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Arsenic Removal from Zimapan Contaminated Water Monitored by the Tyndall Effect

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Abstract

In Zimapan Valley, Mexico, up to 1.1 mg·L^{-1} of arsenic concentrations have been detected in deep wells that are used as drinking water supply for almost 39,000 people, which could have been exposed to levels higher than 10 μg·L^{-1} of arsenic, the maximum level recommended by the World Health Organization. Chronic consumption of water contaminated with arsenic can cause several diseases, including cancer. For it, the implementation of practical and economical methods to remove arsenic from drinking water is crucial to protect the population health. In this work, an electrochemical method to remove arsenic from drinking water is described. The process, monitored by Tyndall effect, utilizes Cu^{2+} and Zn^{2+} ions from a brass electrode in an electrochemical cell with water as electrolyte. Results show that the EC process reduces the concentration of the arsenic diluted in Zimapan water to a level below the limit of detection of the atomic absorption spectrophotometer employed. Arsenic was removed through the formation of Cu and Zn arsenic compounds. Cu^{2+} and Zn^{2+} ions form a hydroxide and eventually polycrystalline precipitation of kottigite and cornubite complexes (identified by energy-dispersive X-ray spectroscopy and X-ray diffraction), which are then filtered to eliminate the precipitated arsenic compounds.

Keywords

Arsenic Removal, Turbidity, Tyndall Effect, Groundwater Arsenic-Contamination,

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Electro-Flocculation, Brass Electrodes

1. Introduction

Arsenic is a toxic metalloid element common on the earth surface, soils, rocks, water and living organisms. It is present throughout the Earth's crust in concentrations of 1.7 mg·Kg^{-1} [1] found in sedimentary, igneous and metamorphic rocks [2]. A combination of natural processes, including weathering and erosion, biological activity, and mainly volcanic eruptions is the main source of arsenic in environment [3]-[6]. Besides, human activities such as mining, combustion of fossil fuels, the use of arsenical pesticides and herbicides in agriculture, crop desiccants, arsenic-based additives for livestock feed, and arsenic use for wood preservation have an additional significant environmental and health impact, because it alters the natural flux and concentrations of arsenic [4].

Although humans can be exposed to arsenic through different pathways like air, food or soil, arsenic contaminated drinking water represents the major threat of all arsenic sources to human health, contributing mainly to the incidence of Chronic Endemic Regional Hydroarsenicism [7]. Toxicity of arsenic depends on the form it is found in nature; it can be present in different oxidation states (−3 Arsine, +1 Arsonium Metals, +3 Arsenites, +5 Arsenates, 0 Elemental Arsenic) [3] [5]. Those compounds with +3 oxidation state are more toxic than compounds with +5 oxidation state, and inorganic arsenic compounds show higher toxicity than organic ones [5]. Arsenic organic compounds are found in food and marine organisms while inorganic arsenic compounds are found in minerals and in many aquifers, where they accumulate by means of natural processes [8]. In several regions of the world, aquifer water is used for drinking purposes. It represents an increased risk to develop serious diseases [3] [9]; since soluble arsenic compounds are extremely toxic [2] [3].

Chronic arsenic exposure affects mainly those organs involved in absorption, accumulation and excretion of arsenic [10]. Ingestion of high doses of arsenic leads to dermal pathologies, gastrointestinal damage, alterations in cardiovascular and nervous systems function, bone marrow depression, haemolysis, hepatomegaly, melanosis, polyneuropathy, encephalopathy and eventually death [3]. Among other effects, arsenic also has an adverse impact on the immune system [3] [10] [11]. Long-term intake of drinking water contaminated with arsenic increases the risk of developing different types of cancer, including skin, lung, bladder and kidney cancer [10]-[14]. In fact, it has been shown that arsenic can cause several alterations in the DNA [10]-[15], making arsenic an important carcinogen [9].

Concentrations of arsenic in natural waters vary over several orders of magnitude, ranging from 0.5 μg·L^{-1} to more than 5000 μg·L^{-1} [4] [16]. Arsenic concentrations in groundwater are typically below 10 μg·L^{-1}. In areas with geological activity and those with mining activities, arsenic has elevated concentrations reaching up to 3 mg·L^{-1}; consequently, groundwater could result highly contaminated [3] [11]. Arsenic content in major problem aquifers ranges in 1 - 20 mg·Kg^{-1} [4]. Groundwater with high arsenic concentrations enough to constitute a menace to human health has been reported in Bangladesh, India, Taiwan, Thailand, China, Hungary, Nepal, Myanmar, Vietnam, Argentina, Chile and Mexico. The scale of the problem represents almost 137 million people from more than 70 countries. They could have been exposed to drinking water containing more than the World Health Organization [WHO], and US Environmental Protection Agency (EPA) recommended a maximum of 10 μg·L^{-1} content of arsenic [3] [17]-[19].

In Mexico, several regions with sources of drinking water contaminated with more than 50 μg·L^{-1} of arsenic have been found, mainly in the north and center of the country [4] [16] [20]. The Comarca Lagunera represents the major health problem for the country with 400,000 inhabitants exposed to high levels of arsenic and fluoride in drinking water [4] [16] [21]. People in this central arid region of the country depend on groundwater as sources for drinking water [23]. Nevertheless, the health potential risk related to the consumption of contaminated water could be higher since almost 75% of drinking water in the country comes from groundwater sources [21].

