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Electrochemical removal of arsenic and remediation of drinking water quality

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ABSTRACT

Arsenic is one of the most abundant elements on the earth and possesses metallic as well as nonmetallic properties. Besides arsenic is very toxic and carcinogenic, it is found in nature both naturally and anthropogenically. Inorganic arsenic species existing in water are arsenite (As^{3+}) and arsenate (As^{5+}). Arsenic toxicity is a global problem because arsenic contamination is naturally coming from water resources. The maximum admissible concentration of arsenic must not exceed 10 μg L^{-1}, so the determination of the total arsenic amount regardless of its species is very important. In this work, the presence of arsenic was electrochemically determined using cyclic, square wave and differential pulse voltammetry, and a spectroscopic determination method including inductively coupled plasma-mass spectrometry (ICP-MS) was applied. A combination of ICP-MS as a sensitive, multi-element capable and reliable method with electrochemistry as a simple, cost-efficient and powerful method was performed to determine and remove arsenic for the first time. Newly modified nano-dimensional surfaces were developed to obtain specific arsenic behavior and effective electrodeposition of arsenic in the removal process. With the water supply research, regional differences in drinking waters were discovered, and different kinds of drinking water samples were put into a common form in terms of drinkable, arsenic-free, high-grade standards.

Keywords: Arsenic; Drinking water; Spectroscopy; Electrochemistry; Remediation

1. Introduction

Arsenic is classified as a metalloid and found in the VA group of the periodic table. Arsenic is naturally present in Earth's crust but endangers all living beings from humans to animals because of its carcinogenic effects [1]. Besides arsenic is widely used as a raw material in agriculture, pharmacy and other industrial branches, it can naturally appear in water because of water's transition within soil and rock. Although arsenite (As^{3+}) is more toxic than arsenate (As^{5+}) in inorganic forms of As, a great number of countries worldwide are planning to decrease total arsenic levels below the recommended guideline value of 10 μg L^{-1} reported by the World Health Organization (WHO) [2]. In such a dangerous environment, the determination of As is very critical and analytical techniques are capable to measure trace and ultra-trace levels of As. Among a number of analytical methods, electrochemical methods such as linear sweep anodic stripping voltammetry [3], differential pulse anodic stripping voltammetry [4] and chronoamperometry [5] are especially applied because of their low-cost instrumentation, rapid analysis, reagentless procedure, high sensitivity, and low limit of detection (LOD).

Although inorganic arsenic species can be used in the treatment of most diseases such as malaria, syphilis, leukemia and psora, skin lesions are observed in patients using these remedies [6]. Arsenic can be taken into the human body in three ways: aspiration, food and water consumption, and dermatic adsorption. After exposure to arsenic; skin, respiration, heart and blood vessels, immunity, reproductivity, digestion and nerve systems can be affected [7]. When arsenic is absorbed, it deposits in the liver, lung, kidney and heart; even in low doses, accumulates in muscular and nerve tissue. Arsenic toxicology depends on its intake, exposure way and frequency [8]. Therefore, arsenic toxicology can be reduced by determination and removal of it using new technologies. In one of these technologies, inductively coupled plasma-mass spectrometry (ICP-MS) measures the emission instead of absorption from an atomization/excitation/ionization source. A great emission is obtained due to the high temperature in the operation of ICP-MS, and the wavelength of each element is specific. At the same time, ICP-MS is more sensitive, reliable than any other techniques, and can detect samples with extremely low LOD from μg L^{-1} to ng L^{-1} level [9].

As another developing technology, nanotechnology is widely used to modify and increase the analytical performance of electrodes. Different kinds of nanomaterials are recently reported to detect arsenic successfully [10]. Graphene oxide (GO) creates a conductive platform with advantages of their easy fabrication, high conductivity, low cost, robust mechanical properties and large surface to volume ratio in electrochemical sensors, so graphene-based materials have great attention [11]. Carbon nanotubes (CNTs) are another extensively used nanomaterials due to their excellent properties and applications including electrochemical detection and removal of heavy metals from water [12].

