

Identification Arsenic (V) by cyclic voltammetry and recovery of Arsenic by electrodeposition

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ABSTRACT

This work is focuses in to develop an As(V) identification technique in an aqueous medium with KCl and KI as background electrolytes, in concentrations ranging from 1.33×10^{-5} M (1 mg/L) to 1.33×10^{-4} M (10 mg/L) applied in drinking water and 1.33×10^{-4} M (10mg/L) to 1.33×10^{-3} M (100mg/L) applied to identification to As in rejection water from capacitive deionization and Inverse osmosis. A technique of electro recovery of arsenic was developed by the application of a potential in acid solution in order to reduce As(V) and As(III) present in drinking and rejection water coming to mining activities, and process like Capacitive deionization and inverse osmosis.

INTRODUCTION

Exposure to arsenic through contaminated water is a latent threat to human health. Arsenic is carcinogenic and its consumption can cause harmful effects to health leading to death. Taking into account the toxicity of arsenic, the World Health Organization (WHO) and US Environmental Protection set the maximum permissible limit of arsenic in drinking water to 0.010 mg/L (US EPA, 2001, World Health Organization, 1993 and 2006).

According to McClintock et al., 2012, in Mexico the Secretary of Health through the official norm, NOM-127-SSA1-1994 establishes that the maximum concentration of arsenic is 0.025 mg/L, in the Mexican Republic arsenic has been found in water

bodies that exceed the limits established in the Standard in the north and central regions of the country (Nuevo Leon, Coahuila, Durango, Hidalgo, Guanajuato, Zacatecas, Chihuahua, Morelos, Aguascalientes, Puebla, Sonora, Jalisco and San Luis Potosí), There is also an important contamination by As in different countries such as the United States of America, China, Chile, Bangladesh, Taiwan, Argentina, Vietnam, Pakistan, Poland, Hungary, New Zealand, Mexico, Japan and India that exceed the limits Maximum permissible 0.025 mg/L indicated by WHO. In general arsenic is found in the environment by natural sources, such as: mineralization, biological activity and volcanic emissions; or by anthropogenic activities such as: industrial processes, mining, metal smelting, pesticides, pesticides of cotton crops or as a wood preservative (Litter et al., 2009).

The oxidation state of As and its mobility are controlled mainly by redox conditions (redox potential, Eh) and pH. Under oxidizing conditions, As (V) predominates over As (III), being found mainly as H_2AsO_4^- at low pH values (below 6,9), whereas at higher pH, the dominant species is HAsO_4^{2-} (under conditions of extreme acidity, the dominant species will be H_3AsO_4^0 and while under conditions of extreme basicity, the dominant species will be AsO_4^{3-}). The conditions favoring oxidation (chemical or biological) induce the change to pentavalent species and, conversely, those favoring the reduction will change the equilibrium to the trivalent state (Lillio, 2002).

The most used instrumental methods of quantification of As in water are by atomic absorption spectroscopy (NMX-AA-051-SCFI-2001) and chromatography; The electrochemical technique by voltammetry has been developed for the quantification of As (III), presenting advantages as being a field technique, of low cost and of less time however no references have been found to have been applied for the identification of As(V). In the voltammetric analysis the current intensity is measured through an electrode by applying a potential difference. The different voltamperometric techniques are distinguished essentially by the different form of variation of the potential applied with the aim of reducing the limits of detection (Litter et al., 2009). Among the great variety of voltammetric techniques, the most used in the quantification of arsenic are anodic and cathodic redissolution (Cavicchioli et al, 2004; Hung et al., 2004).

Electrochemical methods are an alternative for the determination of arsenic in its reduced state, determinations have been reported in the range of 0.007 to 270.0 mg/L and have the advantage over the spectroscopic in sensitivity, selectivity and especially in speciation (Mays and Hussam, 2009).

The redissolution voltammetry technique is characterized by its selectivity to As(III), high sensitivity and low detection limits that can be compared with other techniques. Considering the advantages of electrochemical methods such as Anodic Redissolution Voltammetry (AVS), the present work aims to develop a technique to identify the As(V) metalloid in an aqueous medium different process, like inverse osmosis and capacity deionization for low concentration and reject water from mines, for the investigation was using a platinum working electrode with a KCl bottom solution.

EXPERIMENTAL

The As(V) solutions used in the experiments were prepared from $\text{HAsNa}_2\text{O}_4 \cdot 7\text{H}_2\text{O}$ (Sigma-Aldrich brand) at low concentrations of 1 to 10 mg/L, and highs of 30, 50, 80 and 100 mg/L, As carrier electrolyte 0.001 mol/L KCl. All As (V) samples were added with IK and adjusted to pH 2 with 0.1 mol/L HCl.

In order to corroborate the concentrations of arsenic in the water using in the experimental work, the Arsenator Wagtech: Photometer Palestintest P2000272 was used, whose technique is spectrophotometric.