Zimapan (Hidalgo state, Mexico, 20°40'N and 99°22'N), in the center of the country, is one of the arid regions characterized by its high levels of arsenic in groundwater: 1.097 mg·L^{-1} [21]. This contamination comes from the oxidation of arsenic-bearing minerals that pollute the deeper waters. In addition, there is an anthropogenic contamination from the mining activities in the region [21]-[23]. In Zimapan, water is a scarce resource, and population, estimated at 39,000 [24], totally depends to survive on groundwater. Water with more than 0.3

$mg \cdot L^{-1}$ of arsenic is widely consumed in this region; several health problems related to chronic exposure to high levels of arsenic have been found [21] [23].

An environmental and public health problem on a global scale is the arsenic contamination of groundwater. Therefore, attention to arsenic contamination is growing today due to the public health problems arising around the world caused by groundwater highly enriched with this ubiquitous element [4] [25] [26]. Different technologies for the treatment of groundwater have been developed to remove arsenic from laboratory and field conditions [11] [27]. Almost all technologies for arsenic removal depend on two types of interactions: 1) Coulombic or ion-exchange interactions based on negative charges of As^{+5} oxyanions; 2) acid-base interactions of As^{+5} and As^{+3} [11] [27]. Many of these techniques are at the experimental stage, and some have not been demonstrated at large scale, continuing in an experimental phase. Besides, although some processes may be technically viable, their cost could be considerably high to make them prohibitive [11].

In this paper, a low-cost electrochemical method (EC) is proposed. The process utilizes Zn^{2+} and Cu^{2+} ions from brass electrodes in an electrochemical cell with the test water as the electrolyte and a power supply as the energy source. The Zn^{2+} and Cu^{2+} ions form a hydroxide, and eventually crystalline precipitation of minerals kottigite and cornubite complexes, which are then filtered to remove the arsenic content. The EC process was monitored by turbidity measurements and the chemical species were identified by energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction techniques (XRD).

2. Materials and Methods

Procedures carried out in this work can be summarized as follows: 1) obtaining and preparation of aqueous samples; 2) EC removal of As^{+5} content; 3) monitoring As^{+5} content in the water sample by a modified Crecelius method of quantification; 4) monitoring the electrical current and of the light scattered from the aqueous samples produced by gradual flocculation using the Tyndall effect method; 5) quantification of Zn and Cu compounds obtained from the generated floccules. In **Figure 1** these procedures are described.

2.1. Water Samples

In order to test the EC method developed to remove As, two types of water samples were used, as indicated in **Table 1**:
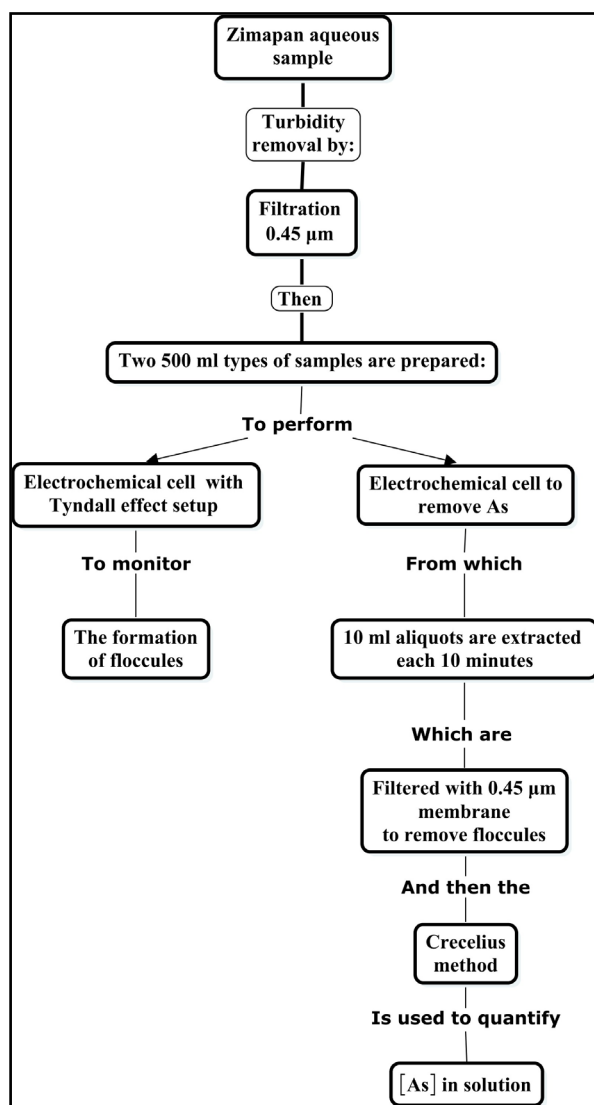
a) Sample A (contaminated water, problem sample). Water from a contaminated well in Zimapan, Hidalgo, Mexico was obtained to perform the study. The initial concentration of As of this sample was determined to be 249.3 $\mu g \cdot L^{-1}$ (see methods below for quantification of As). Since this sample showed high turbidity, the suspended particles in the water were filtered using Millipore (Billerica, MA, USA) sterile membrane filter with pore size of 0.45 μm. By means of filtration, 75.2% of the total As was removed to get a final concentration of 61.9 $\mu g \cdot L^{-1}$. The filtrated solution was treated by the EC method for As removal.

b) Sample B (artificially contaminated tap water). For comparison purpose, tap water from Mexico City was artificially contaminated with As ($Na_2HAsO_4 \cdot 7H_2O$; Sigma-Aldrich; 99% purity) at a concentration of 500 $\mu g \cdot L^{-1}$.

