

Article

Silver/Magnetite Modified Carbon Paste Electrode for Arsenic (III) Quantification

Diana E. Soto-Nájera ¹, María Teresa Alarcón-Herrera ¹, José Rafael Irigoyen-Campuzano ¹ and Liliana Reynoso-Cuevas ^{2,*}

¹ Departamento de Ingeniería Sustentable, Centro de Investigación en Materiales Avanzados, S.C. Calle CIMAV 110, Colonia 15 de Mayo, Durango 34147, Mexico; diana.soto@cimav.edu.mx (D.E.S.-N.); 20.alarconherrera.teresama@gmail.com (M.T.A.-H.); jose.irigoyen@cimav.edu.mx (J.R.I.-C.)

² Secihti-Centro de Investigación en Materiales Avanzados, Calle CIMAV 110, Ejido Arroyo Seco, Durango 34147, Mexico

* Correspondence: liliana.reynoso@cimav.edu.mx

Abstract

In this study, a carbon paste electrode modified with silver and magnetite nanoparticles was used to quantify arsenic via square-wave anodic stripping voltammetry. Under optimized parameters, a deposition potential of -0.4 V for a period of 70 s, the setup achieved a linear quantification range from 0 to $40 \mu\text{g L}^{-1}$ of As (III) ($R^2 = 0.982$). Electrochemical characterization was performed using cyclic voltammetry and electrochemical impedance spectroscopy (EIS). The evaluated arsenic quantification framework encompasses the World Health Organization (WHO) limit and the Mexican maximum permissible level for arsenic in drinking water ($10 \mu\text{g L}^{-1}$), as well as arsenic concentrations frequently reported in groundwater wells throughout northern Mexico. Key advantages of this electrode include its low fabrication cost, ease of operation, and analytical stability spanning a 30-day period. Additionally, selectivity tests revealed that Cu(II) masked the arsenic stripping signal at a 1:1 Cu(II): arsenic concentration ratio, whereas no modification of the target signal was observed in the presence of cadmium.

Keywords: anodic stripping voltammetry; carbon paste electrode; magnetite nanoparticles; silver nanoparticles

1. Introduction

Arsenic contamination is a global problem as over 200 million people are exposed to high concentrations of arsenic in drinking water [1]. It has been determined that the main source of human exposure is the consumption of contaminated water, causing diseases such as vascular problems, and ischemic heart disease, in addition to increasing the risk of generating tumors in the bladder, lungs, kidneys, and liver [2], and skin problems [3]. Additionally, chronic arsenic exposure has been associated with cognitive impairment [4].

Water contamination by arsenic occurs through both lithogenic and anthropogenic pathways [5], with the latter being exacerbated by overexploitation [6]. It is estimated that between 94 and 220 million people worldwide are at risk of exposure to high levels of arsenic [7].

Among the countries reporting arsenic concentrations above the WHO drinking water safety limit, India presents a major issue [8]. For Latin America, arsenic contamination

Received: 8 June 2026

Revised: 23 July 2026

Accepted: 24 July 2026

Published: 28 July 2026

Copyright: © 2026 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

of groundwater has been considered a serious problem in 20 countries [9]. Mexico is among the countries with the highest probability of groundwater concentrations above $10 \mu\text{g L}^{-1}$ [10]. Arsenic concentrations above $100 \mu\text{g L}^{-1}$ have been reported in northern Mexico [11]. For this reason, it has been necessary to establish different regulations for water quality assurance. In Mexico, the NOM-127-SSA1-2021 [12] standard establishes a maximum allowable arsenic concentration of $10 \mu\text{g L}^{-1}$ for government-provided drinking water. Additionally, the arsenic concentration in bottled water is set at $10 \mu\text{g L}^{-1}$, as regulated by NOM-201-SSA1-2015 [13]. The latter is equal to the maximum value recommended by the World Health Organization (WHO) and complements the regulations. Arsenic monitoring is another important issue.

The analytical techniques currently used for arsenic determination in water, spectroscopic, chromatographic, and hybrid approaches remain the most common [14]. However, chromatographic procedures for arsenic quantification and speciation require complex sample preparation steps to accurately determine the different arsenic species [15]. In addition, these techniques present several limitations, such as long analysis times [16], the need for specialized personnel [17], and high investment costs in equipment and reagents [18].

Portable colorimetric assays provide a practical means for performing onsite measurements efficiently [19], and their results represent only an approximation of the actual arsenic content in water samples [20]. Current challenges in arsenic quantification encompass the need for precise speciation, the development of low-cost, user-friendly devices, and enhanced analytical performance [21]. On-site arsenic analysis relies on innovative methods based on biosensors, nanomaterials, and electroanalytical technologies [14]. Relevant electrochemical methods include potentiometry, conductimetry, and voltammetry [21].

Ongoing research aims to develop portable devices capable of quantifying arsenic directly on site [22]. Electrochemical techniques, together with the use of modified electrodes, have a high potential to develop devices that are easy to use and capable of quantifying contaminants at low concentrations with high sensitivity [14,23,24].

Although significant progress has been made in environmental monitoring, quantifying arsenic in real water samples remains a complex analytical challenge [25]. In this scenario, the selection of the working electrode material is crucial for the success of the determinations [26]. Gold, for instance, has historically been one of the preferred materials for this task, but its use considerably increases production costs [27]. Added to this are major operational limitations of current systems, such as the need for rigorous electrode conditioning, chemical modification of the sample [28], and constant verification of surface conditions via cyclic voltammetry to ensure reproducibility [29]. Carbon paste electrodes have been widely studied due to their ease of modification, their low cost, chemical stability [30] and easy renewal [31]. It is necessary to incorporate a modifier that provides selectivity and an electrochemical response to the analyte [32]. The use of metallic materials provides a high electroactive surface area and facilitates efficient mass transport [33]. Moreover, incorporating metallic nanoparticles offers the additional advantage of enabling direct adsorption of arsenic species onto the electrode surface [34].

Regarding arsenic, the synergistic effects of two materials have been studied: one with analyte adsorption properties and the other with electrical conducting properties [35].

One of the desired characteristics of electrodes used in arsenic quantification is selectivity.

Therefore, it was decided to study the effect of copper, since these metals are often found as contaminants along with arsenic. In addition, copper is one of the main interfering elements in arsenic quantification [36].

One of the main difficulties is that the oxidation peak of As (0) to As (III) overlaps with the Cu(0) to Cu(II) peak [37]. In addition, Cu can form intermetallic compounds with As during the deposition process [38,39].

Magnetite (Fe_3O_4) is used due to its adsorptive properties for arsenic [40] and it has been reported that the reduction of As(III) is promoted by the redox cycle of Fe(II)/Fe(III) [41]. Further, it exhibits selectivity for arsenic ions [42]. Silver, as a nanoparticle, is used due to its excellent electric conductivity, in addition to the report of being used as a modifier for the determination of arsenic III and V [43], achieving a limit of detection (LOD) of $1.5 \mu\text{g L}^{-1}$ and $0.1 \mu\text{g L}^{-1}$ respectively [44,45].

Although several modified electrodes have been reported for electrochemical arsenic determination, most studies have focused primarily on improving analytical performance. In the present work, the analytical evaluation is complemented with electrochemical characterization to better understand the sensing mechanism of the Ag- Fe_3O_4 NPs-CPE. Cyclic voltammetry, electrochemical impedance spectroscopy, and kinetic analysis were used to explain the synergistic contribution of Ag and Fe_3O_4 nanoparticles to the electrochemical response. In addition, the influence of Cu(II) and Cd(II) on the arsenic signal was investigated to assess the selectivity of the proposed electrode under conditions relevant to water analysis.

2. Materials and Methods

2.1. Reagents and Apparatus

Paraffin oil, density $0.827\text{--}0.890 \text{ g mL}^{-1}$; Fe_3O_4 , particle size $50\text{--}100 \text{ nm}$; graphite powder and KBH_4 were purchased from Sigma-Aldrich, St. Louis, MO, USA. The AgNO_3 crystal was J.T. Baker, Phillipsburg, NJ, USA. All reagents were used without further purification. Cyclic voltammetry and sweep-potential measurements were performed on an Autolab PGSTAT 204 potentiostat/galvanostat (Metrohm Autolab B.V., Utrecht, The Netherlands), and impedance measurements were performed on a Bio-Logic model SP-300 multi-channel galvanostat (Bio-Logic Science Instruments, Seyssinet-Pariset, France). For silver nanoparticle synthesis, the method of chemical reduction was used [46], obtaining a particle size range of $20\text{--}90 \text{ nm}$.

The active surface area of the working electrode was determined using potassium hexacyanoferrate (III) ($\text{K}_3\text{Fe}(\text{CN})_6$) (Sigma-Aldrich).

Atomic Absorption for Cu (AA15N-1) and Cd (AA08N-1) were purchased from AccuStandard (New Haven, CT, USA) and used for interferences measurements.

2.2. Fabrication of Working Electrodes

The composition of the carbon paste electrode modified with Ag and Fe_3O_4 (Ag- Fe_3O_4 NPs-CPE) was selected based on the component reported by Toor et al. [33]. Carbon paste electrode modified with silver nanoparticles (Ag NPs-CPE) and carbon paste electrode modified with magnetite nanoparticles (Fe_3O_4 NPs-CPE) maintain the same proportions of nanoparticles in Ag- Fe_3O_4 NPs-CPE, as described in Table 1, to determine the effect of each of the components of the electrode.

Table 1. Composition of working electrodes in weight percentage.

Electrode	Graphite Powder	Ag NPs	Fe_3O_4 NPs	Paraffin Oil
Ag- Fe_3O_4 NPs-CPE	63	8	4	25
Ag NPs-CPE	67	8		25
Fe_3O_4 NPs-CPE	71		4	25
Bare CPE	75			25

The solid components of each electrode were weighed and homogenized in 5 mL of hexane and stirred for 300 s in a vortex. The mixture was left to rest for 12 h to allow the hexane matrix to evaporate. The paraffin oil was incorporated manually by mixing in an

agate mortar for 30 min. The resulting mixture was packed into 2 mm diameter plastic cylinders, and a copper wire was placed as a conductor. The photo of the working electrode is shown in Figure 1, and the approximate cost is \$8.00.



Figure 1. Working electrode.

2.3. Cell Characteristics and Potential Sweep

A conventional three-electrode voltametric cell was used. A 3 M Ag/AgCl electrode (BASi) was used as a reference electrode, a platinum wire (BASi) was used as an auxiliary electrode, and bare CPE and modified CPEs were used as working electrodes.

Measurements were performed using square-wave anodic stripping voltammetry, with phosphate buffer as the supporting electrolyte. During the preconcentration period, the migration of arsenic species was promoted by magnetic stirring at 200 rpm, with pertinent adjustments to improve the signal. The system was purged with argon for 300 s prior to preconcentration. Baseline correction was applied to each calibration curve measurement using the Nova 2.1.1 program, the potentiostat's software.

2.4. Determination of Redox Potential

Redox potential measurements were performed using an ORION STAR A329 (Thermo Scientific Waltham, MA, USA) equipped with an ORP electrode (HI3230B, Hanna Instruments, Woonsocket, RI, USA). The measurements were conducted in accordance with Standard Method 2580 [47].