Measurements of cyclic voltammetry were carried out using a Potentiostat/ Galvanostat/ ZRA 09096 - Gamry instruments and for data analysis a Gamry Instruments Redefining Electrochemical Measurement Framework Version 6.31, with an electrochemical window of initial potential of 0.0 to +0.800 V with a scanning potential of 100 mV/s. All working solutions were prepared from analytical grade reagents and deionized water on the same working day to avoid degradation thereof.

In the detection of arsenic, a conventional three electrode cell was used. A double-jacketed $\text{Ag}^0 / \text{AgCl}$ electrode with external 10% KNO_3 solution ($E = \text{ECS}$) as the reference electrode (RE), a platinum electrode as the working electrode (WE), that was manufactured with a glass tube and epoxy resin and a graphite electrode as an auxiliary electrode (AE). The electrodes mentioned above were treated with 0.01 mol/L HCl and washed with deionized water prior to each experiment, are the purpose of avoiding impurities on their surface. The study of the solutions was carried out in a glass reactor, the oxygen present in the As(V) samples was displaced by the bubbling of N_2 for a period of 10 min.

Arsenic recovery tests were carried out with solutions containing a mixture of 5 mg/L As(V) and As(III) with a pH adjusted to 2 by HCl, this solutions were prepared with analytical grade reagents. Potential sweeps were performed in a range of 0.8 V at -0.6 V in a potentiostat / Galvanostat / ZRA 09096 - Gamry instruments, in order to observe at cathodic or reduction potential necessary to electrodeposit the arsenic in the metal electrodes, as well as the influence of the oxygen and hydrogen in the electrochemical procedures, the electrodes used for the potential sweeps were a copper working electrode, with 1cm^2 area, encapsulated and mirror polished, a double jacket $\text{Ag}^0 / \text{AgCl}$ reference electrode with external solution Of 10% KNO_3 ($E = \text{ECS}$) and the graphite auxiliary electrode, said process was carried out in a hermetically sealed glass cell. Subsequently, the electrodeposition of As(III) and As (V) at 5 mg/L was performed using 5 x 5 cm, two-sided copper electrodes 25cm^2 of area, for 60 minute at different voltages of 0.5, 1.0 and 1.5 V using an Agilent brand energy source, model E3642A. In order to eliminate the oxygen present and avoid undesirable reactions was maintained constant bubbling of N_2 .

RESULTS

Tests with KCl electrolyte at a concentration of 0.001 mol/L, as reported by Galina et al. (2012) were performed in which the presence of potassium chloride KCl influences the detection of the anode peak. However, As(V) was not detectable in

the presence of KCl as background electrolyte alone, to facilitate detection different volumes of potassium iodide (IK) were added as a reductant of As(V) to As(III) (Figure 1) where it was observed that the anodic peak shifts as the amount of solution of IK in the sample increases: 1 mL (0.462 V), 2 mL (0.436 V), 3 mL (0.430 V), 4 mL (0.424 V), 5 mL (0.418 V). Electro analytical detection of arsenic As(V) requires acidic conditions (Salaün et al., 2007), therefore the experiments were carried out in a pH 2 adjusted with the HCl that helps to reduce and avoid the accumulation of hydrogen or bubbles in the electrode, since at a neutral pH the determination is considered impossible due to the electro inactivity of As (V) (Gibbon and Salaün, 2012).

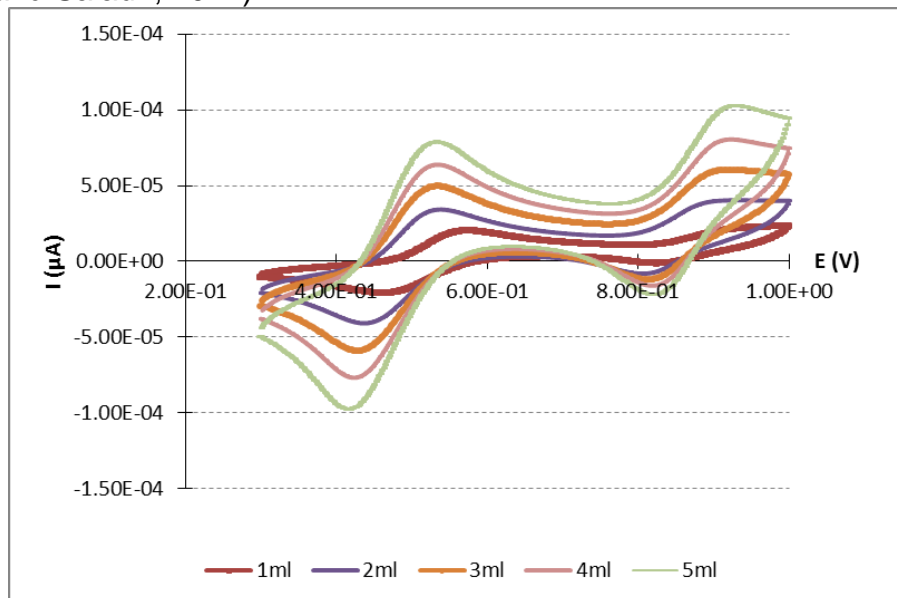


Figure 1. Voltamperogram of As(V) as a function of KI concentration of 1 to 5 ml with 0.001 M KCl and 1.33×10^{-4} M (10mg/L) As (V).