2.2. EC Method

The EC method to remove inorganic As from water consisted in submerging two brass pipeline pieces with 2.54 cm in diameter and 11.76 cm length. These pipelines were sealed in their extremes and used as electrodes. The elementary composition of the electrodes was 62% Cu, 34% Zn, 3% O, and 1% Al, as obtained by means of EDS. A bias of 3 volts was applied to the electrodes once they were immersed in 500 mL of each water sample in a beaker. The elapsed time of the EC treatment was 60 min. Besides, water samples were continuously stirred

Table 1. Aqueous samples used to test the EC treatment.

Sample	Raw sample	Preparation	Sample obtained for EC treatment
A: Zimapan	Turbid water with [As] = 249.3 $\mu g \cdot L^{-1}$	0.45 μm filtration	[As] = 61.9 $\mu g \cdot L^{-1}$
B: Tap water	Water with [As] = 10 $\mu g \cdot L^{-1}$	Addition of $Na_2HAsO_4 \cdot 7H_2O$	[As] = 500 $\mu g \cdot L^{-1}$

Figure 1. General procedure of the EC method.

and maintained at room temperature (25˚C). During the EC treatment, aliquots of 10 mL were taken every 10 min. Further, aliquots were filtrated using a Millipore (Billerica, MA, USA) sterile membrane filter (pore size of 0.45 μm) in order to remove the generated floccules. The As^{+5} content from filtrated solutions was then quantified as explained below.

At the end of experiments, the remnant solutions in the beaker were filtrated, and the filter was removed using sterile forceps and submitted to digestion process to recover the total arsenic retained. In addition, the final As remnant was also quantified from filtrated solution.

2.3. Quantification of As+5 in Water Samples

In order to quantify arsenic concentration of the samples (diluted in water and suspended sediments), the Crecelius method [28], modified and described in Del Razo and coworkers [29] was followed, which consists of the sequential processes shown in **Figure 2**.

2.3.1. Sample Preparation

Aliquots of 10 mL were taken every 10 minutes from 500 mL of the water sample submitted to continuous stirring during the EC process in order to determine As^{+5} concentration.
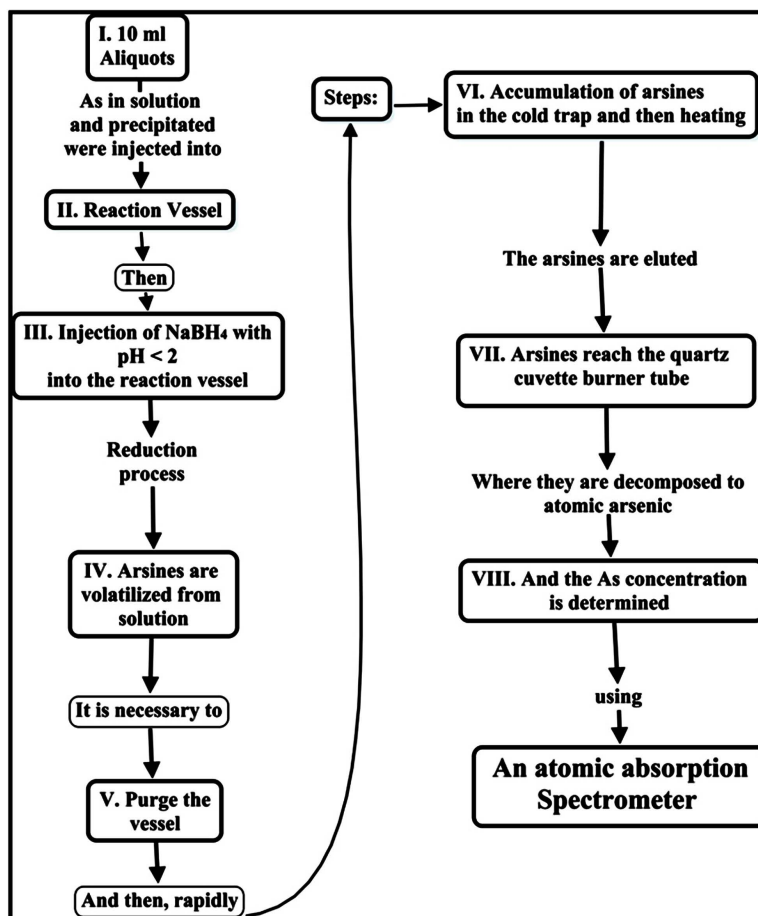
Figure 2. The Crecelius method to quantify [As^{+5}].

2.3.2. Digestion

Homogenized 10 mL aliquots taken every 10 minutes were digested with 0.4 mL of 1:1 HNO$_3$ diluted and 2 mL 1:1 HCl diluted. They were placed to reach 90°C on a hot plate until the total volume was reduced to 2.5 mL. After this, volume was raised to 10 mL with deionized water according with the HNO$_3$/HCl 3030F digestion procedure for recuperation of As established in standard methods [30].

2.3.3. As^{+5} Quantification

A modified Crecelius and coworkers method [28] described in [29] was followed to quantify As^{+5}. All reagents employed were of a ultra-pure degree from Merck. Likewise, acids used were of analytical degree. Once the solution digested was raised to 10 mL with deionized water, 1 mL aliquots of each sample were taken and mixed with 10 mL of deionized water, 1 mL of HCl 6 N. Then, in this solution it was injected 2 mL of 4% (weight/volume) solution of NaBH$_4$ in NaOH 0.02 M (weight/volume) in the cylinder of reaction. The total volume injected into the cylinder of reaction was 14 mL.