2.5. Preparation of Tap Water Samples

Analytical measurements were performed using the standard addition method. To ensure matrix uniformity, a fixed volume of 2.0 mL of phosphate buffer and a 2.5 mL aliquot of tap water (containing $23 \mu\text{g L}^{-1}$ of As) were transferred to 10 mL volumetric flasks. Each flask was then spiked with the corresponding volume of an As(III) standard solution, according to the required fortification level. Finally, the flasks were diluted to volume with deionized water.

2.6. Impedance Spectroscopy Measurements

The working electrodes used were Ag NPs-CPE, Fe_3O_4 NPs-CPE, bare CPE, and Ag- Fe_3O_4 NPs-CPE; Ag/AgCl 3 M was used as the reference electrode, and a platinum wire was used as the auxiliary electrode. Working solutions (phosphate buffer 1 M pH 4.8) were added. For measurements, 7 points per decade were determined, with an amplitude of 10 mV over a frequency range from 100 kHz to 10 MHz. The adjustments were made with the Zview 2 software (Scribner Associates Inc., Southern Pines, NC, USA) program.

2.7. Electrode Aging

The test was performed using Ag-Fe₃O₄ NPs-CPE, whose surface was renewed by polishing on filter paper before each measurement. Three measurements were carried out every five days at a solution of As(III) 10 µg L⁻¹.

2.8. Data Analysis

The data obtained were analyzed with Minitab 17 Statistical Software. Five measurements per point on the calibration curve were performed, using concentrations prepared starting at 5 µg L⁻¹, 10 µg L⁻¹, and then increasing in 10 µg L⁻¹ up to 90 µg L⁻¹ of As(III).

3. Results and Discussion

For peak identification, cyclic voltammetry was applied at a scan rate of 100 mV s⁻¹ in the anodic direction. Figure 2a shows the measurements in the presence and absence of arsenic in water, (b) under the experimental conditions applied, H₃AsO₃ was identified as the arsenic species present in the water samples. The redox potential (Eh) was measured using an oxidation–reduction potential (ORP) electrode.

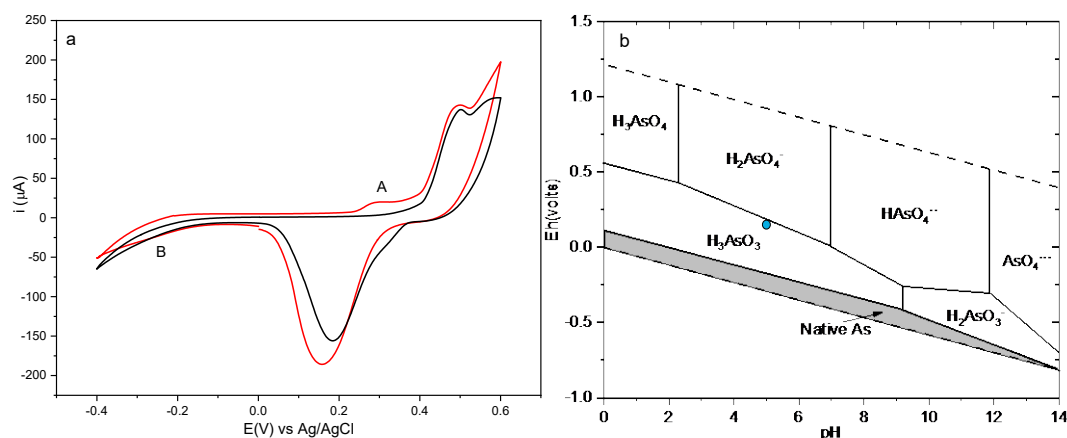
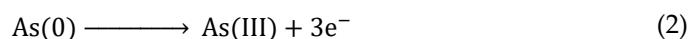
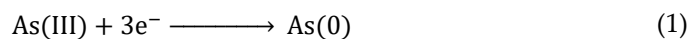


Figure 2. (a) Cyclic voltammetry with Ag-Fe₃O₄ NPs-CPE. The black line corresponds to the blank solution, and the red line shows the measurement in an As(III) in phosphate-buffered solution. Scanning rate of 100 mV s⁻¹ in an anodic direction. Peak A corresponds to redissolution, and Peak B corresponds to deposition. (b) The marked point indicates the experimental redox potential and pH conditions used in this study within the Eh–pH (Pourbaix) diagram of the As–O–H system at 25 °C and 1 bar. Reproduced from [48].

By applying cyclic voltammetry, it was possible to identify the redissolution peak (A, Figure 2), corresponding to reaction (2), and peak B, corresponding to



To identify the response of each Ag-Fe₃O₄ NPs-CPE component, the working electrodes were evaluated and compared through cyclic voltammetry, the results are in Figure 3.

From the comparison made in Figure 3, it is possible to identify peaks A and B in Ag-Fe₃O₄ NPs-CPE, smaller peaks for Ag NPs-CPE, bare and Fe₃O₄ NPs-CPE electrodes; it is not possible to identify a response to the presence of As(III) in A or B.

Once the peaks of interest were identified, the potential for impedance spectroscopy measurements were defined: −400 mV for arsenic deposition and 200 mV for redissolution potential.

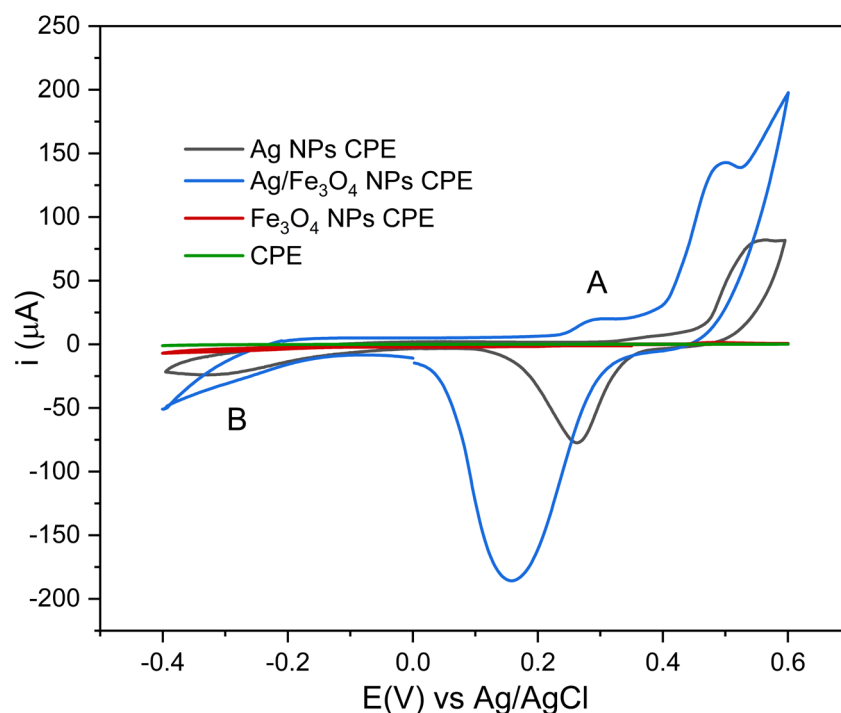


Figure 3. Cyclic voltammetry with the different working electrodes. Experimental conditions: phosphate buffer and As(III) $1000 \mu\text{g L}^{-1}$ solution, at a scan rate of 100 mV s^{-1} in the anodic direction. The peaks marked A and B correspond to redissolution and deposition, respectively.

3.1. Operation Parameters and Calibration Curve

In Figure 4, the peak height is shown as a function of deposition time and deposition potential, respectively. This information was used to optimize the operating conditions of the square-wave technique with Ag-Fe₃O₄ NPs-CPE.

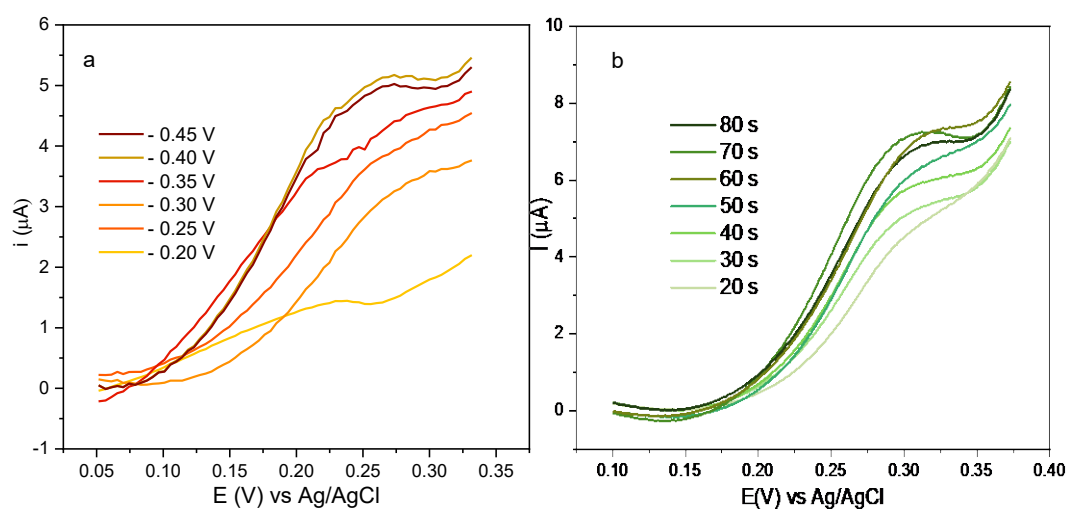


Figure 4. Influence of (a) variation in deposition potential, and (b) variation in deposition time using Ag-Fe₃O₄ NPs-CPE in a $10 \mu\text{g L}^{-1}$ As(III) solution.

As a result of operating parameter optimization, -0.40 V was defined as the deposition potential and 70 s as the deposition time. In Figure 4b, it is observed that a higher peak could be achieved with a longer deposition time.

With the operating parameters, measurements were made at different arsenic concentrations with Ag-Fe₃O₄ NPs-CPE. The results are presented in Figure 5.

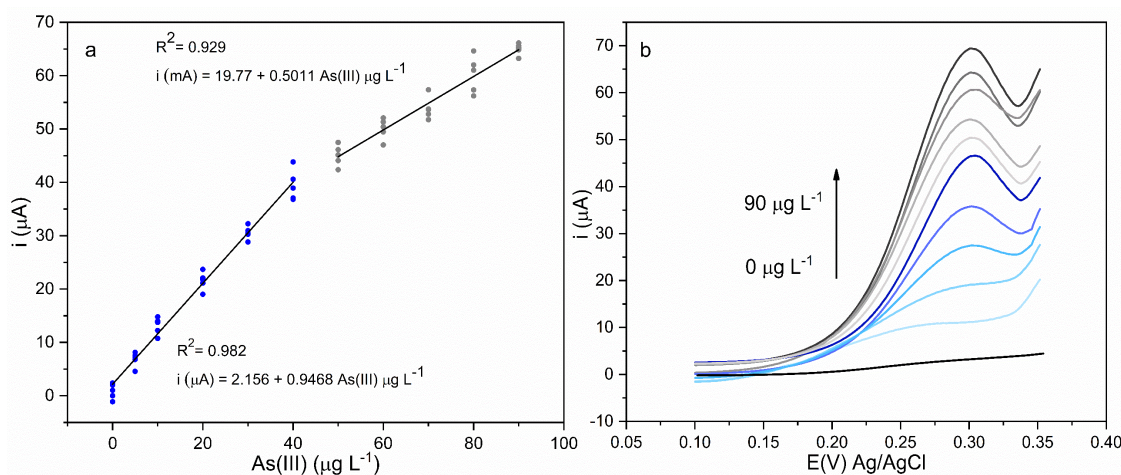


Figure 5. Application of square-wave anodic stripping voltammetry to solutions with arsenic concentrations ranging from 0 to 90 $\mu\text{g L}^{-1}$ As(III) using Ag-Fe₃O₄ NPs-CPE. Measurements were performed with a preconcentration time of 70 s at -0.4 V. A square-wave frequency of 25 Hz, an amplitude of 25 mV, and a step potential of 5 mV. **(a)** Calibration plot showing the bilinear response. Blue symbols and the blue regression line correspond to the concentration range of 0–40 $\mu\text{g L}^{-1}$, whereas gray symbols and the gray regression line correspond to the concentration range of 50–90 $\mu\text{g L}^{-1}$. **(b)** Square-wave voltammograms obtained for increasing As(III) concentrations.