As can be seen in Figure 1, the signal intensity of the presence of As (V) is proportional to the amount of potassium iodide (IK), to increase the amount of IK, the signal of As(V) increases. For this reason, the decision was made to add 5 ml of IK for all experiments.

In order to verify the presence of As(V) in the study solution (synthetic medium) by voltammetry cyclic (Figure 2) the samples were studied: 1) 5mL of IK with 0.001M KCl. 2) 5 ml of IK with 0.001 M KCl plus 1.33×10^{-4} M (10 mg/L) As(V), experiment was exposed to constant bubbling to N_2 . The difference between the two samples is only the presence of arsenic. Figure 2 shows the presence of As(V) at a potential reading of 0.418 V.

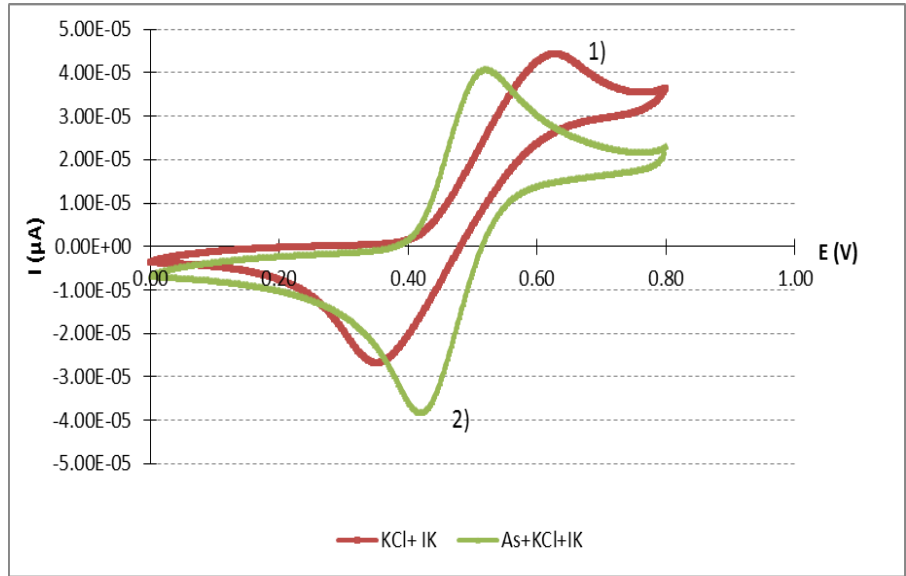


Figure 2. Voltamperogram comparison of IK and KCl. 1) 5 mL of 0.01 M IK with 0.001 M KCl, 2) 5 mL of 0.01 M IK with 0.001 M KCl + 1.33×10^{-4} M As (V).

After experimentally identifying the As(V) with IK signal, experimental tests were performed with high concentrations of As(V) at 1.33×10^{-4} M (10 mg/L), 4.00×10^{-4} M (30 mg/L), 6.67×10^{-4} M (50 mg/L), 1.06×10^{-3} M (80 mg/L), 1.33×10^{-3} M (100 mg/L), with a concentration of 0.001 M KCl, a volume of 5 mL of IK, PH 2 adjusted with HCl, experiment was exposed to constant bubbling to N_2 . Figure 3 shows the displacement of the anodic peak by identifying As(V) at 10 mg/L at an amperage of $-3.84 \mu A$ and $-4.39 \mu A$ at a concentration of 100 mg/L confirming that the magnitude of the anodic peak is proportional to the Amount of As present. Identifying the oxidation and reduction of the metalloid.

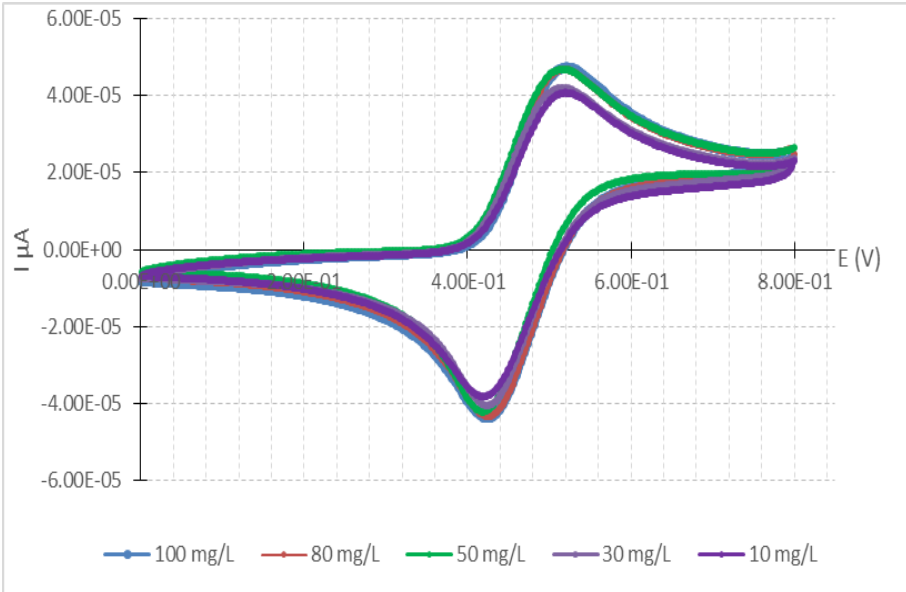


Figure 3. Voltamperogram high concentrations of As(V) at 1.33×10^{-4} M, 4.00×10^{-4} M, 6.67×10^{-4} M, 1.06×10^{-3} M, 1.33×10^{-3} M, plus 0.001 M KCl and a concentration of 5 mL 0.01 M IK.