Once all arsines are generated in an acidic medium (pH = 2 or lower), they are retained in the chromatographic trap immersed in liquid nitrogen, which is gradually warmed to collect separated arsines according with their differences in boiling points. Then, arsines suffer atomization by an air/hydrogen flame in the quartz combustion cell and are converted to elemental arsenic atoms. The releasing arsenic atoms are detected by atomic absorption spectrophotometry (Perkin Elmer model 3100, equipped with an EDL II Perkin-Elmer electrodeless discharge lamp, coupled with a Perkin Elmer integrator, model Nelson) operating at $\lambda = 197.3 \pm 0.7$ nm which corresponds to one of the most probable transitions for As.

In order to quantify As from water samples, the next procedures were performed. Working standards of 20 µg·L^{-1} of As were daily prepared from a stock solution of 1000 µg·L^{-1}, whose spectrophotometric curve was

used as a reference to determine As concentration in the water samples. These standards were prepared triplicate, presenting less than 10% coefficient of variation accepted by standard methods [30]. To evaluate the accuracy of As content in quantification procedures, it was used the NIST 1640 reference water (National Institute Standards and Technology, Gaithersburg, MD) which had a concentration of 26.67 ± 0.41 mg·Kg^{-1}. In the standard and NIST water samples, to measure As content, both of them were also submitted to the digestion process before quantification by spectrophotometry. A blank (prepared with both acids, HNO$_3$, and HCl) was also prepared as control for reagents, included in each As determination. Once As quantification from NIST water was 99.5% accuracy, measurements from water samples were carried out.
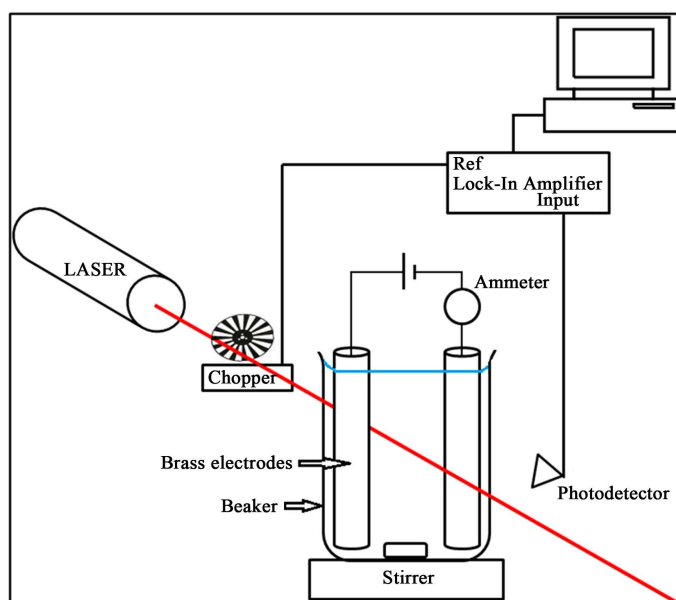
2.4. Arsenic Products Quantification and Identification during the EC Process

Identification of arsenic products of precipitated arsenic was performed through X-ray diffraction crystallography using a diffractometer (Siemens, D5000) equipped with a Cu target tube.

To quantify the products formed during the EC process from ions released by the electrodes, an atomic absorption spectrophotometer with flame (F-AAS) method to measure Cu^{2+} and Zn^{2+} arsenic products (Perkin Elmer model 3100 user manual) was used. In summary, samples (from arsenic suspended and diluted) were digested with acid and then nebulized, in a similar arrangement of that used for quantification of As described above, to convert the sample into small particles. Then, the samples (filters and water aliquots) were burned with a flame of air and acetylene in order to separate the compounds in atomic elements. Finally, samples were quantified by spectrophotometry at $\lambda = 324.7$ nm for Cu^{2+} compounds, and at $\lambda = 213.8$ nm for Zn^{2+} compounds. Data obtained were quantified by interpolation in calibration curves according with the user manual.

2.5. Monitoring Flocculation of As during the EC Process by the Tyndall Effect

As the EC process produces the formation of particles of Cu^{2+} and Zn^{2+} arsenic compounds (flocculates), it is feasible to observe and measure the rate of such particle formation, and provide information about the dynamics of the process. To monitoring the formation of particles in the water samples during the EC process, the Tyndall effect was used (see the experimental setup in **Figure 3**). The light beam from a He-Ne laser (Melles Griot) with a wavelength $\lambda = 632.8$ nm, 1 mW, is periodically interrupted by an optical chopper (SRI). A lock-in amplifier (SRI, mod. SR530) is tuned to the chopper frequency through the reference channel, which permits the detection of the scattered light through the solution by means of a silicon photodetector (EG & G). The output is connected to a current-voltage operational amplifier. The photodetector is positioned at 30˚ with respect to the beam. The lock-in amplifier is linked to a PC using a GPIB parallel port.
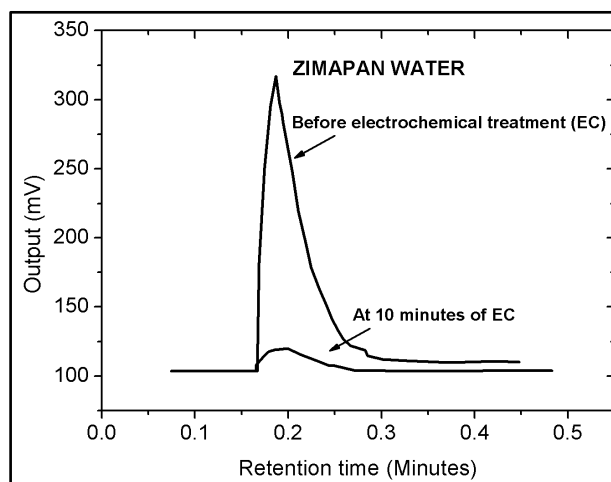