The analytical performance of Ag-Fe₃O₄ NPs-CPE in arsenic quantification was measured using the scanning technique under optimized conditions. Figure 5a shows the calibration curve, which exhibits bilinear behavior in the 0–90 $\mu\text{g L}^{-1}$ range. The lower portion of the curve, from 0 to 40 $\mu\text{g L}^{-1}$, represents the range of greatest environmental significance. The upper range, from 50 to 90 $\mu\text{g L}^{-1}$, shows a decrease in sensitivity of approximately 47% compared to the lower range. This loss of linearity may be due to surface saturation and the interaction between the adsorbed species and the analyte [49]. However, the range in which Ag-Fe₃O₄ NPs-CPE performs efficiently allows the quantification of 10 $\mu\text{g L}^{-1}$, a value established as safe for drinking water.

3.2. Analytical Application in Real Water Samples

To evaluate the practical applicability of the developed Ag-Fe₃O₄ NPs-CPE platform, analytical determinations were conducted in tap water using the standard addition method. To guarantee matrix uniformity across all experimental runs, a fixed volume of 2.5 mL of tap water (natively containing 23 $\mu\text{g L}^{-1}$ of As) was transferred into a series of 10 mL volumetric flasks. Each flask was subsequently treated with 2.0 mL of phosphate-buffered solution (pH 4.8, 1 M) and spiked with the appropriate aliquot of an As(III) standard solution to achieve the target fortification levels. Finally, the mixtures were diluted to volume with deionized water prior to square-wave anodic stripping voltammetry.

The analytical performance of the Ag-Fe₃O₄ NPs-CPE was evaluated in a real tap water matrix using the standard addition method to compensate for potential matrix effects. Figure 6 shows the square-wave anodic stripping voltammetric responses and the corresponding calibration curve obtained within a fortification range from 0 to 40 $\mu\text{g L}^{-1}$ As(III). As observed in Figure 6, well-defined stripping peaks correspond to the oxidation of As(0) to As(III). The stripping peak current exhibited a linear dependence relative to the concentration of the spiked As(III). Despite the inherent complexity of the tap water matrix, which typically features co-existing ions and natural components that can foul electrochemically active sites, the modified electrode exhibited a remarkably stable baseline and well-defined, sharp peak morphologies. The high sensitivity achieved (0.8827 $\mu\text{A } \mu\text{g L}^{-1}$) highlights that the synergistic effect between the silver and magnetite nanoparticles plays

a crucial role in minimizing matrix interferences. This structural combination efficiently protects the active surface, ensuring reliable analytical responses even in complex real-world water samples.

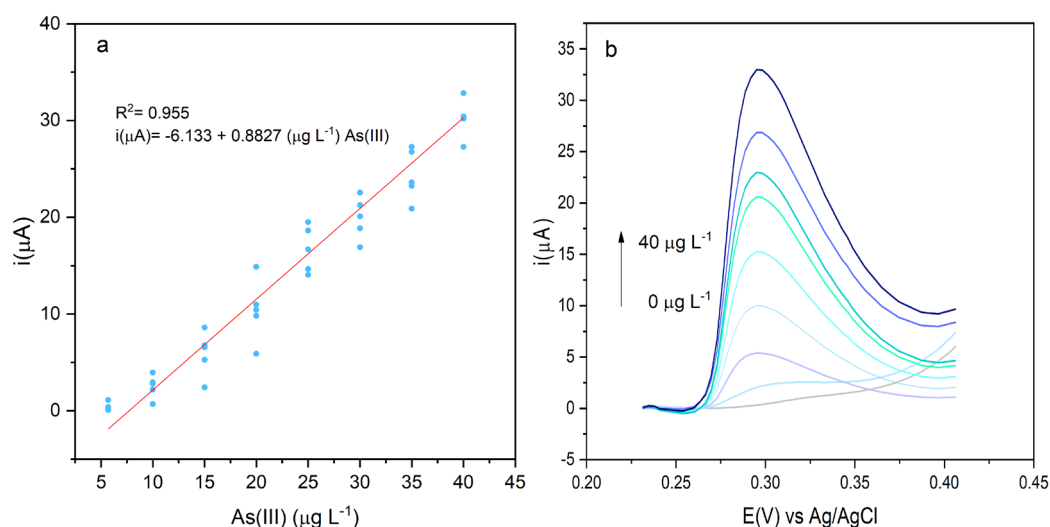


Figure 6. (a) Linear calibration curve of stripping peak current (i) as a function of As(III) concentration in the tap water matrix. Blue symbols represent experimental data, and the red line corresponds to the linear regression. (b) Corresponding square-wave anodic stripping voltammetric for different concentration levels from 0 to 40 $\mu\text{g L}^{-1}$. Experimental conditions: deposition potential -0.4 V ; deposition time 70 s.

3.3. Interference Measurement

When designing an electrochemical sensor for practical water monitoring, ensuring selectivity is just as critical as achieving a low detection limit. In the case of arsenic, copper is notoriously known as one of the most troublesome interfering ions [36]. This usually occurs for two reasons, the stripping peaks of As(0) to As(III) and Cu(0) to Cu(II) heavily overlap in the same potential region [37], and copper tends to form intermetallic compounds with arsenic during the deposition step [38,39].

To see how this interaction played out, we ran cyclic voltammograms in the anodic direction while step-by-step raising the Cu(II) concentration (Figure 7a).

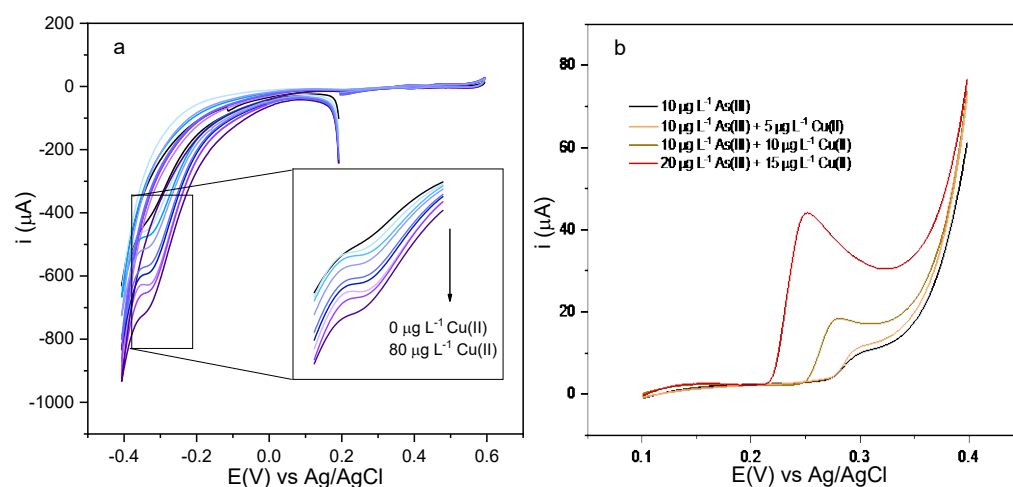


Figure 7. (a) Cyclic voltammetry in anodic direction with variation in Cu(II) concentration. (b) Comparison in the As(III) and Cu(II) mixture signal.

The copper reduction point can be identified; in b, the results obtained show that the Ag-Fe₃O₄-CPE electrode is stable, since increasing the Cu(II) concentrations from 5 to 15 µg L⁻¹. For (b), the peak resulting from the arsenic measurement in the presence of copper increases the resulting signal. This phenomenon has been previously reported using a gold electrode [50], as well as with a silver-modified electrode [51].

Cadmium is another contaminant frequently found alongside arsenic in water sources [52,53]. The results of this study are shown in Figure 8.

In Figure 8a it can be seen that the increase in the concentration of Cd(II) is not reflected in working potential window; in b) the result of the potential sweep is shown in which it can be observed that the presence of Cd(II) does not affect the arsenic signal, which agrees with what was reported by Zhu et al. [54] who report the possibility of identifying the signal of several elements with an electrode with noble metals and iron structures.

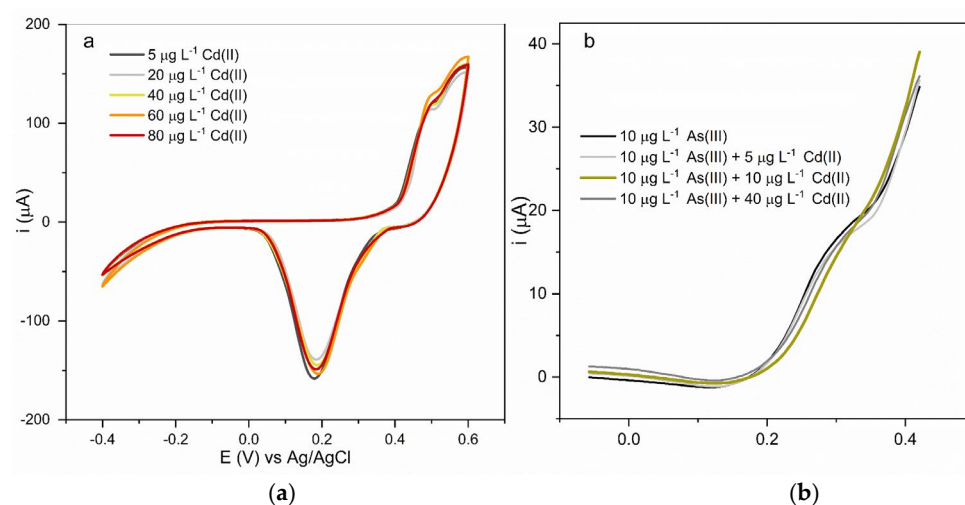


Figure 8. (a) Cyclic voltammetry in anodic direction with variation in Cd(II) concentration. (b) Comparison in the As(III) and Cd(II) mixture signal.

3.4. Electrode Aging

The aging of the working electrode was evaluated by measurements in a 10 µg L⁻¹ As(III) solution, three measurements per day for a period of 44 days. The electrode's performance is summarized in Figure 9.

