

Article

Electrochemical Treatment of Arsenic in Drinking Water: Effect of Initial As^{3+} Concentration, pH, and Conductivity on the Kinetics of Oxidation

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Abstract: Many technologies for the treatment of arsenic-containing drinking water are available, but most of them are more effective on arsenic oxidized forms. Therefore, the pre-oxidation of As^{3+} is necessary. The electrochemical processes represent a very promising method due to the simultaneous oxidation of compounds using electrochemical conditions and the reactive radicals produced. In this work, As^{3+} oxidation was experimentally studied at a pilot scale using an electrochemical oxidation cell (voltage: 10 V; current: 1.7 A). The effect of the initial arsenite concentration, pH, and conductivity of drinking water on the oxidation of As^{3+} into As^{5+} was investigated. The results showed that the initial As^{3+} concentration strongly directly influences the oxidation process. Increasing the initial arsenite concentration from 500 to 5000 $\mu\text{g L}^{-1}$, the pseudo-first order kinetic constant (k) strongly decreased from 0.521 to 0.038 min^{-1} , and after 10 min, only 21.3% of As^{3+} was oxidized (vs. 99.9% in the case of As^{3+} equal to 500 $\mu\text{g L}^{-1}$). Slightly alkaline conditions ($\text{pH} = 8$) favored the electrochemical oxidation into As^{5+} , while the process was partially inhibited in the presence of a more alkaline or acidic pH. The increase in conductivity up to 2000 $\mu\text{S cm}^{-1}$ enhanced the kinetic of the oxidation, despite remaining on the same order of magnitude as in the case of conductivity equal to 700 $\mu\text{S cm}^{-1}$. After 10 min, 99.9 and 95% of As^{3+} was oxidized, respectively. It is the opinion of the authors that the influence of other operational factors, such as voltage and current density, and the impact of the high concentration of other pollutants should be deeply studied in order to optimize the process, especially in the case of an application at full scale. However, these results provide helpful indications to future research having highlighted the influence of initial As^{3+} concentration, pH, and conductivity on the electrochemical oxidation of arsenic.



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1. Introduction

In natural water, the inorganic arsenic species arsenite (As^{3+}) and arsenate (As^{5+}) are the most abundant species. Due to its better affinity towards proteins, lipids, and other biomolecules that facilitate uptake by human cells, As^{3+} is considered the most toxic form of As [1]. The occurrence of arsenic (As) in nature can be related both to natural and anthropogenic causes. Exposure to low concentrations of arsenic in drinking water for a long time can cause severe health effects, such as bladder cancer, renal cancer, liver cancer, and skin cancer [2,3]. Although the mechanisms which determine disorders in human health are not completely clear, non-carcinogenic issues have also been related with a chronic exposure to arsenic in polluted water, such as cardiovascular, dermatological, developmental, endocrinological, immunological, neurological, and respiratory problems [4]. Some



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authors highlighted that although the number of studies about the presence and toxicity of As in groundwater has enhanced in recent years, some challenges in research remain, such as the need for more data (especially in the case of populations in rural regions) and the importance of including in epidemiological studies the co-presence in drinking water of other elements (e.g., F^- , U, Se . . .) that could have an impact on human health [5].

Arsenic can also concentrate in the environment, especially in crops and animals. For instance, Upadhyay et al. [6] highlighted that As in rice can reach very high concentrations depending on the type of rice, irrigation regime, location, and other environmental conditions. Rahman et al. [7] reported that As concentration in vegetables cultivated in a severely As-contaminated area of Bangladesh reached $90 \mu\text{g kg}^{-1}$. Another study found a mean arsenic concentration in the caps of edible mushrooms of up to 163 mg kg^{-1} dry weight [8]. In addition, animals, such as fish and cows, can concentrate and accumulate arsenic [6].

The presence of As both in water and in the environment could be a problem because As can enter humans through different pathways causing health issues [7]. The World Health Organization (WHO) reported that the sources of exposure to arsenic for humans are represented by contamination of water and food, release by industrial products (in some cases, arsenic is used during the production of glass, pigments, and textiles products), and the smoke of tobacco (arsenic in the soil can be absorbed by plants) [9]. Based on the literature, ingestion through contaminated water remains the main source of exposure, especially when the concentration of arsenic is very high, and the drinking water is not properly treated [10]. For these reasons, almost 20 years ago, the WHO reduced the suggest provisional guideline value for arsenic in drinking water from 50 to $10 \mu\text{g L}^{-1}$ [11], confirming this approach in the first addendum in 2017 [12]. In accordance with this guideline, the European Union established the arsenic standard level in drinking water as $10 \mu\text{g L}^{-1}$ [13] and confirmed this value in the new Drinking Water Directive approved in 2020 [14]. However, several concerns remain about possible health issues due to chronic exposure also at low concentrations of As [15].