Figure 3. Experimental setup for the Tyndall effect method.
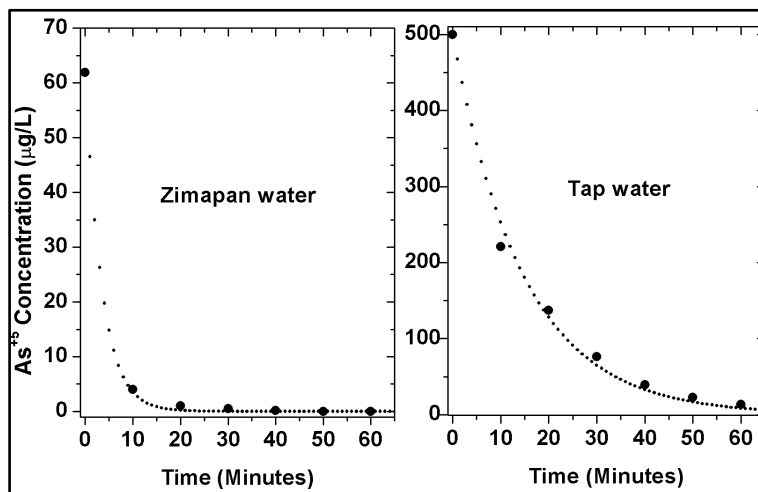
3. Results and Discussion

3.1. Evolution of As[+5] Removal during the EC Process

In **Figure 4** is shown a typical chromatogram of the water of Zimapan before EC (large peak), in which one can observe the evolution time for As[+5]. In the same figure, it is also shown a chromatogram of water of Zimapan at 10 minutes of EC treatment (small peak). The retention time starts at the moment in which the cold trap begins to be heated. The As[+5] concentration is proportional to the area under the peak and above the baseline signal, according to the NIST sample mentioned above for calibration purposes, as mentioned in Materials and Methods section.
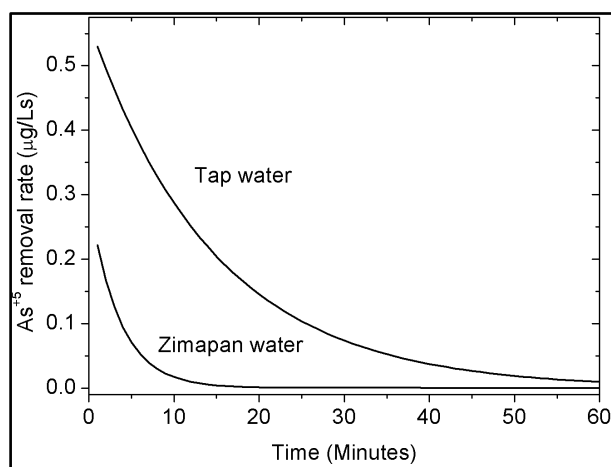
In **Figure 5** the aqueous arsenate concentration as a function of time in samples A and B are shown. It can be observed that As[+5] concentration in Zimapan water diminishes below the detection limit of the equipment between 10 and 20 minutes of EC treatment. Besides, it can also be noted that, for absolute values, the arsenic removal for Zimapan sample is faster than in the tap water sample, as observed in **Figure 6**. For instance, at ten minutes, the EC method removes 93.54% of the arsenic content in Zimapan sample (from an initial concentration of 61.9 $\mu g \cdot L^{-1}$) at an average rate of 0.07 μg/sec. By contrast, in the tap water sample, 55.84% of the arsenic (from an initial concentration of 500 $\mu g \cdot L^{-1}$) was removed after 10 minutes of EC treatment at an average rate of 0.4 μg/sec. However, it is necessary consider that the initial concentrations in both samples were quite differ-

Figure 4. Change of the chromatograms of Zimapan water with the EC treatment.

Figure 5. As[+5] content in the water samples as a function of the EC treatment.

Figure 6. As^{+5} removal rate obtained from the decaying exponential fitting indicated by the dots in **Figure 5**.

ent: 61.9 μg·L^{-1} for the Zimapan sample and 500 μg·L^{-1} for the tap water sample. For the Zimapan water sample, it is necessary an elapsed time between 10 and 20 minutes to reach [As] < 1 μg·L^{-1}. In contrast, for the tap water sample an hour is needed to diminish [As] to 13 μg·L^{-1}. The corresponding theoretical fits for both graphs (**Figure 5**), were used to establish the rate of arsenic removal during the process (**Table 2**). From this fit, it was obtained the time in which the concentration of arsenic becomes half of the initial value, namely $t_{1/2}$ for each water sample. For the Zimapan sample $t_{1/2}$ = 2.43 minutes (with a removal rate of 0.14 μg/sec), and for the tap water sample $t_{1/2}$ = 10.19 minutes (at a rate of 0.28 μg/sec). In fact, the removal of arsenic is faster in the tap water sample than in the Zimapan sample water during the whole process, despite the concentration of arsenic in the tap water sample is higher. Thus, although there is a lower concentration of arsenic in the Zimapan sample, the electrochemical reaction is faster in the tap water.