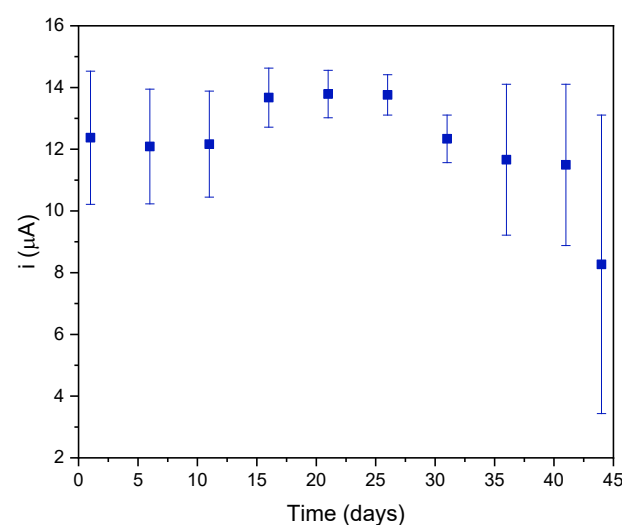


Figure 9. Long-term stability response of the Ag-Fe₃O₄ NPs-CPE over a period of 44 days. The measurement was performed in a solution of 10 µg L⁻¹ As(III) ($n = 3$).

From day 1 to approximately day 15, the peak current showed minor variations, fluctuating between 10 and 14 μA . However, the electrochemical response became considerably more stable and reproducible between days 16 and 31.

This phenomenon may be due to a phenomenon described by Švancara et al. [55] called “Self-Homogenization,” which refers to changes that occur in the carbon paste with respect to the processing time. After day 31, the electrode signal drops, approximately 33% compared to the initial signal. This decay marks the end of the sensor’s operational lifetime. To place both the analytical performance and operational stability of the proposed electrode in context, Table 2 compares its main analytical characteristics with those reported for other electrochemical platforms used for arsenic determination.

Table 2. Application of different electrochemical platforms for the quantification of arsenic.

Arsenic Species	Electrochemical Platform	Sweep Technique	LOD ($\mu\text{g L}^{-1}$)	Stability (Days)	Sensitivity ($\mu\text{A}(\mu\text{g L}^{-1})^{-1}$)	Linear Range ($\mu\text{g L}^{-1}$)	Reference
III	GO-g- Fe_3O_4 -PAMAM-COOH/AuNPs	SWASV	0.47	15 *	-	1 to 125	[56]
III	Fe_3O_4 -Au-IL/GCE	SWASV	0.22	-	122	0 to 100	[57]
III	Chitosan-Catechol modified carbon paper	DP	0.82	30	7.79	1 to 100	[58]
III	Au nano/ Fe -MOFs	SWASV	0.0085	-	4.708	0.2 to 2 2 to 30	[54]
III	$\text{Fe}_3\text{O}_4/\text{Co}_3\text{S}_4$ -SPCE	SWASV	0.691	10	4.359	1 to 10	[59]
III	rGO/AuNP/ MnO_2	SWASV	2.4	42	0.03015	25 to 200	[60]
III	AuNPs-L-Cyst/SPCE	LSASV	0.91	-	4.679	1 to 200	[61]
III	Fe_3O_4 -rGO	SW	1.19	-	2.15	1 to 20	[42]
III	$\text{Ag}@\text{SiO}_2/\text{PANI}$ NFs/SPCE	SWASV	0.013	-	0.83	0.1 to 100	[62]
III	Gold electrode modified with AgNPs	DP	1.03	-	0.0459	3.75 to 15	[45]
V	Ag-NP-SPCNFEs	DP	0.6	-	0.000109	1.9 to 25.1	[63]
III	Nanocomposite silane grafted bentonite CPE	DP	0.0036	-	0.0469	0.5 to 20	[64]
III	NS-Pt-doped NiCo_2O_4 CPE	SW	0.05	28	0.1438	0.1 to 125	[65]
III	ZnO -GO/MCPE	DP	0.03	-	-	10 to 80	[66]
III	$\text{Ag}/\text{Fe}_3\text{O}_4$ NPs CPE	SW	0.51396	30	0.9468	4.68 to 40	This work

DP—differential pulse; SW—square-wave; SPCE—screen-printed carbon electrode; CPE—carbon paste electrode; PAMAM—poly(amidoamine) dendrimer; Fe_3O_4 -Au-IL—linker-free magnetite-decorated gold nanoparticles; MOFs—hybrid of amino-containing Fe-based metal–organic frameworks; PANI—polyaniline; SPCNFEs—carbon-nanofiber-based screen-printed electrodes; MCPE—modified carbon paste electrode. * The sensor retained 97.8% of its initial response after 7 days and 90.3% after 15 days.

The $\text{Ag}/\text{Fe}_3\text{O}_4$ NPs-CPE developed in this work achieved a limit of detection (LOD) of $0.514 \mu\text{g L}^{-1}$, which is comparable to those reported for several Fe_3O_4 and Au-based electrochemical platforms. Although lower detection limits have been reported for some nanostructured electrodes, the proposed sensor provides adequate analytical performance while maintaining a simple electrode design and fabrication procedure. Only a limited number of studies reported the limit of quantification (LOQ), making a direct comparison difficult. The proposed electrode exhibited a LOQ of $4.68 \mu\text{g L}^{-1}$, which falls within the range of the few values available in the literature. In addition, the linear working range ($4.68\text{--}40 \mu\text{g L}^{-1}$) includes the World Health Organization (WHO) guideline value for arsenic in drinking water ($10 \mu\text{g L}^{-1}$), supporting its potential application for routine environmental monitoring.

3.5. Impedance Spectroscopy

We used electrochemical impedance spectroscopy to see how electrons move at the electrode surface. Looking at the Nyquist plots in Figures 10 and 11, all modified electrodes show a smaller loop compared to the bare CPE. This means that adding nanoparticles drops the interface resistance.

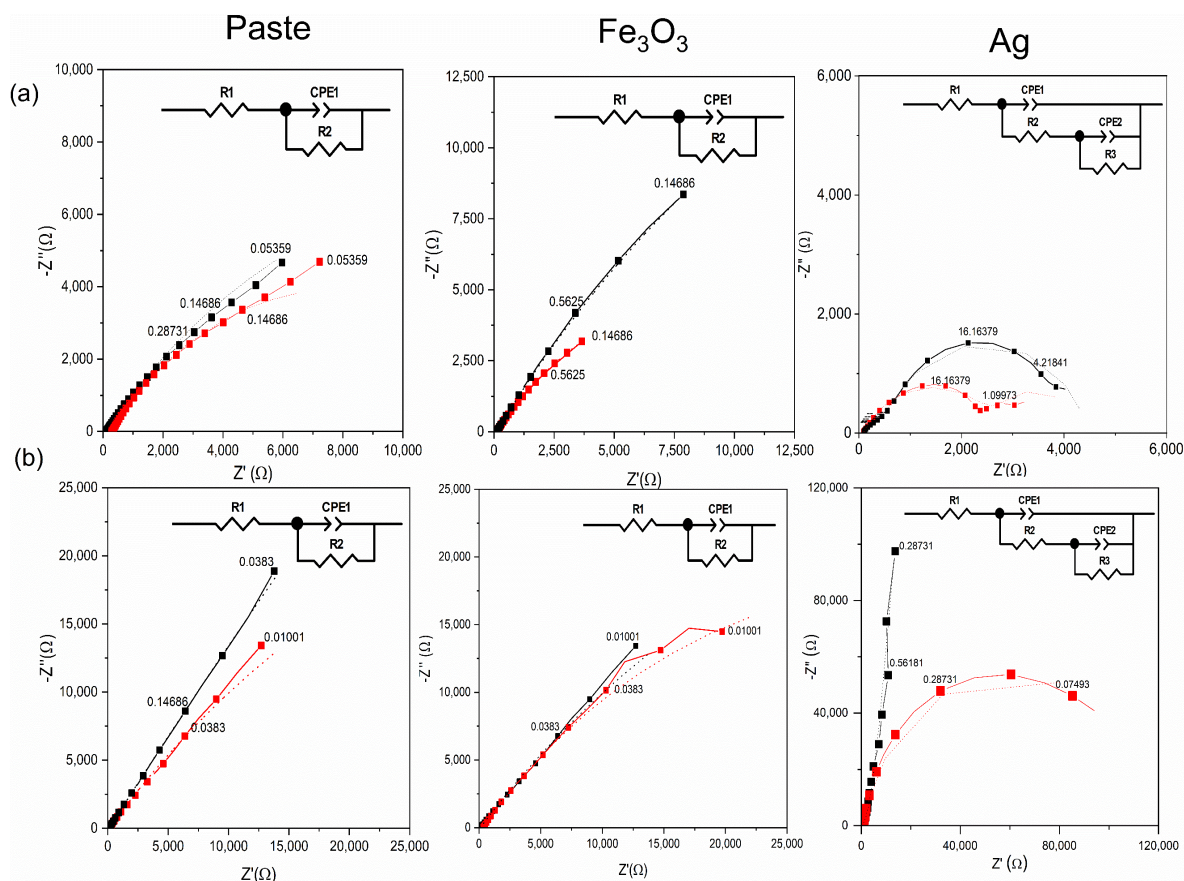


Figure 10. Nyquist diagram, (a) corresponds to -0.4 V deposition and (b) to 0.2 V redissolution, for each of the components; black line, measurements in phosphate buffer support electrolyte solution, red line, measurement in $100 \mu\text{g L}^{-1}$ As(III) solution.

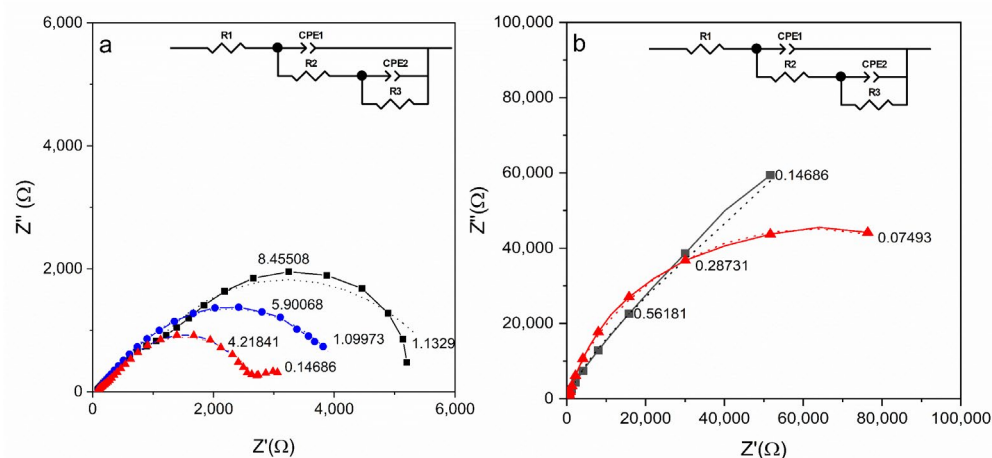


Figure 11. Nyquist diagrams for Ag-Fe₃O₄ NPs-CPE, (a) corresponds to deposition potential and (b) redissolution potential, black line measurement in support electrolyte and red measurement in $100 \mu\text{g L}^{-1}$ As(III), blue line $50 \mu\text{g L}^{-1}$ As(III).