According to the results obtained and the working conditions, a calibration curve for the determination of arsenic in high concentrations was elaborated: 10, 30, 50, 80, and 100 mg/L. The curve showed a R^2 of 0.999, with a standard deviation of 2.8 and a media of -42.17. Figure 4. It is important to say that in concentrations greater than 80 mg/L the readings are not reliable for this reason in the graphic the last concentration is 80 mg/L.

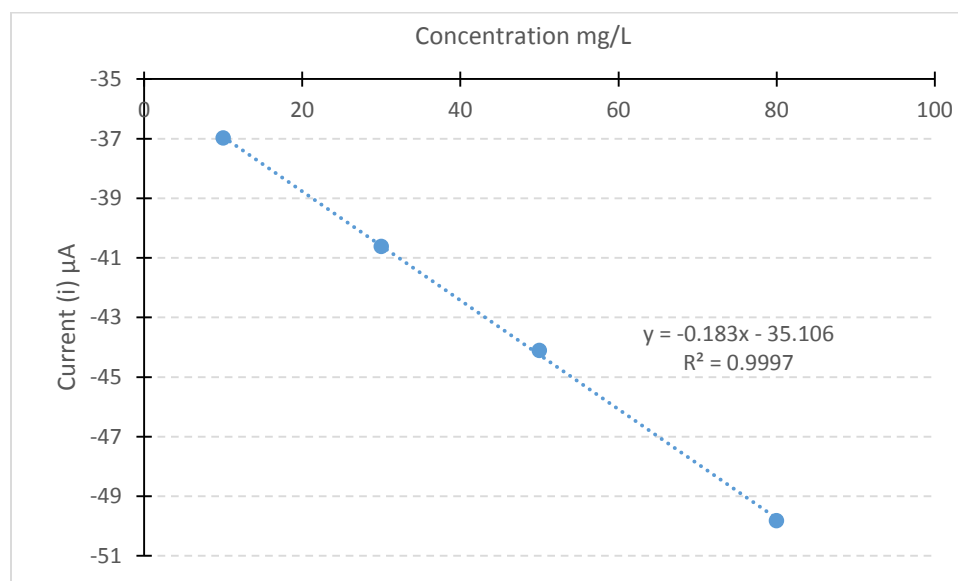


Figure 4. Calibration curve of As(V) High concentrations. Base electrolyte 0.001M KCl, pH 2 adjusted with HCl, 5 mL of IK.

The same test was performed at low concentrations of Arsenic (V) 1.33×10^{-5} M (1 mg/L), 2.66×10^{-5} M (2 mg/L), 4.00×10^{-5} M (3 mg/L), 5.33×10^{-5} M (4 mg/L), 6.67×10^{-5} M (5 mg/L), 8.00×10^{-5} M (6 mg/L), 9.34×10^{-5} M (7 mg/L), 1.06×10^{-4} M (8 mg/L), 1.20×10^{-4} M (9 mg/L), 1.33×10^{-4} M (10 mg/L), plus the addition of 0.001 KCl and 5 mL IK. The behavior of the oxidation reduction is shown in Figure 5, it being observed that the magnitude of the anodic peak with reference to the current is proportional to the concentration of As(V), taking as a reference that at a concentration of 1 mg/L it is identify the arsenic at -3.82 µA and in a concentration of 10 mg/L to - 3.84 µA.