To date, several treatment methods are available for arsenic removal, such as coagulation with ferric or aluminum salts, adsorption on conventional or alternative activated carbon, membrane processes (e.g., reverse osmosis), and anion exchange [16,17].

However, these treatments are more effective on As^{5+} (abundant in well-oxygenated superficial water and less hazardous for human health) than As^{3+} (more present in groundwater and more toxic) [18].

For instance, membranes, especially nanofiltration and reverse osmosis could help in arsenic removal, although they present high costs in terms of construction and energy consumption [19]. Zakhar et al. [19] pointed out that the rejection of As^{5+} can be very high (85–99%) with lower values observed for As^{3+} (61–87%). However, they also suggested that a preliminary oxidation phase to convert arsenite into arsenate through chemicals is not recommended due to the possible damage to the membranes [19]. In addition, adsorption has been tested for As, and Alka et al. [20] reported a removal of almost 95% of arsenic with the advantage of a sludge-free technology but the need for the periodic replacement of exhausted beds which is more frequent in the presence of highly polluted water. Moreover, Gregor [21] evaluated the removal of arsenic in three case studies in New Zealand through aluminum-based coagulation–flocculation treatment. He highlighted that As^{5+} is effectively removed by the process, while As^{3+} passed the treatment and was oxidated by the final chlorination phase [21].

Therefore, As^{3+} oxidation in arsenate using chemical and biological processes could help to simultaneously (i) reduce the hazardousness of water and (ii) facilitate the removal of arsenic compounds [22–25].

Among the non-conventional processes, electrochemical oxidation represents an effective solution for the transformation of As^{3+} into As^{5+} [26–29]. The advantages of this process are (i) high compactness, (ii) easy operation and automation, (iii) high kinetics of oxidation, (iv) no necessity to add chemical additives, and (v) low production of sludge [30]. In electrochemical processes, two important phenomena are exploited: (i) the direct oxidation

of the pollutants on the anode surface by hydroxyl radicals and (ii) indirect oxidation due to other compounds (e.g., chlorine, hypochlorous acid, hypochlorite, . . .) formed at the electrodes [31].

One of the factors which influences the effectiveness of the electrochemical processes is the material of the electrodes. The main characteristics of a good electrode should be (i) high electrical conductivity and catalytic activity, (ii) high stability, and (iii) low cost/life ratio [32]. Electrodes for water treatment can be made from different materials, such as IrO_2 , SnO_2 , and TiO_2 , and the choice also depends on the pollutant that needs to be treated. In recent years, metal oxides based on silicon have been demonstrated to be optimal low-cost electrodes for drinking water treatment [33–35], overcoming some disadvantages, such as the short lifetime, which hindered the large-scale application of other types of electrodes [36].

Previous studies observed conversion rates from As^{3+} to As^{5+} ranging from 70 to 90% using an electrooxidation cell operating with a current density varying from 0.15 to 30 mA cm^{-2} [37]. The electrocatalytic oxidation of arsenite in arsenate was also investigated using electrochemically immobilizing Pd nanoparticles on a Pt surface to obtain a more efficient catalyst. The results highlighted that, during the process, both catalytic efficiency and electron transfer were enhanced [38]. In another study, nearly complete oxidation of As^{3+} into As^{5+} was observed by an electro-oxidation through a dimension stable anode with a current density of 0.24 mA cm^{-2} [39]. High arsenic removal from aqueous solution was observed by combining the electrochemical oxidation with nanofiltration membranes. As^{3+} was electrochemically completely oxidized in less than 2 h using an electro cell with water soluble polymers as supporting electrolytes in the electrochemical process [40]. Nidheesh et al. [41] tested anodic oxidation and electro-Fenton as effective for As^{3+} oxidation using Pt/Ti-graphite-felt electrodes. Once arsenate has been obtained, a variety of technologies, including adsorption, ion exchange, coagulation followed by filtration, and membrane processes can be used to remove arsenates from water [33,34].