We fitted our experimental data using equivalent electrical circuits to calculate the parameters of the interface (Table 3). The solution resistance, represented by R1 [67], stayed stable between 2 and 3 $\Omega \text{ cm}^2$ across most tests, which confirms that our supporting electrolyte remained stable throughout the experiments. The real variations appeared in R2, which represents the charge-transfer resistance. When we applied a deposition potential of -400 mV in the buffer solution, the bare CPE showed a resistance of $0.634 \times 10^3 \Omega \text{ cm}^2$ in the buffer solution. Testing the evaluation of the single-modifier Fe_3O_4 NPs-CPE yielded a slightly higher value of $R2 = 0.872 \times 10^3 \Omega \text{ cm}^2$ which makes sense given the semiconductor nature of magnetite [68]. On the other hand, adding silver nanoparticles alone (AgNPs-CPE) successfully lowered the opposition to electron transport. In contrast, the addition of silver nanoparticles alone (Ag NPs-CPE) effectively minimized opposition to electron transfer, dropping R2 to $0.133 \times 10^3 \Omega \text{ cm}^2$ due to the high conductivity of silver.

We found a completely different behavior for the hybrid matrix Ag/ Fe_3O_4 NPs-CPE. In the blank supporting electrolyte at -400 mV , the hybrid surface displayed a high resistance of $2.40 \times 10^3 \Omega \text{ cm}^2$. However, as soon as we added $100 \mu\text{g L}^{-1} \text{ As(III)}$, R2 suffered a massive drop to $0.00417 \times 10^3 \Omega \text{ cm}^2$. This sharp drop represents the highest conductivity among all the systems we studied. This occurs because As(0) deposits rapidly onto the electrode surface, building a temporary metallic network that works in perfect synergy with the silver nanoparticles.

The constant phase element values CPE describe the double-layer capacitance as a function of surface texturing [69]. Additionally, the second relaxation loop which appears at lower frequencies, modeled by R3 and CPE2 for the silver and hybrid setups, represents mass transport and adsorption dynamics at the surface. When we changed the potential to a redissolution value of 200 mV , the bare CPE remained highly resistive, showing an R2 of $402 \times 10^3 \Omega \text{ cm}^2$ in both solutions. In contrast, the Ag/ Fe_3O_4 NPs-CPE maintained remarkably low values of $0.00454 \times 10^3 \Omega \text{ cm}^2$ in buffer and $0.00172 \times 10^3 \Omega \text{ cm}^2$ with analyte. This behavior confirms that the combination of magnetite as an active anchor and silver as an electron pathway successfully enhances charge-transfer kinetics during both the deposition and stripping steps.

Equivalent circuits are a key part of interpreting impedance data because they help us visualize how electrochemical reactions take place at the electrolyte/electrode interface [70]. In our simulations, we used constant phase elements to achieve a better fit, calculating the true capacitance values through Equation (3):

$$Y_0 = (Capp)^p \quad (3)$$

where Y_0 is a coefficient calculated from the capacitance (Capp) and p is a parameter < 1 for a non-ideal capacitor [71]. The circuit element values obtained from the simulation are listed in Table 3.

Table 3. Values of equivalent circuit elements.

Electrode	Potential (mV)	Solution	R1 ($\Omega \text{ cm}^2$)	R2 ($\Omega \text{ cm}^2 \times 10^3$)	CPE1 ($\text{F/cm}^2 \times 10^{-6}$)	R3 ($\Omega \text{ cm}^2 \times 10^4$)	CPE2 ($\text{F/cm}^2 \times 10^{-6}$)
Fe_3O_4 NPs-CPE	200	Phosphate buffer	3.18	3.55	395		
Fe_3O_4 NPs-CPE	200	As	10.56	2.28	237		
Fe_3O_4 NPs-CPE	-400	Phosphate buffer	2.96	0.872	355		
Fe_3O_4 NPs-CPE	-400	As	8.95	0.484	233		
Paste	200	Phosphate buffer	3.58	402	164		
Paste	200	As	3.58	402	164		
Paste	-400	Phosphate buffer	3.26	0.634	318		
Paste	-400	As	3.13	0.224	1380		
Ag NPs-CPE	200	Phosphate buffer	2.89	210	157	31,400	6.50

Ag NPs-CPE	200	As	2.44	3.80	6.19	729	8.95
Ag NPs-CPE	−400	Phosphate buffer	2.60	0.133	89.4	0.0203	136
Ag NPs-CPE	−400	As	2.73	0.126	461	0.000170	12.2
Ag/Fe ₃ O ₄ NPs-CPE	200	Phosphate buffer	2.29	0.00454	11.9	1.10	7.64
Ag/Fe ₃ O ₄ NPs-CPE	200	As	2.43	0.00172	9.57	0.405	5.19
Ag/Fe ₃ O ₄ NPs-CPE	−400	Phosphate buffer	2.29	2.40	19.4	0.00846	3.85
Ag/Fe ₃ O ₄ NPs-CPE	−400	As	2.71	0.00417	14.4	0.00922	4.64

The electrodes that resulted in the most notable change were Ag NPs-CPE and Ag-Fe₃O₄ NPs-CPE. For these electrodes, a decrease in resistance to electron transport was observed; in addition, the adsorptive capacity of the materials was identified by the shape of the last semicircle in the Nyquist diagram (Figures 10a and 11a).

3.6. Electrochemical Characterization

To evaluate the electroactive area of the Ag-Fe₃O₄ NPs-CPE, cyclic voltammetry experiments were carried out using the ferricyanide–ferrocyanide redox system over a scan rate range of 10 to 60 mV·s^{−1} (Figure 12).

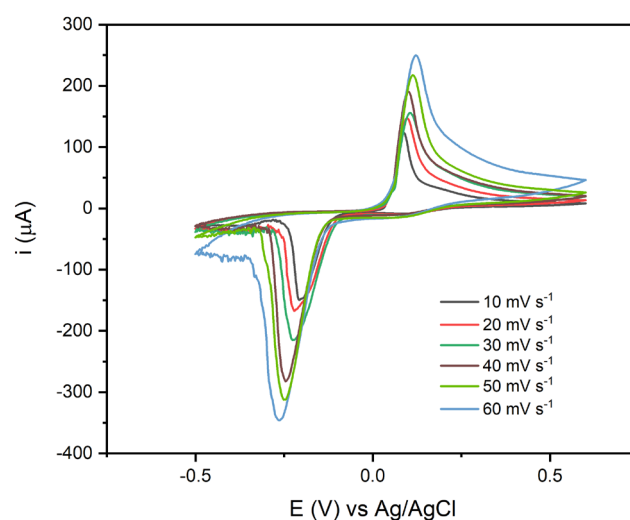


Figure 12. Cyclic voltammetry was performed in a 4.0 mM K₃Fe(CN)₆ solution at scan rates of 10–60 mV·s^{−1}.

The linear dependence between the peak current (I_p) and the square root of the scan rate ($v^{1/2}$) was employed to estimate the electroactive area, according to the Randles–Sevcik equation:

$$I_p = 2.69 \times 10^5 n^{3/2} A C D^{1/2} v^{1/2} \quad (4)$$

where I_p denotes the peak current, n represents the number of electrons in the redox reaction ($n = 1$), A is the electroactive surface area of the electrode, C corresponds to the concentration of potassium ferrocyanide (4.0 mM), D is the diffusion coefficient (7.603×10^{-6} cm²·s^{−1}), and v is the scan rate applied during the measurement. The average electroactive area is 0.0527 cm².

To further characterize the electron-transfer kinetics, a Tafel analysis was performed using the voltammogram recorded at a scan rate of 80 mV s^{−1}. The linear region preceding the oxidation peak, where the current is primarily governed by activation-controlled kinetics, was selected for analysis. The faradaic current was obtained by subtracting the background current from the measured response, and the electrode potential was plotted against the logarithm of the faradaic current (Figure 13).

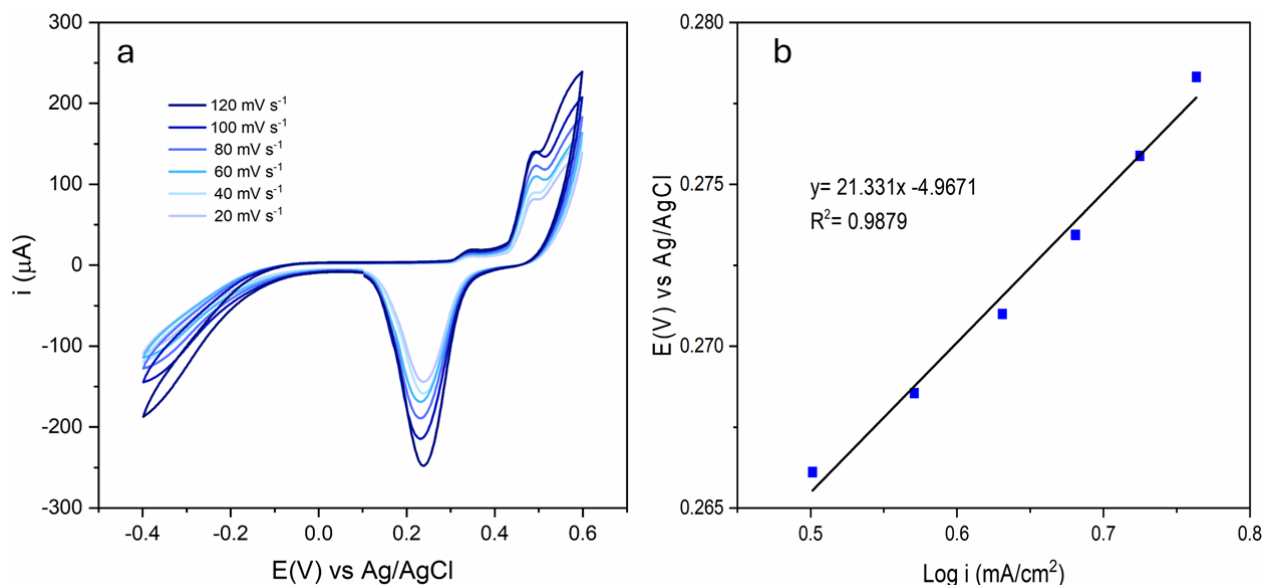


Figure 13. Electrochemical characterization of Ag-Fe₃O₄ NPs-CPE. (a) Cyclic voltammograms recorded in a 10 μg L⁻¹ As(III) solution at scan rates ranging from 20 to 120 mV s⁻¹. The different shades of blue correspond to increasing scan rates from 20 to 120 mV s⁻¹, as indicated in the inset legend. (b) Tafel plot used to determine the apparent charge-transfer coefficient.

The resulting linear fit was used to calculate the apparent charge-transfer coefficient (α) and the exchange current (I_0) based on the Butler–Volmer model.

3.7. Electrochemical Kinetic Analysis

The electron-transfer kinetics of the modified electrode were investigated by cyclic voltammetry at scan rates of 20–120 mV s⁻¹. The anodic peak current (I_p) was measured from each voltammogram, and a linear relationship between I_p and the square root of the scan rate ($v^{1/2}$) was established. This relationship was analyzed according to the Randles–Sevcik equation [72] to evaluate the charge transport mechanism governing the electrochemical process.

The slope of the linear fit was used to estimate kinetic parameters for mass transport and electron transfer, accounting for the number of transferred electrons, arsenic concentration, electroactive surface area, and diffusion coefficient. In addition, the coefficient of determination (R^2) was used to assess whether the electrochemical response was predominantly diffusion-controlled or influenced by charge-transfer limitations.

The combined electrochemical evidence obtained from cyclic voltammetry, Tafel analysis, and electrochemical impedance spectroscopy supports the sensing mechanism proposed in Figure 14. The schematic summarizes the role of Fe₃O₄ nanoparticles in As(III) preconcentration through surface adsorption and the contribution of Ag nanoparticles to enhanced electron-transfer kinetics, ultimately leading to an improved anodic stripping response.