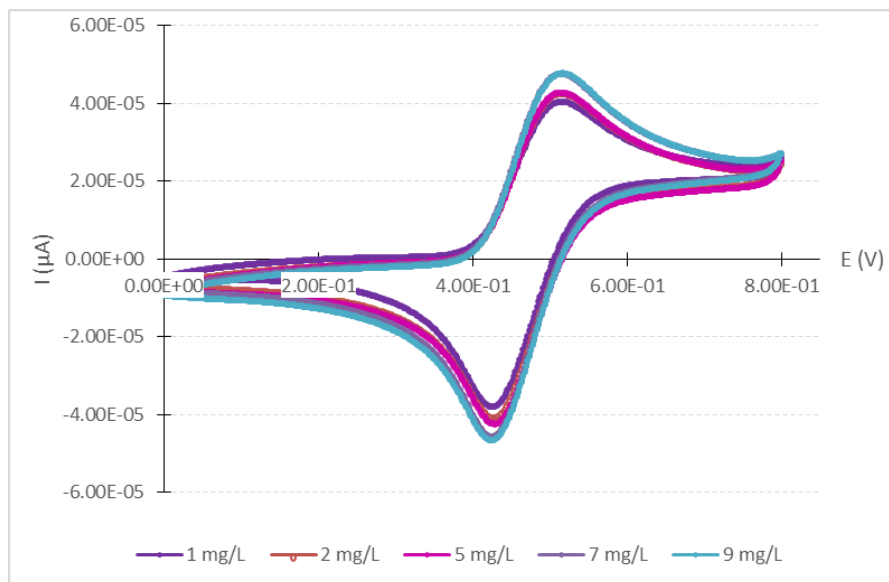


Figure 5. Voltamperogram high concentrations of As (V) 1.33×10^{-5} M, 2.66×10^{-5} M, 4.00×10^{-5} M, 5.33×10^{-5} M, 6.67×10^{-5} M, 8.00×10^{-5} M, 9.34×10^{-5} M, 1.06×10^{-4} M, 1.20×10^{-4} M, 1.33×10^{-4} M, plus the addition of 0.001 KCl and 5 mL of 0.01M IK.

A calibration curve was prepared for the determination of Arsenic at low concentrations: 1, 2, 5, 7 and 9 mg/L. The curve presented an R^2 of 0.998, with a standard deviation of 2.8 and a media of -42.24.

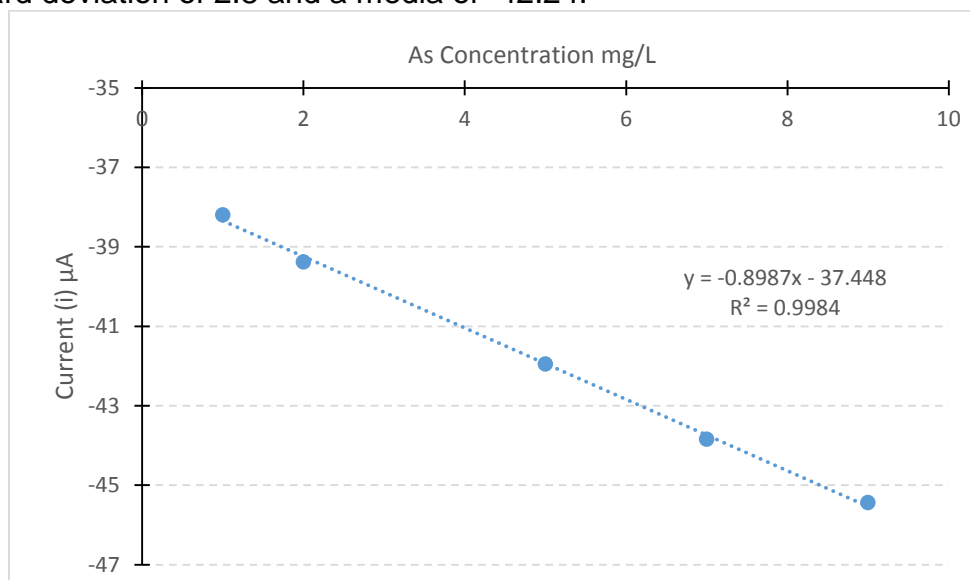


Figure 6. Calibration curve of As (V) low concentrations. Base electrolyte 0.001M KCl, pH 2 adjusted with HCl, 5 mL of IK.

Electrodeposition

Potential scans of the solutions involved in the electrodeposition were performed in a range of 0.8 mV to -0.6 mV in order to find the cathodic potential required to reduce As(V) and As(III) to its elemental state As(0). KCl at 0.001 M, As(V) at 6.67×10^{-5} M and As(III) at 6.67×10^{-5} M was used as background electrolyte, the pH of the solution was adjusted to 2 with HCl. Figure 7 shows potential sweeps where it can be seen that the potentials for reducing arsenic are visible for As(III) at -0.30 mV, As(V) -0.12 mV and the mixture of As(V) and As(III) at 5 mg/L at -0.39mV and a current of 0.0015 A, while no background signal is observed when applying the background electrolyte KCl without As.