It is plausible to assume that, despite the arsenic available in both samples diminishes as the EC process takes place, the saturation in the system may occur in an important way when the electrode becomes coated, probably with an oxide surface layer product of the reaction of the electrode components (Zn, Cu, etc.) and the ions and salts present in the solution. Once the electrode is covered with the coated formed by the own electrode ions and the ions and salts from the solution, the amount of ions of zinc and copper (which are released to the solution), may be reduced progressively as the coat becomes thicker. As a result, since there are less arsenic and less Cu^{2+} and Zn^{2+} ions (reactants), the rate of the reaction diminishes to form the products following the law of mass action [31]. This electrochemical effect is the cause of the decrease in the velocity of the removal of arsenic in the tap water sample although it remains enough arsenic available in the solution.

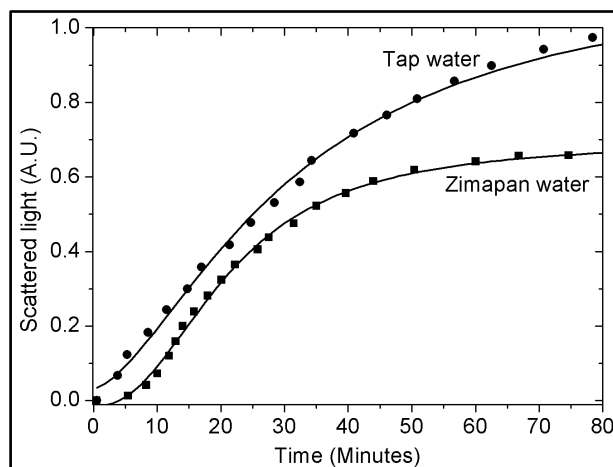## 3.2. Evolution of the Tyndall Effect

The generated floccules during the EC treatment were monitored by the Tyndall effect, which is proportional to the optical turbidity. According to **Figure 7**, the light dispersion in the solution increases until saturation is reached after 60 minutes for Zimapan sample and after 80 minutes for tap water sample. The continuous lines represent the logistic fittings to the experimental points, given by the following equation:

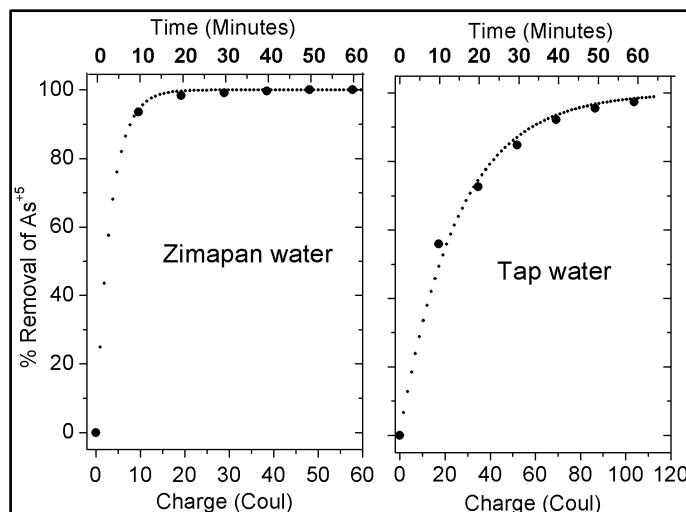$$Y = A_2 + \left(A_1 - A_2\right)\Big/\left(1 + \left(\frac{t}{t_{01}}\right)^p\right). \tag{1}$$

The fitting parameters are shown in **Table 2**.

In **Figure 8**, it can be seen that in Zimapan sample although the arsenic concentration has been diminished about 95% at the minute 10 and below 1 μg at the minute 20 (**Figure 5**), turbidity (**Figure 7**) continues increasing until the minute 60 (in fact, after the minute 10, there is no more arsenic detectable in the Zimapan sample water). After the minute 60, turbidity increases at a low rate almost reaching asymptotic values. On the other side, in the tap water sample, turbidity only continues growing after the minute 60 at a low rate, time in which

Figure 7. Evolution of the turbidity as a function of the elapsed time for both water samples. The continuous lines result from the fitting to logistic curves, whose fitting parameters are indicated in the turbidity columns of **Table 2**.

Figure 8. Arsenic percentage removal and charge involved during the EC. Filled large dots correspond to data and small points to exponential fit.

Table 2. Fitting parameters of As concentration (A, t_o, $t_{1/2}$), and turbidity (A_1, A_2, t_{01}, and p) as a function of time, using a decreasing exponential, and a logistic curve, respectively.

Sample	$[As] = A\exp(-t/t_0)$					Turbidity $Y = A_2 + (A_1 - A_2)/(1 + (t/t_{01})^p)$			
	A	t_o	$t_{1/2}$	pH_i	pH_f	A_1	A_2	T_{01}	p
Zimapan	61.9	3.5	2.43	7.92	8.13	−0.014	0.696	21.24	2.306
Tap water	500	14.7	10.19	7.30	7.90	0.033	1.165	31.32	1.58

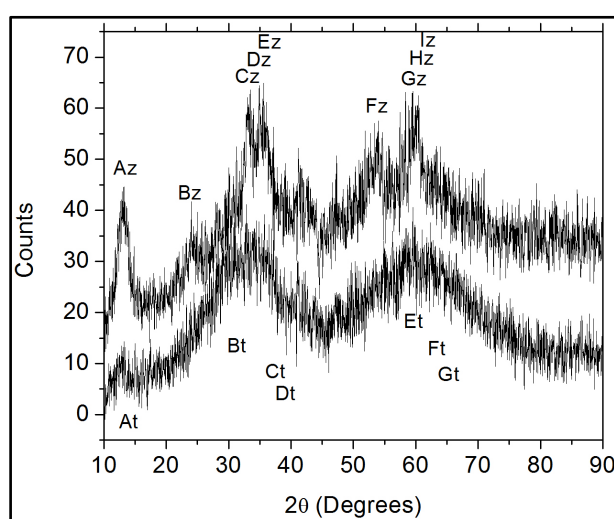remains 13.5 μg of arsenic in the water (**Figure 5**).