This work presents the formation of newly developed surfaces for electrochemical determination and removal of arsenic from drinking water samples. Gold electrode surfaces were electrochemically modified using GO and CNT to obtain a specific arsenic response. Analysis methods of today mainly focus on wastewater or industrial water, but too little effort is made for drinking water coming from various resources such as soil, rock or spring. Three kinds of water samples were obtained from three resources to compare regional differences in the quality of water. As a spectroscopic reference method, ICP-MS was used to determine the total As the concentration of drinking water samples with a very low LOD. These two strong methods including electrochemistry and ICP-MS were combined for the first time in arsenic determination from drinking water. In this manner, As content in water was determined both electrochemically and spectroscopically, excess of arsenic exceeding guideline value of WHO was successfully removed, and a high grade, drinkable and reliable drinking water was obtained for all resources according to limitations accepted by the whole world.

2. Materials and methods

2.1. Chemicals

Drinking water samples were collected from three different resources, and named as rural water, well water and urban water. Each water sample was acidified using concentrated nitric acid (HNO_3) obtained from Merck (Kenilworth, New Jersey). 0.01 mol L^{-1} acetate buffer solution (ABS) was prepared using sodium acetate from AFG Bioscience (Northbrook, USA) and acetic acid from Carlo Erba Reagents (Barcelona, Spain), and pH was adjusted to 5.25 by means of 1.00 mol L^{-1} HCl from Carlo Erba Reagents (Barcelona, Spain) and 1.00 mol L^{-1} NaOH from AFG Bioscience (Northbrook, USA). The 2.00 mg mL^{-1} graphene oxide (GO) suspension was obtained dispersing GO sheets from Aldrich in 0.01 mol L^{-1} ABS. COOH functionalized multi-walled carbon nanotubes (CNTs) were purchased from Nanografi (San Francisco, USA) (N95%, OD: 20–30 nm) and dissolved in 0.01 mol L^{-1} ABS to get the concentration of 1.00 mg mL^{-1}. Heavy metal mix III including As, Cd, Hg and Pb in 12% HNO_3 from Sigma-Aldrich (St. Louis) was prepared in 0.01 mol L^{-1} ABS as 1% by weight. Other reagents were in analytical grade. In all analyses, pure N_2 gas was passed from the solutions to remove oxygen.

2.2. Electrochemical measurements

Electrochemical measurements were performed on PalmSens potentiostat and PS Trace 4.0 software with a conventional three-electrode system including platinum (Pt) wire as the counter electrode, silver/silver chloride (Ag/AgCl) as the reference electrode, and gold (Au) electrode with 0.031 cm^2 area as the working electrodes. The modification of Au surfaces was made in 2.00 mg mL^{-1} GO and 1.00 mg mL^{-1} CNT solutions using cyclic voltammetry (CV) between −0.50 V and +0.50 V vs Ag/AgCl, and the surfaces were called Au/GO and Au/CNT, respectively. As was electrochemically determined using various techniques including differential pulse voltammetry (DPV), square wave voltammetry and CV. Scanning electron microscopy (SEM) images of the modified surfaces were obtained using the Thermo Scientific Apreo S model device (Waltham, Massachusetts). Indium tin oxide (ITO) coated rectangular glass (surface conductivity 70–100 Ω/sq) was purchased from Sigma (St. Louis) and used in SEM studies.

2.3. ICP-MS measurements

ICP-MS measurements were obtained using the Agilent 7900 model ICP-MS Instrument and quadrupole mass analyzer. In the ICP-MS MassHunter software, The general purpose plasma and He modes were used. Before the analytical runs, the instrument was optimized with a tuning solution containing Ce, Co, Li, Tl, Y purchased from Agilent Technologies (Santa Clara, USA), and it was stabilized in rising mode with a 2% v/v HNO_3 for half an hour. QC standard including As was obtained from Redoks LAB and prepared in an acid solution of 2% v/v HNO_3. To improve the ICP-MS performance, an internal solution containing Bi, Ge, In, Li, Lu, Rh, Sc, Tb purchased from Agilent Technologies (Santa Clara, USA) was used. All other operating conditions are listed in Table 1.