As illustrated in Figure 14, the electrochemical evidence obtained in this work provides a comprehensive interpretation of the proposed sensing mechanism for As(III) detection using Ag-Fe₃O₄ NPs-CPE. Cyclic voltammetry identified the redox processes associated with arsenic deposition and stripping, while kinetic analysis provided information on the apparent electron-transfer characteristics of the modified electrode. In parallel, electrochemical impedance spectroscopy revealed a significant decrease in charge-transfer resistance (R_{ct}), indicating that the incorporation of Ag and Fe₃O₄ nanoparticles facilitates interfacial electron transfer. Rather than considering these techniques independently, their combined interpretation allows the deposition, adsorption, electron-

transfer, and stripping processes to be explained within a single electrochemical mechanism. This approach is consistent with previous studies emphasizing that Tafel analysis should be interpreted together with impedance measurements and complementary electrochemical techniques to obtain a more reliable description of reaction kinetics and interfacial processes [73–75].

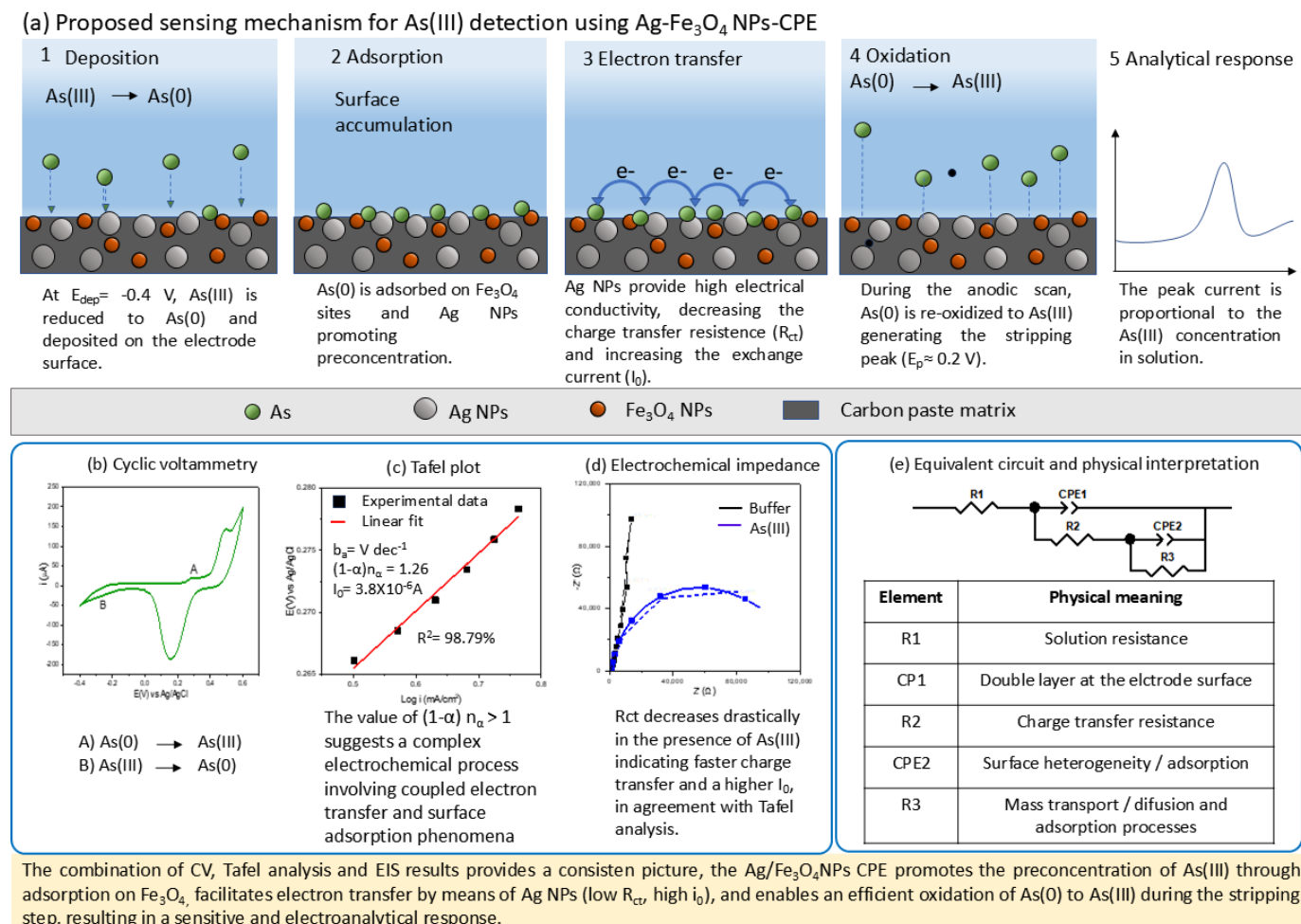


Figure 14. Proposed sensing mechanism of As(III) at the Ag-Fe₃O₄ NPs-CPE based on CV, Tafel, and EIS analyses.

4. Conclusions

A carbon paste electrode modified with silver and magnetite nanoparticles was successfully developed for the electrochemical quantification of As(III) by square-wave anodic stripping voltammetry. The proposed Ag-Fe₃O₄ NPs-CPE exhibited a linear working range between 4.68 and 40 $\mu\text{g L}^{-1}$, a limit of detection of 0.514 $\mu\text{g L}^{-1}$, and adequate analytical stability over a period of 30 days. The analytical range includes the maximum arsenic concentration established by the World Health Organization and the Mexican drinking water regulation, demonstrating its suitability for the determination of environmentally relevant concentrations.

The electrochemical characterization carried out by cyclic voltammetry, electrochemical impedance spectroscopy, and kinetic analysis contributed to a better understanding of the behavior of the modified electrode during arsenic detection. Cyclic voltammetry allowed the identification of the deposition and stripping processes, while impedance measurements showed a decrease in the charge-transfer resistance after incorporating Ag and Fe₃O₄ nanoparticles. Likewise, the kinetic analysis indicated that the electrochemical

response is governed by a diffusion-controlled process with favorable electron-transfer characteristics. Altogether, these results support the proposed sensing mechanism, in which Fe_3O_4 nanoparticles promote arsenic accumulation on the electrode surface through adsorption, whereas Ag nanoparticles facilitate electron transfer during the stripping step, resulting in an enhanced analytical response.

The combination of both nanomaterials produced a synergistic effect that was not observed when each modifier was evaluated individually, confirming that the simultaneous incorporation of Ag and Fe_3O_4 improves the electrochemical performance of the carbon paste electrode. In addition, the interference study showed that Cd(II) did not significantly affect the arsenic signal, whereas Cu(II) remained the main interfering species because of the overlap between the stripping signals of both metals.

Overall, the proposed Ag- Fe_3O_4 NPs-CPE combines low fabrication cost, simple preparation, good analytical performance, and adequate operational stability, making it a promising alternative for routine arsenic monitoring in water samples. Furthermore, the electrochemical characterization presented in this work not only demonstrates the analytical capability of the electrode but also provides a mechanistic explanation for enhanced sensing performance, which may contribute to the rational design of future electrochemical sensors for environmental monitoring.

Author Contributions: D.E.S.-N.: Conceptualization, methodology, investigation, formal analysis, data curation, writing—original draft. L.R.-C.: Methodology, investigation, data curation, writing—review and editing. J.R.I.-C.: Formal analysis, validation, writing—review and editing. M.T.A.-H.: Supervision, resources, funding acquisition, project administration, visualization, writing—review & editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data will be made available on request.

Acknowledgments: The authors acknowledge the academic support of Luis Arturo Torres Castañón, as well as the assistance of Rubí Resendiz Ramírez and Azucena Osornio Villa in the measurements and interpretation of electrochemical impedance spectroscopy data. Soto-Nájera gratefully acknowledges the financial support provided by Secretaría de Ciencia, Humanidades, Tecnología e Innovación for the scholarship.

Conflicts of Interest: The authors declare no conflicts of interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Rahaman, M.S.; Rahman, M.M.; Mise, N.; Sikder, M.T.; Ichihara, G.; Uddin, M.K.; Kurasaki, M.; Ichihara, S. Environmental Arsenic Exposure and Its Contribution to Human Diseases, Toxicity Mechanism and Management. *Environ. Pollut.* **2021**, *289*, 117940. <https://doi.org/10.1016/j.envpol.2021.117940>.
2. Palma-Lara, I.; Martínez-Castillo, M.; Quintana-Pérez, J.C.; Arellano-Mendoza, M.G.; Tamay-Cach, F.; Valenzuela-Limón, O.L.; García-Montalvo, E.A.; Hernández-Zavala, A. Arsenic Exposure: A Public Health Problem Leading to Several Cancers. *Regul. Toxicol. Pharmacol.* **2020**, *110*, 104539. <https://doi.org/10.1016/j.yrtph.2019.104539>.
3. Boffetta, P.; Zunarelli, C.; Borron, C. Dose-Response Analysis of Exposure to Arsenic in Drinking Water and Risk of Skin Lesions: A Systematic Review of the Literature. *Dose-Response* **2020**, *18*, 1559325820957823. <https://doi.org/10.1177/1559325820957823>.