It is possible that the pH is involved, at least in some extent: the change in pH before and after the EC treatment (**Table 2**). At the beginning of the EC process, the Zimapan sample water has a pH = 7.92 and the tap water sample a pH = 7.30, a difference of 0.62. Consider, for instance, the change in pH for the Zimapan water sample, *i.e.*, $\Delta_{pHZimapan} = +0.21$, and the change in pH for the tap water sample, *i.e.*, $\Delta_{pHTapWater} = +0.6$. The slight

higher acidity of the tap water sample before and after the EC process could have generated a slightly more detachment of ions, Cu^{2+} and Zn^{2+}, from the brass electrode, giving rise to an increase of the As removal from the solution.

The analysis of the filtered sediments obtained from the EC treatment analyzed by EDS, revealed the presence of 50.07% Zn, 3.9% Cu, 29.42% O, 0.64% Ca, 3.71% As, and 9.09% Si, as shown in **Table 3**. **Table 3** and **Table 4** display the identification of the main peaks, which were obtained taking into account the elemental analysis by EDS previously mentioned and the database of the XRD system. The crystallographic phases of the precipitates were identified by X-ray diffraction. In **Figure 9** the XRD spectra for both samples are shown. The spectra reveal nanometric and/or micrometric structures in an amorphous background.

3.3. Energy Consumption during the Arsenic Removal Process

It is worth to indicate that it is useful to describe the evolution of the removal of Arsenic by plotting the content of arsenic as a function of the electric charge through the solution.

Figure 9. X-Ray diffractograms for sediments of sample A (Zimapan water whose features are labeled with *z*), and for sample B (Tap water, whose features are labeled with *t*).

Table 3. Identification of XRD main peaks of sediments obtained from Zimapan water (sample A).

Peak	Position (2θ)	Compound	Structure	Planes	JCPDS-lCDD file
Az	13.164	$Zn_3(AsO_4)_2 \cdot 8H_2O$ Kottigite	Monoclinic	020	33-1467
Bz	24.907	$ZnCO_3$ Smithsonite	Rombohedric	004 202	8-449
Cz	30.569	$Zn(OH)_2$ Sweetite	Tetragonal	213 220	38-356
Dz	34.412	Ca_3SiO_5	Monoclinic	225	42-551
Ez	34.994	$Cu_5(AsO_4)_2(OH)_4$ Cornubite	Triclinic	212	38-441
Fz	52.210	Co_2O_3	Hexagonal	203	02-770
Gz	58.559	$Cu_5(AsO_4)_2(OH)_4$ Cornubite	Triclinic	014	38-441
Hz	60.720	$Cu_5(AsO_4)_2(OH)_4$ Cornubite	Triclinic	212 412	38-441
Iz	61.119	$Cu_5(AsO_4)_2(OH)_4$ Cornubite	Triclinic	221	38-441

Table 4. Identification of XRD main peaks of sediments obtained from Tap water (sample B).

Peak	Position (2θ)	Compound	Structure	Planes	JCPDS-lCDD file
At	13.164	$Zn_3(AsO_4)_2 \cdot 8H_2O$ Kottigite	Monoclinic	020	33-1467
Bt	30.569	$Zn(OH)_2$ Sweetite	Tetragonal	213 220	38-356
Ct	34.412	Ca_3SiO_5	Monoclinic	225	42-551
Dt	34.994	$Cu_5(AsO_4)_2(OH)_4$ Cornubite	Triclinic	212	38-441
Et	58.559	$Cu_5(AsO_4)_2(OH)_4$ Cornubite	Triclinic	212	38-441
Ft	60.720	Co_2O_3	Triclinic	212	38-441
Gt	61.119	$Cu_5(AsO_4)_2(OH)_4$ Cornubite	Triclinic	212	38-441

Thus, the amount of electric charge that passes through the electrodes is given by the equation:

$$Q(t) = \int_0^t I(t')\,dt' \tag{2}$$

where $I(t')$ is the electrical current (in the SI units ampere, A) monitored while the aqueous sample is EC treated. In the case of Zimapan water a constant current has been observed:

$$I(t) = 0.016\text{A} \tag{3}$$

And for the tap water:

$$I(t) = A_1 e^{-t/t_1} + y_0.$$

where

$A_1 = 0.0072$ A.

$t_1 = 686.87$ sec. $\tag{4}$

$y_0 = 0.027$ A.