3. Results and discussion

3.1. Electrochemical determination of As

Fig. 1 shows the electrochemical determination of As using DPV between −0.10 V and +0.20 V vs. Ag/AgCl. With the adding of 1% As by weight (red) to the 0.01 mol L^{-1} ABS (blue), a well defined As peak was observed at −0.04 V vs. Ag/AgCl. Thus, As signal was obtained in parallel with the literature [13] and all electrochemical measurements were applied in this condition.

Formation of the most stable and effective interaction of an analyte with an electrode is an essential parameter

Table 1
Operating parameters of ICP-MS for drinking water analysis

Operating specification	Parameters
RF power (W)	1,300
Plasma mode	General purpose, He
Omega lens (V)	8.8
Deflect lens (V)	0.0
Cell gas flow rate (mL min^{-1})	4.3
Energy discrimination (V)	5.0
Sample uptake (mL min^{-1})	0.5
Peristaltic pump rotation speed (rpm)	20.0
Analytical mass (amu)	^{75}As

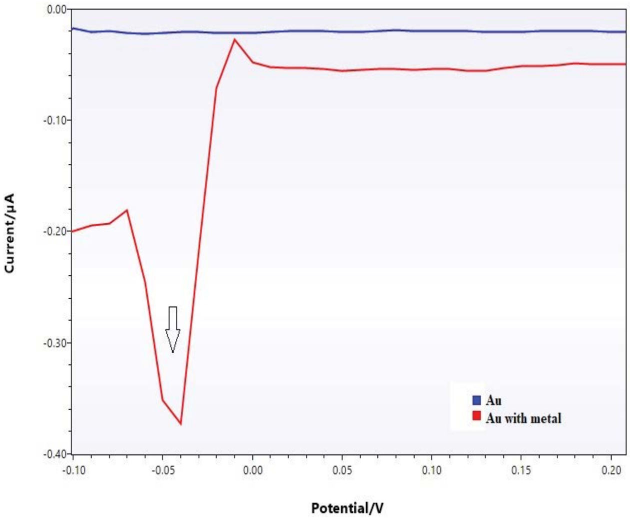

Fig. 1. Differential pulse voltammograms of Au electrode in 0.01 mol L^{-1} ABS (blue) and in 0.01 mol L^{-1} ABS containing 1% As (red) by weight between −0.10 V and +0.20 V vs. Ag/AgCl.

in electrochemistry and Au electrodes with their inertness are the best surfaces for As and Au interaction [14]. Another critical point in electrochemistry is the modification of the electrode with auxiliary materials. In Fig. 2, differential pulse behaviors of bare Au (green), Au/GO electrodeposited in 2.00 mg mL^{-1} GO solution for 10 cycles (red) and Au/CNT electrodeposited in 1.00 mg mL^{-1} CNT solution for 10 cycles (blue) were compared in 0.01 mol L^{-1} ABS containing 1% As by weight between −0.10 V and +0.20 V vs. Ag/AgCl. As it was seen, differential pulse voltammogram of Au/CNT (blue) gave a peak current at −0.04 V vs. Ag/AgCl almost 2 times higher current response than bare Au (green), and Au/GO (red) showed no current response. Therefore, the surface of the electrode was selected as Au/CNT in all electrochemical studies.

3.1.1. Characterization of surfaces

The surface morphologies of bare ITO, ITO/GO and ITO/CNT was compared in Fig. 3 using the SEM technique. The graphene nanosheets (Fig. 3a) and carbon nanotubes (Fig. 3b) were obviously seen as a difference from bare ITO (Fig. 3c). The nanopores less than 5 µm^2 allowed the free entry of As in ITO/CNT with its more compact, uniform and layer by layer surface characteristics than ITO/GO.