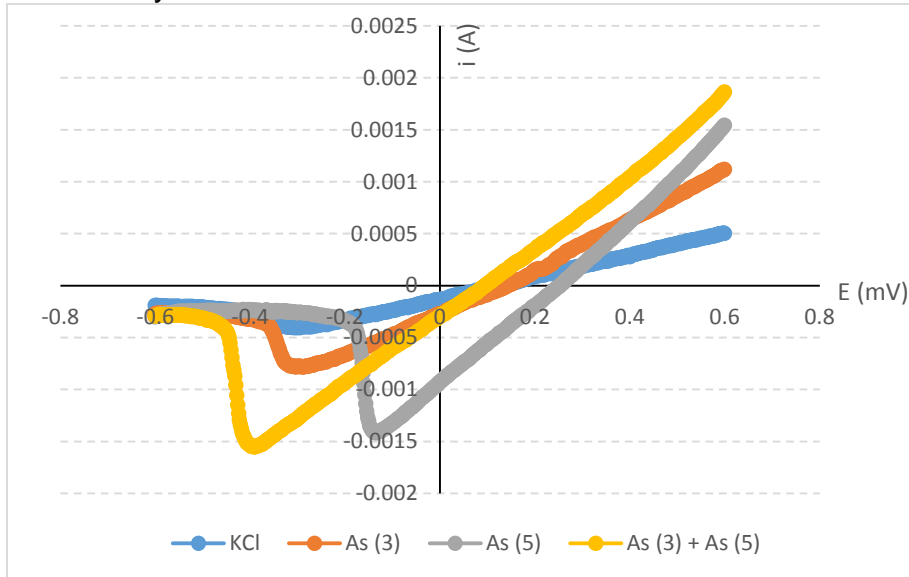


Figure 7. Potential scans of the solutions involved in the electrodeposition, a) 0.001M KCl, b) 6.67×10^{-5} M (5 mg/L) As(III), c) 6.67×10^{-5} M (5 mg/L) As(V), d) mixture As(V) and As(III) at 6.67×10^{-5} M (5 mg/L) respectively, pH 2 adjusted with HCl.

It is possible to observe that the reduction potential of the mixture of As (V) and As (III) is observed at a potential of -0.39 mV and a current of 0.0015 A. Figure 8, which is the potential required to perform the electrodeposition of As(V) and As(III) by its reduction to its elemental state As(0).

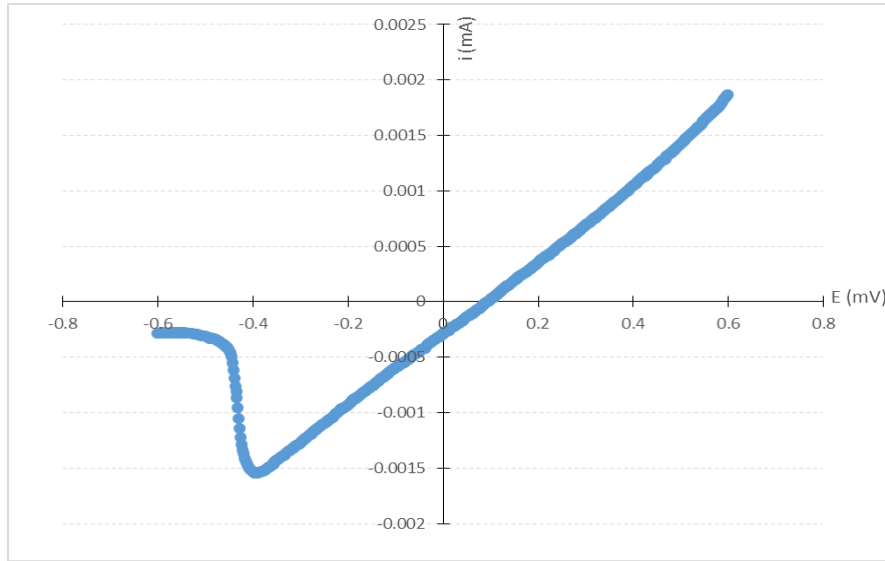


Figure 8. Potential scanning of As(V) and As(III) $6.67 \times 10^{-5} \text{M}$ (5 mg / L) potential, KCl 0.001 M, adjusted pH 2 with HCl.

For the calculation of the percentage of electrodeposited arsenic a calculation was made by the Faraday equation, where (m) is the mass to be deposited (mol), (i) is the observed current (A), (t) is the reaction time (s), (n) is the number of electrons involved in the reaction and the Faraday constant (96485 C/mol).

$$m = \frac{it}{nF} = \frac{(0.0015 \text{ A})(8000 \text{ s})}{(5) \left(96485 \frac{\text{As}}{\text{mol}}\right)} = \frac{12 \text{ As}}{482425 \frac{\text{As}}{\text{mol}}} = 2.487 \times 10^{-5} \text{ mol}$$

It can be observed that the time 8000 seconds with the current observed, it can be electrodeposited 2.487×10^{-5} mol corresponding to 37% of the arsenic present in the solution.

Once the potential and current of arsenic reduction was identified, a potentiostatic test was performed in which the observed potential was applied -0.39mV (Figure 9), background electrolyte 0.001 KCl, $6.67 \times 10^{-5} \text{M}$ As(V), $6.67 \times 10^{-5} \text{M}$ As(III), pH adjusted to 2 with HCl. In this figure it can be seen how the current to the passage of time tends to zero. This happens because the arsenic is electro deposited in the copper decreasing the initial concentration in the solution.