This work aims to evaluate the effectiveness of the electrochemical oxidation of As^{3+} in spiked drinking water to assess the impact of the initial arsenite concentration, pH, and conductivity of the water. A semi-batch reactor equipped with an electrochemical cell with cylindrical electrodes made of mixed metal oxides based on silicon was used to study the kinetics of the oxidation process. This study aims to provide important information about the optimal water characteristics (initial As^{3+} concentration, pH, and conductivity) for the electrochemical oxidation of arsenic in drinking water.

2. Materials and Methods

2.1. Chemical and Solutions

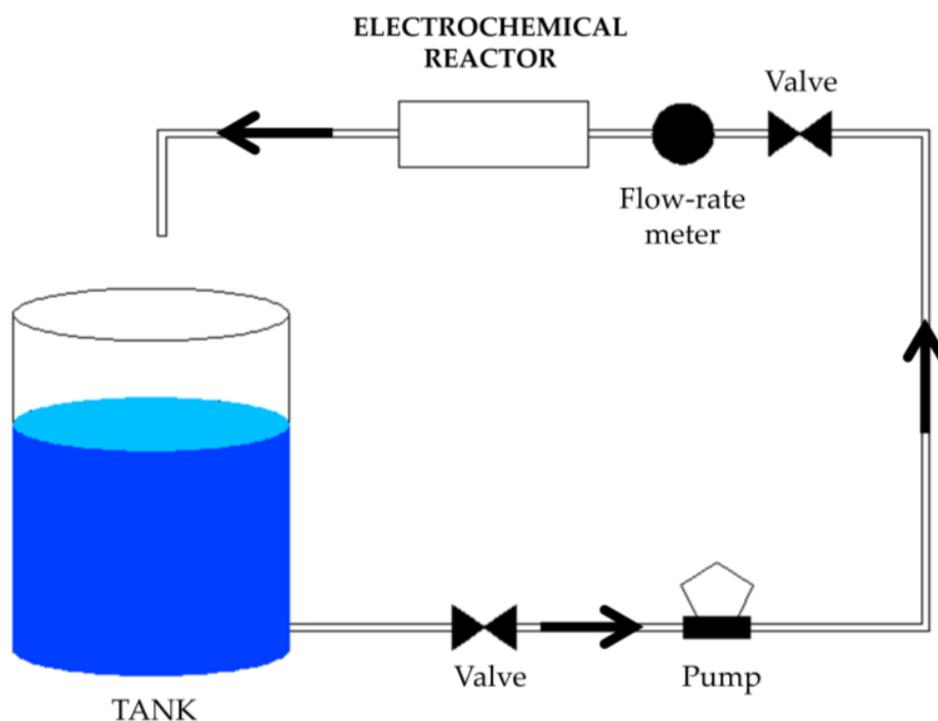
To take into consideration conditions more similar to the real ones, this experimental study was carried out using tap water with pH equal to 7.20 and conductivity of 700 $\mu\text{S cm}^{-1}$. The detailed composition (cations and anions) is reported in Table 1. The untreated water contained relatively high concentrations of magnesium, calcium, potassium, bicarbonate, sulphate, chloride, and nitrate, but no arsenic was detected.

2.2. Experimental Set-Up

A simplified diagram of the electrochemical plant used is presented in Figure 1. The electrochemical reactor consisted of 2 Izumrud-STO[®] cells (IZUMRUD, Sankt Petersburg, Russia) equipped with cylindrical electrodes made of mixed metal oxides based on silicon. Each of the cells contained two compartments, anodic and cathodic, separated by a ceramic diaphragm. This ion selective membrane plays the role of a barrier between the liquids in both compartments.

Table 1. Analytical characterization of the tap water used for preparing arsenic-containing water solutions ($n = 3$). C.I.: confidence interval.

Parameter	Concentration \pm C.I. (mg L^{-1})	Parameter	Concentration \pm C.I. (mg L^{-1})
Aluminium	0.015 ± 0.003	Molybdenum	0.0016 ± 0.005
Calcium	80.46 ± 1.2	Sodium	14.21 ± 1.8
Cadmium	<0.001	Nickel	0.0008 ± 0.0001
Chromium	0.0003 ± 0.0001	Lead	0.0010 ± 0.002
Copper	0.0003 ± 0.0001	Zinc	0.0251 ± 0.007
Iron	0.0078 ± 0.0010	Fluoride	<0.1
Potassium	1.276 ± 0.3	Chloride	35.6 ± 1.1
Lithium	0.0044 ± 0.001	Nitrate	34.8 ± 3.4
Magnesium	31.86 ± 2.7	Sulphates	101 ± 9.2
Manganese	<0.001	HCO_3^-	280 ± 12.1

**Figure 1.** Experimental set-up for the electrochemical oxidation.

The electrochemical plant operated in a semi-batch mode with a 35 L water tank, and flow rate kept constant at 60 L h^{-1} . Samples were periodically taken from the water tank.