3.1.2. Validation of electrochemical arsenic removal

A comprehensive study on the removal of arsenic was made using electrochemical characteristics for validation. The effect of the scan rate on the peak current of As was investigated at a range of scan rates between 10 and 250 mV s^{-1}. The cyclic voltammograms of Au/CNT in 0.01 mol L^{-1} ABS containing 1% As by weight between −0.50 V and +0.50 V vs. Ag/AgCl at scan rates of 10–250 mV s^{-1} are represented in Fig. 4. The cathodic peak currents increased with the increased scan rate, while the potential is stable [15]. In a slow scan rate, the diffusion layer will grow much further from the electrode in

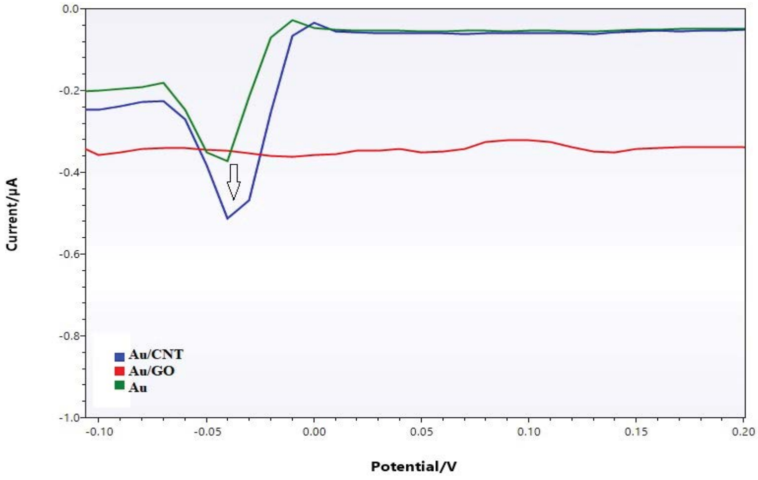

Fig. 2. Differential pulse voltammograms of bare Au (green), Au/GO electrodeposited in 2.00 mg mL^{-1} GO solution for 10 cycles (red) and Au/CNT electrodeposited in 1.00 mg mL^{-1} CNT solution for 10 cycles (blue) in 0.01 mol L^{-1} ABS containing 1% As by weight between −0.10 V and +0.20 V vs. Ag/AgCl.