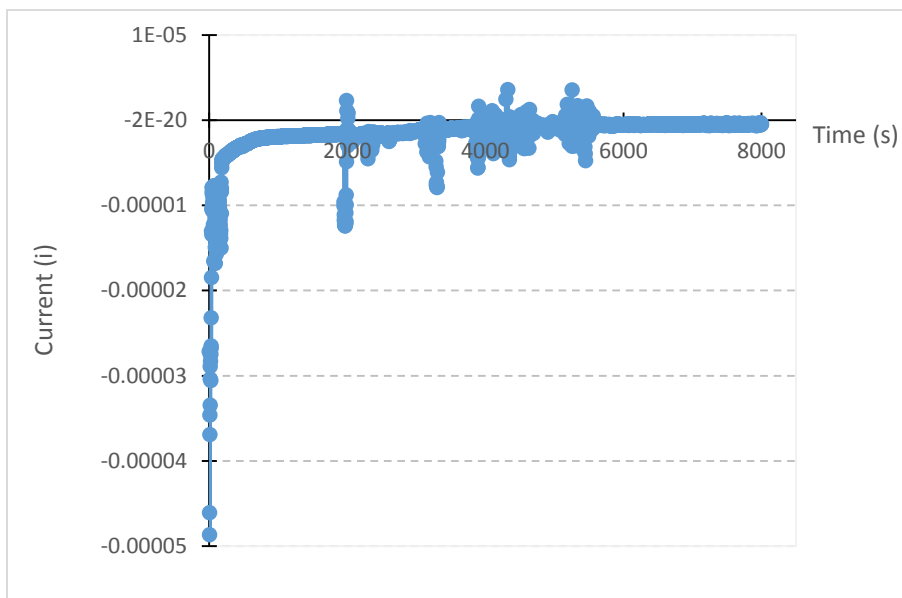


Figure 9. Potentiostatic test. 6.67×10^{-5} M As(V) + 6.67×10^{-5} M As(III) + 0.001 M KCl, pH 2 adjusted with HCl. Potential applied -0.039mV.

Once the arsenic electrodeposition was verified with the previous tests, the electrodeposition of arsenic was carried out on a larger scale using 0.001 M KCl as background electrolyte, the pH was adjusted to 2 using HCl, the arsenic concentration was a mixture of As(V) and As(III) at 6.67×10^{-5} M that is 5 mg/L respectively, all in a hermetically sealed glass cell and the oxygen present in the solution was displaced by the nitrogen bubble (N_2) with the purpose of avoiding other reactions in which the oxygen influences.

The potentials applied were 0.5V, 1.0V and 1.5V for 60 minutes, when applying these potentials it was observed that the arsenic is removed from the solution almost in its entirety. It was necessary to design a system configuration for washing by means of silver diethyldithiocarbamate, the gas (arsine gas) generated in the electrodeposition process. To verify that the arsenic was electrodeposited efficiently, analytical chemical tests were performed with the Arsenator in the initial sample (before the electrodeposition process) and the final sample obtained after one hour of work. The results show that the arsenic is removed in percentages greater than almost in its totality, however part of this removal is by the generation of arsine gas. An arsenic identification test was performed by voltammetry and the following. Figure 10 was obtained. It can be observed that the potential obtained was -37.42 μ A and is located in a concentration of less than about 0.08 mg/L with which it is verified that the arsenic is removed from the initial solution.

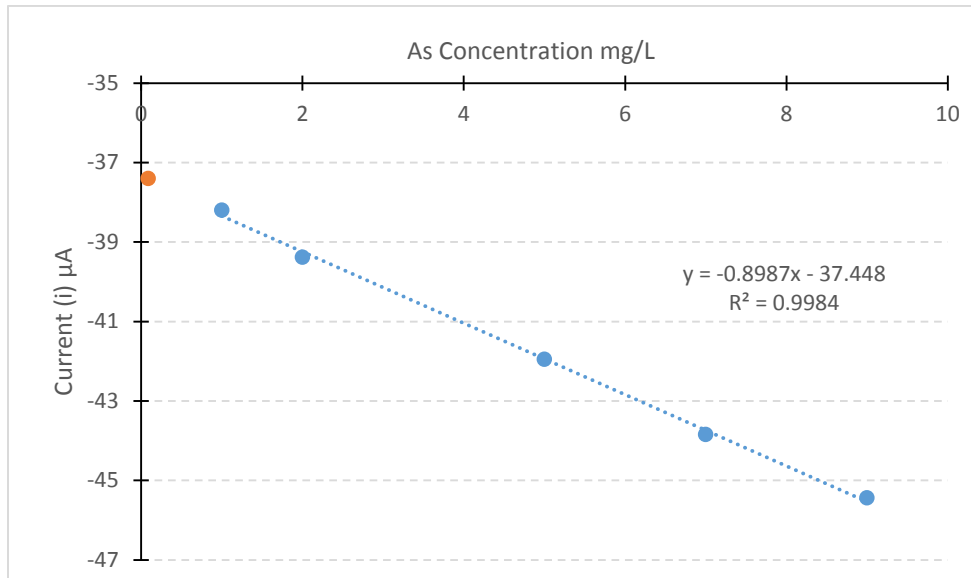


Figure 10. As(V) identification location on the calibration curve of low concentrations. Identification potential $-3.38 \times 10^{-5} \mu\text{A}$.

It is observed that more than 90% of arsenic was removed but much of it is removed by the arsenic reaction to generate arsine gas.