4. Vahter, M.; Skröder, H.; Rahman, S.M.; Levi, M.; Derakhshani Hamadani, J.; Kippler, M. Prenatal and Childhood Arsenic Exposure through Drinking Water and Food and Cognitive Abilities at 10 Years of Age: A Prospective Cohort Study. *Environ. Int.* **2020**, *139*, 105723. <https://doi.org/10.1016/j.envint.2020.105723>.
5. Chandio, T.A.; Khan, M.N.; Muhammad, M.T.; Yalcinkaya, O.; Wasim, A.A.; Kayis, A.F. Fluoride and Arsenic Contamination in Drinking Water Due to Mining Activities and Its Impact on Local Area Population. *Environ. Sci. Pollut. Res.* **2021**, *28*, 2355–2368. <https://doi.org/10.1007/s11356-020-10575-9>.
6. López Porras, G.; Allard, P. Making Waves: Public Health Risks from Arsenic in Mexico's Water Extraction Practices. *Water Res. X* **2025**, *26*, 100283. <https://doi.org/10.1016/j.wroa.2024.100283>.
7. WHO; World Bank Group; UNICEF. *State of the World's Drinking Water*; WHO: Geneva, Switzerland, 2022.
8. Patel, A.K.; Singh, A.; Das, N.; Kumar, M. Health Risk Associated with Consumption of Arsenic Contaminated Groundwater in the Ganga and the Brahmaputra Floodplain of India. *Case Stud. Chem. Environ. Eng.* **2021**, *3*, 100103. <https://doi.org/10.1016/j.cscee.2021.100103>.
9. Bundschuh, J.; Armienta, M.A.; Morales-Simfors, N.; Ayaz, M.; López, D.L.; Dietrich, S.; Schneider, J.; Delgado, V.; Tapia, J.; Sracek, O.; et al. Arsenic in Latin America: New Findings on Source, Mobilization and Mobility in Human Environments in 20 Countries Based on Decadal Research 2010–2020. *Crit. Rev. Environ. Sci. Technol.* **2021**, *51*, 16. <https://doi.org/10.1080/10643389.2020.1770527>.
10. Podgorski, J.; Berg, M. Global Threat of Arsenic in Groundwater. *Science* **2020**, *368*, 845–850. <https://doi.org/10.1126/science.aba1510>.
11. Irigoyen-Campuzano, J.; Barraza-Barraza, D.; Gutiérrez, M.; Reynoso-Cuevas, L.; Alarcón-Herrera, M.T. Hydrogeochemical Characterization of an Intermontane Clustering Analysis. *Hydrology* **2024**, *11*, 6. <https://doi.org/10.3390/hydrology11060076>.
12. NOM-127-SSA1-2021; Agua Para Uso y Consumo Humano. Límites Permisibles de la Calidad del Agua. Secretaría de Salud: Mexico City, Mexico, 2022.
13. NOM-201-SSA1-2015; Productos y Servicios. Agua y Hielo Para Consumo Humano, Envasados y a Granel. Secretaría de Salud: Mexico City, Mexico, 2015.
14. Bhat, A.; Hara, T.O.; Tian, F.; Singh, B. Review of Analytical Techniques for Arsenic Detection and Determination in Drinking Water. *Environ. Sci. Adv.* **2023**, *2*, 171–195. <https://doi.org/10.1039/d2va00218c>.
15. Reid, M.S.; Hoy, K.S.; Schofield, J.R.M.; Uppal, J.S.; Lin, Y.; Lu, X.; Peng, H.; Le, X.C. Arsenic Speciation Analysis: A Review with an Emphasis on Chromatographic Separations. *TrAC Trends Anal. Chem.* **2020**, *123*, 115770. <https://doi.org/10.1016/j.trac.2019.115770>.
16. Borrill, A.J.; Reily, N.E.; Macpherson, J.V. Addressing the Practicalities of Anodic Stripping Voltammetry for Heavy Metal Detection: A Tutorial Review. *Analyst* **2019**, *144*, 6834–6849. <https://doi.org/10.1039/c9an01437c>.
17. Rath, B.S.; Kumar, P.S.; Vo, D.-V.N. Critical Review on Hazardous Pollutants in Water Environment: Occurrence, Monitoring, Fate, Removal Technologies and Risk Assessment. *Sci. Total Environ.* **2021**, *797*, 149134. <https://doi.org/10.1016/j.scitotenv.2021.149134>.
18. Rajawat, D.S.; Kumar, N.; Satsangee, S.P. Trace Determination of Cadmium in Water Using Anodic Stripping Voltammetry at a Carbon Paste Electrode Modified with Coconut Shell Powder. *J. Anal. Sci. Technol.* **2014**, *5*, 19. <https://doi.org/10.1186/s40543-014-0019-0>.
19. Kolya, H.; Hashitsume, K.; Kang, C.W. Recent Advances in Colorimetric Detection of Arsenic Using Metal-Based Nanoparticles. *Toxics* **2021**, *9*, 143. <https://doi.org/10.3390/toxics9060143>.
20. Devi, P.; Thakur, A.; Lai, R.Y.; Saini, S.; Jain, R.; Kumar, P. Progress in the Materials for Optical Detection of Arsenic in Water. *TrAC Trends Anal. Chem.* **2019**, *110*, 97–115. <https://doi.org/10.1016/j.trac.2018.10.008>.
21. Ardini, F.; Dan, G.; Grotti, M. Arsenic Speciation Analysis of Environmental Samples. *J. Anal. At. Spectrom.* **2020**, *35*, 215–237. <https://doi.org/10.1039/c9ja00333a>.
22. Merji, A.; Curri, M.L.; Ingrosso, C.; Mars, A. All-in-One Electrochemical Platform with Integrated O₂-Filtering Electrocatalyst towards on-Site Simultaneous Ultratrace Detection of Multiple Heavy Metals in Real Water Samples. *Sens. Actuators B. Chem.* **2026**, *446*, 138633.
23. Kaimal, R.; Maridevaru, M.C.; Dube, A.; Wu, J.J.; Sambandam, A.; Ashokkumar, M. Borophene Nanosheet-Based Electrochemical Sensing toward Groundwater Arsenic Detection. *Ind. Eng. Chem. Res.* **2023**, *62*, 15418–15427. <https://doi.org/10.1021/acs.iecr.3c01922>.
24. Shalvi; Gautam, V.; Lata Verma, K.; Suman; Jain, V.K.; Kumar, A. An Overview of Advanced Approaches for Detecting Arsenic at Trace Levels. *Environ. Nanotechnol. Monit. Manag.* **2022**, *18*, 100730. <https://doi.org/10.1016/j.enmm.2022.100730>.

25. Martynov, L.Y.; Dymova, A.V.; Semyachkin, I.A.; Nikulin, A.V.; Sakharov, K.A.; Yashtulov, N.A.; Zaytsev, N.K. Electrochemical and Microscopic Study of a Rotating Disk Gold-Film Electrode for Voltammetric Determination of Arsenic (III). *Microchem. J.* **2024**, *205*, 111177. <https://doi.org/10.1016/j.microc.2024.111177>.
26. Bhat, A.; Gupta, A.K.; O'Connor, C.; Tian, F.; Singh, B. Emergence of Electroanalytical Techniques for Arsenic Detection in Water: Recent Trends and Future Perspectives. *ChemElectroChem* **2025**, *12*, e202500259. <https://doi.org/10.1002/celec.202500259>.
27. Zamani, M.; Klapperich, C.M.; Furst, A.L. Recent Advances in Gold Electrode Fabrication for Low-Resource Setting Biosensing. *Lab A Chip* **2023**, *23*, 1410–1419. <https://doi.org/10.1039/d2lc00552b>.
28. Touilloux, R.; Tercier-Waeber, M.L.; Bakker, E. Direct Arsenic(III) Sensing by a Renewable Gold Plated Ir-Based Microelectrode. *Analyst* **2015**, *140*, 3526–3534. <https://doi.org/10.1039/c5an00151j>.
29. Luong, J.H.T.; Lam, E.; Male, K.B. Recent Advances in Electrochemical Detection of Arsenic in Drinking and Ground Waters. *Anal. Methods* **2014**, *6*, 6157–6169. <https://doi.org/10.1039/c4ay00817k>.
30. Zhang, Y.; Feng, H.; Wu, X.; Wang, L.; Zhang, A.; Xia, T.; Dong, H.; Li, X.; Zhang, L. Progress of Electrochemical Capacitor Electrode Materials: A Review. *Int. J. Hydrog. Energy* **2009**, *34*, 4889–4899. <https://doi.org/10.1016/j.ijhydene.2009.04.005>.
31. Mesarić, Š.; Dahemen, E.A.M.F. Ion-selective carbon-paste electrodes for halides and silver (I) ions. *Anal. Chim. Acta* **1973**, *64*, 431–438.
32. Zaib, M.; Athar, M.M.; Saeed, A.; Farooq, U. Electrochemical Determination of Inorganic Mercury and Arsenic—A Review. *Biosens. Bioelectron.* **2015**, *74*, 895–908. <https://doi.org/10.1016/j.bios.2015.07.058>.
33. Cox, J.A.; Rutkowska, I.A.; Kulesza, P.J. Critical Review—Electrocatalytic Sensors for Arsenic Oxo Species. *J. Electrochem. Soc.* **2020**, *167*, 037565. <https://doi.org/10.1149/1945-7111/ab697d>.
34. Feng, L.; Cao, M.; Ma, X.; Zhu, Y.; Hu, C. Superparamagnetic High-Surface-Area Fe₃O₄ Nanoparticles as Adsorbents for Arsenic Removal. *J. Hazard. Mater.* **2012**, *217*, 439–446. <https://doi.org/10.1016/j.jhazmat.2012.03.073>.
35. Toor, S.K.; Devi, P.; Bansod, B.K.S. Electrochemical Detection of Trace Amount of Arsenic (III) at Glassy Carbon Electrode Modified with Au/Fe₃O₄ Nanocomposites. *Aquat. Procedia* **2015**, *4*, 1107–1113. <https://doi.org/10.1016/j.aqpro.2015.02.140>.
36. Liang, B.; Xiao, X.Y.; Song, Z.Y.; Li, Y.Y.; Cai, X.; Xia, R.Z.; Chen, S.H.; Yang, M.; Li, P.H.; Lin, C.H.; et al. Revealing the Solid-Solution Interface Interference Behaviors between Cu²⁺ and As(III) via Partial Peak Area Analysis of Simulations and Experiments. *Anal. Chim. Acta* **2023**, *1277*, 341676. <https://doi.org/10.1016/j.aca.2023.341676>.
37. Bu, L.; Xie, Q.; Ming, H. Gold Nanoparticles Decorated Three-Dimensional Porous Graphitic Carbon Nitrides for Sensitive Anodic Stripping Voltammetric Analysis of Trace Arsenic(III). *J. Alloys Compd.* **2020**, *823*, 153723. <https://doi.org/10.1016/j.jallcom.2020.153723>.
38. Lan, Y.; Luo, H.; Ren, X.; Wang, Y.; Liu, Y. Anodic Stripping Voltammetric Determination of Arsenic(III) Using a Glassy Carbon Electrode Modified with Gold-Palladium Bimetallic Nanoparticles. *Microchim. Acta* **2012**, *178*, 153–161. <https://doi.org/10.1007/s00604-012-0827-0>.
39. Zhou, C.; Yang, M.; Shanshan, L.; Tianjia, J.; Jinhui, L.; Xingjiu, H.; Xing, C. Electrochemically Etched Gold Wire Microelectrode for the Determination of Inorganic Arsenic. *Electrochim. Acta* **2017**, *231*, 238–246. <https://doi.org/10.1016/j.electacta.2017.01.184>.
40. Chen, R.; Zhi, C.; Yang, H.; Bando, Y.; Zhang, Z.; Sugiur, N.; Golberg, D. Arsenic (V) Adsorption on Fe₃O₄ Nanoparticle-Coated Boron Nitride Nanotubes. *J. Colloid Interface Sci.* **2011**, *359*, 261–268. <https://doi.org/10.1016/j.jcis.2011.02.071>.
41. Xia, X.; Cheng, X.L.; Liu, Z.; Li, J.J.; Li, S.S. Sensitive Detection of As(III) on Fe₃O₄/MoS₂ through Interfacial Engineering to Accelerate the Fe²⁺/Fe³⁺ Cycle: Identifying the Dominant Role of Electron Transfer Induced by Valence Change in Synergistic Electroanalysis. *Sens. Actuators B Chem.* **2022**, *366*, 132022. <https://doi.org/10.1016/j.snb.2022.132022>.
42. Hu, H.; Lu, W.; Liu, X.; Meng, F.; Zhu, J. A High-Response Electrochemical As (III) Sensor Using Fe₃O₄-RGO Nanocomposite Materials. *Chemosensors* **2021**, *9*, 150. <https://doi.org/10.3390/chemosensors9060150>.
43. Lalhrualtuangi, M.; Lalawmpuia, R.; Tiwari, D.; Dubey, R. Nanocomposite Material in the Trace and Simultaneous Electrochemical Detection of As(III) and As(V). *Environ. Eng. Res.* **2025**, *30*, 240663. <https://doi.org/10.4491/eer.2024.663>.
44. Salunke, R.S.; Chavan, P.G.; Shirale, D.J. Anodic Stripping Voltammetry Studies of Electrochemically Engineered Silver Nanoparticles over Single Polypyrrole Nanowire Device for Tracing of Arsenic(III): An Environmental Perspective. *Nanotechnol. Environ. Eng.* **2018**, *3*, 12. <https://doi.org/10.1007/s41204-018-0042-2>.
45. Sonkoue, B.M.; Tchekwagep, P.M.S.; Nanseu-Njiki, C.P.; Ngameni, E. Electrochemical Determination of Arsenic Using Silver Nanoparticles. *Electroanalysis* **2018**, *30*, 2738–2743. <https://doi.org/10.1002/elan.201800520>.
46. Song, K.C.; Lee, S.M.; Park, T.S.; Lee, B.S. Preparation of Colloidal Silver Nanoparticles by Chemical Reduction Method. *Korean J. Chem. Eng.* **2009**, *20*, 153–155. <https://doi.org/10.1007/s11814-009-0024-y>.