Thus, the total charge involved during the EC process was 19.2 Coulomb after 20 minutes in which arsenic diminishes from 61.9 µg·L^{-1} to <1 µg·L^{-1} for Zimapan sample, and 102.12 Coulombs for the tap water sample after 60 minutes of the experiment in which the arsenic concentration was reduced to 13.5 µg·L^{-1}.
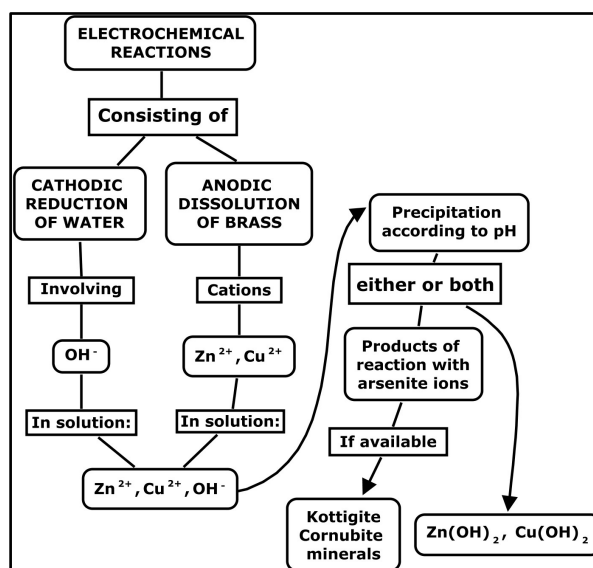
For the Zimapan water sample, the consumed energy to remove arsenic below the limits of detection of the equipment was of 57.6 Joules, while in the tap water sample was 291.6 Joules, to diminish to 13.5 µg·L^{-1}.

The energy cost to remove a µg of As is 0.93 Joules for the Zimapan sample while that corresponding to the tap water sample is 0.58 Joules.

3.4. Chemical Reactions Carried out during the EC Process

In the treatment of arsenic-contaminated water, chemical reactions initiate the nucleation of particles susceptible to be monitored during the EC method by the Tyndall effect. The reactions carried out during the EC process, which produces light scattering floccules are described in the scheme shown in **Figure 10**.

In the EC method, the electrodes play a fundamental role since they are the source of Zn and Cu ions, which form solid complexes with arsenic ions, through oxidation-reduction reactions, to form compounds that grow into floccules that are easy to eliminate from the water. The electrodes exposed to the water solutions can be dissolved or corroded due to the electrode or corrosion potential, which is determined by the equilibrium between the reactions that occur in the anode and the cathode surface. Through the anodic reaction, the anode oxidizes and, thus, corrodes. By applying an electrical potential to the metal surface between the electrodes, this process can be altered [32]. Since zinc and copper are the main elements of brass electrodes, they corrode both in acidic and alkaline solutions, but resist corrosion well in neutral solutions [32].

Figure 10. Formation of light scattering particles precipitated or floccules during the EC treatment. In fact, the light dispersive particles are the mineral compounds containing As and the precipitated hydroxides.

The corresponding anodic reactions of the brass electrodes that take place in the EC method (pH > 7) used are:

$$Zn \rightarrow Zn^{2+} + 2e^- \tag{5}$$

$$Cu \rightarrow Cu^{2+} + 2e^- \tag{6}$$

Also, in the cathode region the water molecule is reduced to produce hydrogen and hydroxyl ions:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH, \tag{7}$$

but the hydrogen ions are not enough to generate hydrogen gas. However, there are too many electrons in the brass electrodes reacting with oxygen molecules, which were adsorbed by the metal surface from the air dissolved in the water samples, to produce the hydroxyl ions. Such hydroxyl ions form a precipitate with the Zn^{2+} and Cu^{2+} ions since the pH of the samples are in the range of precipitation of zinc and copper hydroxide [33]:

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \tag{8}$$

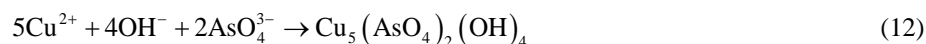$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2. \tag{9}$$

These precipitates could be part of the light scattering particles monitored by the Tyndall effect (see Section 2.5). If there are arsenate ions, the following reaction may take place:

$$OH^- + (HAsO_4)^{3-} \rightarrow H_2O + (AsO_4)^{3-} \tag{10}$$

Thus, according with the identified precipitates, the Zn^{2+} ions may combine with the arsenates ions:

$$(AsO_4)^{3-} + Zn^{2+} \rightarrow Zn_3(AsO_4)_2. \tag{11}$$

In the characterization process, this product resulted to be a mineral of kottigite. Also, combining Cu^{2+} and OH^- ions may also produce cornubite mineral as follows:

$$5Cu^{2+} + 4OH^- + 2AsO_4^{3-} \rightarrow Cu_5(AsO_4)_2(OH)_4 \tag{12}$$

Comparing these reactions with the results showed in **Table 3** and **Table 4** from the Section 3.2, it can be observed that the reaction products numbered 8, 11, and 12, are the corresponding products determined by XRD precipitate analysis. Also, in the precipitate analysis it was found a tiny amount of Cu in solution. It is possible that, for this reason, the precipitate of $Cu(OH)_2$ could not be detected.

4. Conclusions

In this work, an electrochemical process with brass and monitored by the Tyndall effect has been reported as a method to remove As from contaminated water. The method consists in the electro-flocculation of mineral salts including arsenate ions already present in the water samples with the anodic dissolution of the brass electrodes of Cu^{2+} and Zn^{2+} ions, and a final filtration process to separate the floccules from the water. By means of the EC method, it was possible to reduce the arsenic concentration of natural and artificially contaminated water to levels within the limits permitted by the WHO.

The flocculation products were analyzed by EDS, allowing the identification of the corresponding phases by means of X-Ray diffraction. Components of kottigite and cornubite mineral were identified. In addition, the relevant chemical reactions that produced such minerals were proposed and corroborated by analyzing their respective structures consisting of nanometric and/or micrometric sediments in an amorphous background.

The removal rate of arsenic by means of the EC process was higher in the tap water sample artificially contaminated with 500 μg/L of As than in the Zimapan water sample contaminated with 61.9 μg/L. The energy cost to remove 1 μg of As is 0.93 Joules for the Zimapan sample while that corresponding to the tap water sample is 0.58 Joules.

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