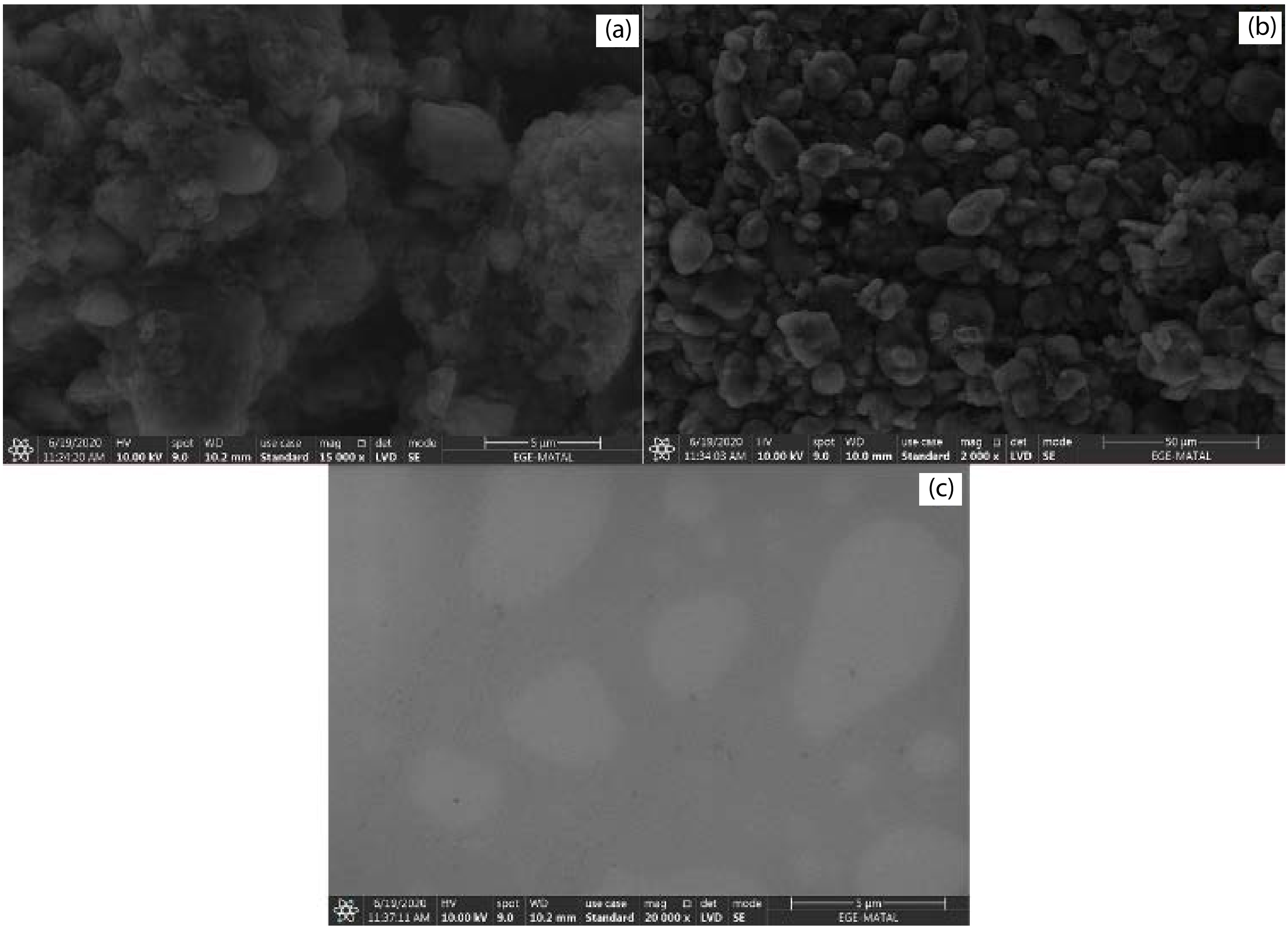

Fig. 3. Scanning electron microscopy images of (a) ITO/GO, (b) ITO/CNT, and (c) bare ITO.

comparison to a fast scan. Flux to the electrode is smaller at slow scan rates than faster rates and the current is proportional to flux towards the electrode. The plot of cathodic peak current (I_c/μA) vs. scan rate (ν/V s^{-1}) is also given in Fig. 4, inset. The linear response of the peak current to the square root of the scan rate between 10–250 mV s^{-1} showed a reversible process, and linear regression expression was expressed as $I_c = 1.5118\ \nu - 0.0667$, $R^2 = 0.9705$.

The effect of concentration on the peak current was also discussed for validation. Fig. 5 displays square wave voltammograms of Au/CNT between −0.06 V and +0.40 V vs. Ag/AgCl in 0.01 mol L^{-1} ABS containing different concentrations of As added in the range of 100 – 220 μL. The peak currents were linearly increased with the addition of As in the range of 120 – 220 μL and the plot of concentration (C/mmol L^{-1}) against peak current (I/nA) was given in Fig. 5, inset. The linear regression equation was obtained as I (nA) = 3.3994C (mmol L^{-1}) – 22.9950 and the direct relation of concentration with current resulted in the strong electrochemical response in higher concentrations of As.

Electrodeposition of Au/CNT to remove As was performed by CV with 10 scans between −0.50 V and +0.50 V vs. Ag/AgCl in water samples. After As removal from drinking water samples, As levels were compared spectroscopically by ICP-MS.