47. American Public Health Association (APHA); American Water Works Association (AWWA); Water Environment Federation (WEF). Standard Methods for the Examination of Water and Wastewater. In *Encyclopedia of Meat Sciences*, 3rd ed.; Three Volume Set; Bair, R.B., Eaton, A.D., Rice, E.W., Eds.; Academic Press: Washington, DC, USA, 2017; Volume 3, pp. 344–351. ISBN 9780323851985.
48. Lu, P.; Zhu, C. Arsenic Eh-PH Diagrams at 25°C and 1 Bar. *Environ. Earth Sci.* **2011**, *62*, 1673–1683. <https://doi.org/10.1007/s12665-010-0652-x>.
49. Robles, A.D.; Vettorelo, S.N.; Gerpe, M.; Garay, F. The Electrochemical Reaction Mechanism of Arsenic on Gold Analyzed by Anodic Stripping Square-Wave Voltammetry. *Electrochim. Acta* **2017**, *227*, 447–454. <https://doi.org/10.1016/j.electacta.2016.12.181>.
50. Casuse-Driovinto, T.Q.; Benavidez, A.; Jemison, N.; Cerrato, J.M.; Feliu, J.; Garzón, F.H. Electrochemical Redox of Arsenic (III) and Cu (II) Mixtures with Ultraflat Au(111) Thin Films in Water. *Electrochim. Acta* **2024**, *489*, 144220. <https://doi.org/10.1016/j.electacta.2024.144220>.
51. Cortés, S.P.M.; Galán-Vidal, C.A.; Ávila, J.A.R.; Romero, G.A.Á.; Páez-Hernández, M.E. Square Wave Anodic Stripping Voltammetry Determination of Arsenic (III) onto Carbon Electrodes by Means of Co-Deposition with Silver. *J. Mex. Chem. Soc.* **2018**, *62*, 314–322. <https://doi.org/10.29356/jmcs.v62i2.430>.
52. Ngoc, N.T.M.; Chuyen, N.V.; Thao, N.T.T.; Duc, N.Q.; Trang, N.T.T.; Binh, N.T.T.; Sa, H.C.; Tran, N.B.; Ba, N.V.; Khai, N.V.; et al. Chromium, Cadmium, Lead, and Arsenic Concentrations in Water, Vegetables, and Seafood Consumed in a Coastal Area in Northern Vietnam. *Environ. Health Insights* **2020**, *14*, 1178630220921410. <https://doi.org/10.1177/1178630220921410>.
53. Khellaf, B.; Bouayad, L.; Benouadah, A.; Hamdi, T.M.; Chekri, R.; Jitaru, P. Arsenic, Mercury, Cadmium and Lead Contents in Algerian Continental and Marine Farming Fish and Human Health Risk Assessment Due to Their Consumption. *Reg. Stud. Mar. Sci.* **2023**, *62*, 102943. <https://doi.org/10.1016/j.rsma.2023.102943>.
54. Zhu, X.; Zhu, G.; Ge, Y.; Zhang, B.; Yang, J.; Hu, B.; Liu, J. Aunano/Fe-MOF Hybrid Electrode for Highly Sensitive Determination of Trace As(III). *J. Electroanal. Chem.* **2021**, *899*, 115642. <https://doi.org/10.1016/j.jelechem.2021.115642>.
55. Švancara, I.; Mikysek, T.; Stočes, M.; Ludvík, J. Graphite Powder and Related Material as the Principal Components of Carbon Paste Electrodes. In *Graphite: Properties, Occurrences and Uses*; Campbell, Q.C., Ed.; Nova Science Publishers: Hauppauge, NY, USA, 2013.
56. Liu, H.; Baghayeri, M.; Amiri, A.; Karimabadi, F.; Nodehi, M.; Fayazi, M.; Maleki, B.; Zare, E.N.; Kaffash, A. A Strategy for As(III) Determination Based on Ultrafine Gold Nanoparticles Decorated on Magnetic Graphene Oxide. *Environ. Res.* **2023**, *231*, 116177. <https://doi.org/10.1016/j.envres.2023.116177>.
57. Sedki, M.; Zhao, G.; Ma, S.; Jassby, D.; Mulchandani, A. Linker-Free Magnetite-Decorated Gold Nanoparticles (Fe₃O₄-Au): Synthesis, Characterization, and Application for Electrochemical Detection of Arsenic (III). *Sensors* **2021**, *21*, 883. <https://doi.org/10.3390/s21030883>.
58. Hu, F.; Hu, H.; Li, Y.; Wang, X.; Shi, X. Signal Amplification Strategy by Chitosan-Catechol Hydrogel Modified Paper Electrode for Electrochemical Detection of Trace Arsenite. *Sensors Actuators B Chem.* **2024**, *400*, 134836. <https://doi.org/10.1016/j.snb.2023.134836>.
59. Huang, H.Q.; Li, Y.Y.; Chen, S.H.; Liu, Z.G.; Cui, Y.M.; Li, H.Q.; Guo, Z.; Huang, X.J. Noble-Metal-Free Fe₃O₄/Co₃S₄ Nanosheets with Oxygen Vacancies as an Efficient Electrocatalyst for Highly Sensitive Electrochemical Detection of As(III). *Anal. Chim. Acta* **2022**, *1189*, 339208. <https://doi.org/10.1016/j.aca.2021.339208>.
60. Wu, Y.; Zhang, T.; Su, L.; Wu, X. Electrodeposited RGO/AuNP/MnO₂ Nanocomposite-Modified Screen-Printed Carbon Electrode for Sensitive Electrochemical Sensing of Arsenic(III) in Water. *Biosensors* **2023**, *13*, 563. <https://doi.org/10.3390/bios13050563>.
61. Wang, W.; Yi, Z.; Liang, Q.; Zhen, J.; Wang, R.; Li, M.; Zeng, L.; Li, Y. In Situ Deposition of Gold Nanoparticles and L-Cysteine on Screen-Printed Carbon Electrode for Rapid Electrochemical Determination of As(III) in Water and Tea. *Biosensors* **2023**, *13*, 130. <https://doi.org/10.3390/bios13010130>.
62. Feng, T.; Chen, K.; Zhong, J.; Cheng, Y.; Zhao, H.; Lan, M. Sensors and Actuators: B. Chemical In-Situ Polymerization of Dendritic Polyaniline Nanofibers Network Embedded with Ag @ SiO₂ Core-Shell Nanoparticles for Electrochemical Determination of Trace Arsenic (III). *Sensors Actuators B Chem.* **2022**, *369*, 132265. <https://doi.org/10.1016/j.snb.2022.132265>.
63. Torres-Rivero, K.; Pérez-Ráfols, C.; Bastos-Arrieta, J.; Florido, A.; Martí, V.; Serrano, N. Direct as(V) Determination Using Screen-printed Electrodes Modified with Silver Nanoparticles. *Nanomaterials* **2020**, *10*, 1280. <https://doi.org/10.3390/nano10071280>.

64. Lalmalsawmi, J.; Tiwari, D.; Lee, S. Low Cost, Highly Sensitive and Selective Electrochemical Detection of Arsenic (III) Using Silane Grafted Based Nanocomposite. *Environ. Eng. Res.* **2020**, *25*, 579–587. <https://doi.org/10.4491/eer.2019.245>.
65. Garkani-Nejad, Z.; Javar, H.A.; Mahmoudi-Moghaddam, H. An Efficient Sensor for Simultaneous Determination of Hg (II) and As (III) Using a Carbon Paste Electrode Modified with Needle-Shaped Pt-Doped NiCo₂O₄ Nanograss. *Sens. Actuators B Chem.* **2022**, *258*, 131445. <https://doi.org/10.1016/j.snb.2022.131445>.
66. Singh, S.; Khasnabis, S.; Anil, A.G.; Kumar, V.; Kumar Naik, T.S.; Nath, B.; Garg, V.K.; Singh, J.; Ramamurthy, P.C. Multifunctional Nanohybrid for Simultaneous Detection and Removal of Arsenic(III) from Aqueous Solutions. *Chemosphere* **2022**, *289*, 133101. <https://doi.org/10.1016/j.chemosphere.2021.133101>.
67. Stanković, A.; Kajinić, Ž.; Turkalj, J.V.; Romić, Ž.; Sikirić, M.D.; Asserghine, A.; Nagy, G.; Medvidović-Kosanović, M. Voltammetric Determination of Arsenic with Modified Glassy Carbon Electrode. *Electroanalysis* **2020**, *32*, 1043–1051. <https://doi.org/10.1002/elan.201900666>.
68. Yan, H.; Hu, S. Electrochemical Sensing of Heavy Metal Ions Based on Monodisperse Single-Crystal Fe₃O₄ Microspheres. *J. Wuhan Univ. Technol. Mater. Sci. Ed.* **2018**, *33*, 1422–1427. <https://doi.org/10.1007/s11595-018-1985-7>.
69. Roughness, S. Quantitative Relation of the Frequency Dispersion of Double Layer Capacitances to Surface Roughness. *Adv. Nanosci. Nanotechnol.* **2018**, *2*, 25–28. <https://doi.org/10.33140/ann/02/01/00003>.
70. Chang, B.-Y.; Park, S.-M. Electrochemical Impedance Spectroscopy. *Annu. Rev. Anal. Chem.* **2010**, *3*, 207–229. <https://doi.org/10.1146/annurev.anchem.012809.102211>.
71. Growcock, F.B.; Jasinski, R.J. *Impedance Spectroscopy*; John Wiley & Sons: Hoboken, NJ, USA, 1989.
72. Bard, A.J.; Faulkner, L.R. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; Harris, D., Swan, E., Robey, C., Aiello, E., Eds.; John Wiley & Sons: Hoboken, NJ, USA, 1976.
73. Khadke, P.; Tichter, T.; Boettcher, T.; Muench, F.; Ensinger, W.; Roth, C. A Simple and Effective Method for the Accurate Extraction of Kinetic Parameters Using Differential Tafel Plots. *Sci. Rep.* **2021**, *11*, 8974. <https://doi.org/10.1038/s41598-021-87951-z>.
74. van der Heijden, O.; Park, S.; Vos, R.E.; Eggebeen, J.J.J.; Koper, M.T.M. Tafel Slope Plot as a Tool to Analyze Electrocatalytic Reactions. *ACS Energy Lett.* **2024**, *9*, 1871–1879. <https://doi.org/10.1021/acsenenergylett.4c00266>.
75. Harrington, D.A.; Van Den Driessche, P. Mechanism and Equivalent Circuits in Electrochemical Impedance Spectroscopy. *Electrochim. Acta* **2011**, *56*, 8005–8013. <https://doi.org/10.1016/j.electacta.2011.01.067>.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.