CONCLUSIONS

The identification of As(V) by cyclic voltammetry is observed at low potentials 0.400 V. For the development of the As(V) identification method, KCl and KI were added to promote As reduction. Also, the use of low cost of electrodes such as platinum and carbon allows the identification of concentrations of 1 to 100 mg/L found in natural and industrial waters.

The identification of As(V) by cyclic voltammetry is a technologically viable option due to the reduction of time and costs, with high sensitivity and friendly to the environment. Based on the above, it is convenient to extend the study by performing the As(V) quantification in the same way as the identification and quantification of As(III) with cyclic voltammetry with a Platinum working electrode. It is possible to read and identify arsenic potential with cyclic voltammetry in smaller range than 100 mg/L.

It is possible to recover the arsenic by electrodeposition with efficiencies greater than 50%, the required working medium is an acidic medium, to avoid the arsenic distribution in the environment by means of arsine gas it is necessary to rinse the gases through silver diethyldithiocarbamate, which avoids poisoning the environment and reduces the risk of poisoning of operators. It is recommended to carry out a detailed study of the reaction generated by the arsine gas to identify the percentages of removal of the electrodeposition.

BIBLIOGRAPHIC REFERENCES

Cavicchioli, A., La-Scalea, M.A. and Gutz, I.G.R. (2004) Analysis and speciation of traces of arsenic in environmental, food and industrial samples by voltammetry: A review.

Electroanalysis, 16: 697-711.

Galina N. Noskova, Elza A. Zakharova, Nina A. Kolpakova, Alexander S. Kabakaev. (2012). Electrodeposition and stripping voltammetry of arsenic (III) and arsenic (V) on a carbon black-polyethylene composite electrode in the presence of iron ions. *J Soil State Electrochem*, 16:2459-2472.

Gibbon-Walsh K, Salaün P, Van den Berg, CMG (2012) Determination of arsenate in natural pH seawater using a manganese coated gold microwire electrode. *Anal Chim Acta* 710:50-57

Hung, D.Q., Nekrassova, O. and Compoton, R.G. (2004) Analytical methods for inorganic arsenic in water: A review. *Talanta*, 64, 269-277. The Filtration Society. The International Journal for Filtration and Separation. Vol 13. (1):21-26.

Lillo, J. (2002.). Peligros geoquímicos: arsénico de origen natural en las aguas. Escuela Superior de Ciencias Experimentales y Tecnología. Universidad Rey Juan Carlos. Madrid, España.

Litter, M.I., Farías, S.S. and Armienta, M.A. (2009) Metodologías analíticas para la determinación y especiación de arsénico en aguas y suelos. CYTED. Argentina (Adobe Digital Editions Versión:<http://docplayer.es/6722881-lberoarsen-metodologias-analiticas-para-la-determinacion-y-especiacion-de-arsenico-en-aguas-y-suelos.html>).

Litter Marta I., María Teresa Alarcón-Herrera, María J. Arenas, María A. Armienta, Marta Avilés, Roberto E. Cáceres, Henrique Nery Cipriani, Lorena Cornejo, Luiz E. Dias, Alicia Fernández Cirelli, Elsa M. Farfán, Sofía Garrido, Liliana Lorenzo, María.E. Morgada, Mario A. Olmos-Márquez, Alejo Pérez-Carrera.(2012). Small scale and household methods to remove arsenic from water for drinking purposes in Latin America. *Science of the Total Environment*, 429:107-122.

Mays, D.E. and Hussam, A. (2009) Voltammetric methods for determination and speciation of inorganic arsenic in the environment A review. *Analytical Chimica Acta*, 646:6-16.

McClintock, T.R., Chen, Y., Bundschuh, J., Oliver, J.T., Navoni, J., Olmos, V., Villaamil L. E., Ahsan, H. and Parvez, F. (2012) Arsenic exposure in Latin America: Biomarkers, risk assessments and related health effects. *Science of the Total Environment*, 429:76-91.

Norma Mexicana NMX-AA-051-SCFI-2001, Análisis de agua - determinación de metales por absorción atómica en aguas naturales, potables, residuales y residuales tratadas - método de prueba. México.

Norma Oficial Mexicana NOM-127-SSA1-1994, Salud ambiental. Agua para uso y consumo humano. Límites permisibles de calidad y tratamientos a que debe someterse el agua para su potabilización. Diario Oficial de la Federación 22 de noviembre de 2000. México.

Organización Mundial de la Salud. Mitigación de los efectos del arsénico presente en las aguas subterráneas. CONSEJO EJECUTIVO EB118/14.118ª reunión 24 de mayo de 2006. Punto 5.4 del orden del día provisional.

Salaün, P., Planer-Friedrich B., Van den Berg CMG. (2007). Inorganic arsenic speciation in the wáter an seawater by anodic stripping voltametry with a gold microelectrode. Anal Chim Acta 585:312-322.

U.S.EPA, Environmental Protection Agency. (2001). National primary drinking water regulations; arsenic and clarifications to compliance and new source contaminants monitoring; final Rule. Federal Register 66 (14), 6976. USA.

World Health Organization, (1993). Guidelines for Drinking-water Quality. In: Recommendations, Vol. 1. Geneva, Zwitzerland.