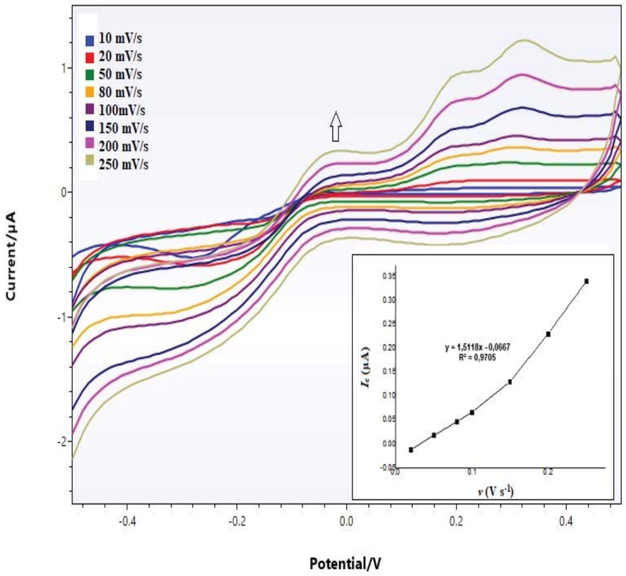

Fig. 4. Cyclic voltammograms of Au/CNT in 0.01 mol L^{-1} ABS containing 1% As by weight between −0.50 V and +0.50 V vs. Ag/AgCl at a scan rates between 10–250 mV s^{-1}. Inset: the plot of I_c (μA) vs. ν (V s^{-1}).

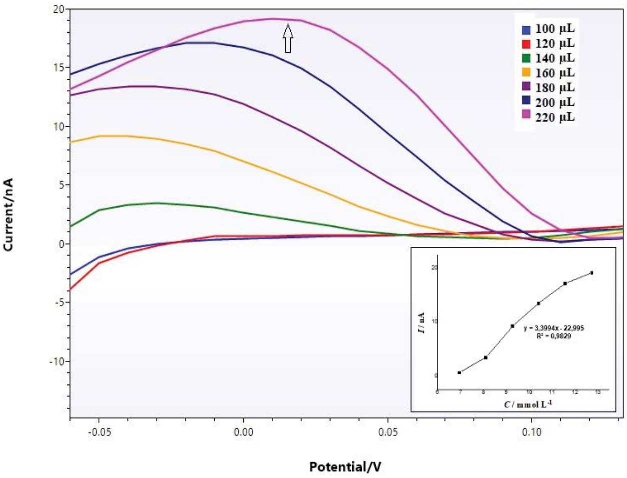

Fig. 5. Square wave voltammograms of Au/CNT between −0.06 V and +0.40 V vs. Ag/AgCl in 0.01 mol L^{-1} ABS containing different concentrations of As added in the range of 100–220 µL. Inset: the plot of concentration (C/mmol L^{-1}) vs. peak current (I/µA).

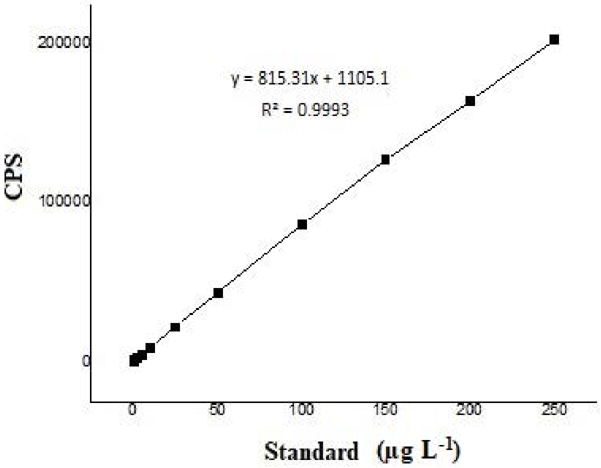

Fig. 6. Measurement of concentration levels according to standards for As in drinking waters.

3.2. Spectroscopic determination of As

For the quantitative analysis of As present in target drinking water samples, ICP-MS was used. 11 different As standard samples of known concentrations (0.5–250.0 µg L^{-1}) of As in the test samples were applied to measure As level. The plot of ICP-MS measurement in CPS (counts per second) against the concentration of standards (ppb) is given in Fig. 6 with the equation and coefficient of determination (R^2) for As in drinking water samples, and the obtained calibration curve was used for the determination of As levels in water samples under those experimental conditions. The linear range of As was obtained between 0.5 and 250.0 µg L^{-1}.

Standard concentration levels of drinking water were regulated by the United States Environment Protection Agency (EPA) [16] and As limiting level is added in Table 2. In the case of the UK, the heavy metals in contact with drinking water must conform to British Standard (BS) 6920 to address regulations regarding the prevention of contamination of the drinking water supply [17]. BS 6920 consists of 5 separate tests: odor and flavor of water, the appearance of water, growth of microorganisms, the extraction of substances and metals. Odor, color and appearance tests for all water samples had been already made with the observation of samples up to 1 month. In the second month, no difference in color, odor or appearance was observed. In the extraction part of As, spectroscopic determination of As in water samples was carried out. Any metal detected in the water samples must be at a concentration less than the maximum admissible concentration (MAC) as given in Table 2 with BS. If the concentration of any metal exceeded the MAC level, the sample would not comply to meet the specification. As it could be seen from Table 2, As levels of all water samples were less than the MAC value of As (10.00 µg L^{-1}) according to both EPA and BS 6920, but As level (8.44 µg L^{-1}) in well water was very close to the limiting values. Such a limited dose of As can pose a danger for all drinking water regions. Therefore, the water samples were purified from As using an electrochemical deposition process.

The average, median and LOD of three different water samples were also shown in Table 2. The LOD was estimated at three times the standard deviation and ranged between 0.03 and 0.16 µg L^{-1} for different supplies. Such a very low LOD of these incorporated methods was superior to most of the single methods [18–22]. As we could also see from Table 2, there was a small difference between the average and median values indicating almost the same concentrations of As in the drinking water resources. Therefore, all water samples were the same as each other in terms of As concentration. Thus, regional variations of water resources were compared with this study [23].

Table 2
List of EPA limiting As level (µg L^{-1}); BS limiting As level (µg L^{-1}); before As removal (µg L^{-1}); after As removal (µg L^{-1}); average (µg L^{-1}); median (µg L^{-1}); LOD (µg L^{-1}) and pH of three different water samples

Sample	EPA	BS	Before removal	After removal	LOD	pH
Rural water	10.00	10.00	3.51 ± 0.03	2.93 ± 0.02	0.16	8.60
Well water	10.00	10.00	8.44 ± 0.01	7.64 ± 0.02	0.14	8.55
Urban water	10.00	10.00	3.71 ± 0.03	3.10 ± 0.01	0.03	8.66
Mean	10.00	10.00	5.22	4.56	0.11	8.60
Median	10.00	10.00	3.51	3.10	0.14	8.60

3.2.1. Arsenic removal performance

Final ICP-MS results of drinking water samples after removal of As were also demonstrated in Table 2. After electrochemical removal, As level decreased from 3.51, 8.44 and 3.71 μg L^{-1} down below to 2.93, 7.64 and 3.10 μg L^{-1} in rural water, well water and urban water, respectively. Removed As amounts are total 16.52%, 9.48% and 16.44% for rural water, well water and urban water, respectively. Such a good removal performance even in low doses proved the success of the process incorporating a reference method such as spectroscopy with a treatment process such as electrochemistry. At the same time, As was determined within the limits of both EPA and BS standards by means of the removal process. The pH values are also compared in Table 2, and pH values of all drinking waters were obtained within the high grade and drinkable water limits (8.00–9.00). Thus, the diversities generating from water resources were eliminated and the content of waters was put into a common form, drinking water quality was remediated.

4. Conclusion

This work developed an electrochemical and spectroscopic determination and removal process of As from drinking water. The convenience of CNT modified Au surfaces to detect As in water samples was demonstrated. Special analytical advantages including high sensitivity, fast and reliable analysis, robust stability, low LOD and ease of use were obtained using a combination of electrochemistry with ICP-MS. The proposed accurate and precise method improved a cost-effective and simple alternative to determine the total amount of As regardless of its species in environment measurements. As the content of different water resources was reduced below the EPA and BS limiting values indicating the suitability of the method for the determination of As concentrations in drinking water samples. At the same time, regional differences of As coming from resources were determined using both ICP-MS and electrochemistry techniques. The developed method was successfully applied to determine the analytical capacity of ICP-MS and the electrochemical removal power of As in routine water analysis providing overall information for trace As determination. Incorporation of these two techniques controlled the quality of drinking waters in terms of both human health and environmental pollution.

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