Before starting the experimental tests, the water sample was continuously mixed in the tank and circulated in the electrochemical plant (switched off) for 1 h to homogenize the solution.

The study focuses on the operational conditions which depend on the water characteristics and not the electrochemical system. Voltage and current have been assumed by the authors based on previous studies (10 V and 1.7 A, respectively) [33]. Therefore, the electrochemical oxidation tests were performed in order to assess the influence of the following parameters on the oxidation efficiency in the following ranges:

- Initial As^{3+} concentration: $500 \mu\text{g L}^{-1}$ – $5000 \mu\text{g L}^{-1}$
- Conductivity: $700 \mu\text{S cm}^{-1}$ – $2000 \mu\text{S cm}^{-1}$
- pH: 5–10

To investigate the effect of electrochemical oxidation on these cations, the concentration of As^{3+} in the tap water was adjusted with sodium arsenite (NaAsO_2) 0.05 M. As^{3+} was spiked in the raw water up to $5000 \mu\text{g L}^{-1}$. The range of As^{3+} concentration was chosen based on two reasons: (i) many literature studies which highlighted the possible presence of a huge amount of arsenic in un-treated drinking water [42–44], also up to $5000 \mu\text{g L}^{-1}$ [45]; (ii) electrochemical oxidation represents a valid alternative for As^{3+} removal, especially when the initial concentration in water is very high, and other non-electrochemical treatments can be ineffective.

To study the influence of conductivity, sodium chlorite (NaCl) was added into the raw water in order to increase the conductivity to $1000 \mu\text{S cm}^{-1}$ (5.59 g), $1500 \mu\text{S cm}^{-1}$ (14.12 g), and $2000 \mu\text{S cm}^{-1}$ (23.13 g).

pH was modified with sodium hydroxide (NaOH) and phosphoric acid (H_3PO_4) to alkaline and acidic conditions, respectively.

2.3. Sampling Activities and Analytical Methods

During tests, 50 mL of treated water was periodically sampled up to 120 min. To stop the oxidation process of the reactive species, 1 mL of H_3PO_4 (1 M) was added and mixed for 30 min immediately after the sampling. Before the analysis, the samples were stored in dark plastic flasks at 6°C .

As^{5+} was analyzed using an inductively coupled plasma mass spectrometry (ICP-MS) (Model ELAN 6100, PerkinElmer, Inc., Waltham, MA, USA). For detection of As^{3+} , a combination of high-performance liquid chromatography (HPLC) system (LC 200, PerkinElmer, Inc., Waltham, MA, USA) with ICP-MS was applied.

To separate both inorganic forms (As^{3+} and As^{5+}), an ion chromatography column PRP-X100 (Hamilton Company, Reno, NV, USA) was used. The limits of determination (LOD) and quantification (LOQ) were set at 10 and $20 \mu\text{g}_{\text{As}} \text{L}^{-1}$, respectively. To determine the effectiveness of the oxidation process, the amount of As^{3+} oxidized was evaluated based on the As^{5+} produced.

The conductivity and pH were measured using a conductometer WTW-LF340 (Xylem Inc., Washington, NY, USA) and a pH meter VWR-pH100 (VWR International, Radnor, PA, USA).

3. Results and Discussion

During the experimental tests, the effect of As^{3+} concentration, water conductivity, and pH on the oxidation efficiency was investigated.

3.1. Influence of Initial As^{3+} Concentration

In Figure 2, the results of kinetic studies on different trivalent arsenic initial concentrations are reported. In these tests, pH and conductivity were maintained at 8 and $780 \mu\text{S cm}^{-1}$, respectively. In tests where the initial As^{3+} concentration was up to $1000 \text{As}^{3+} \mu\text{g L}^{-1}$, arsenic was completely oxidized in almost 10 min (Figure 2a). At higher As^{3+} concentrations, a longer time is needed to completely oxidize As^{3+} into As^{5+} . More than 30 min are required at initial As^{3+} concentrations of $2000 \mu\text{g L}^{-1}$ and more than 2 h in the case of $5000 \mu\text{g L}^{-1}$.

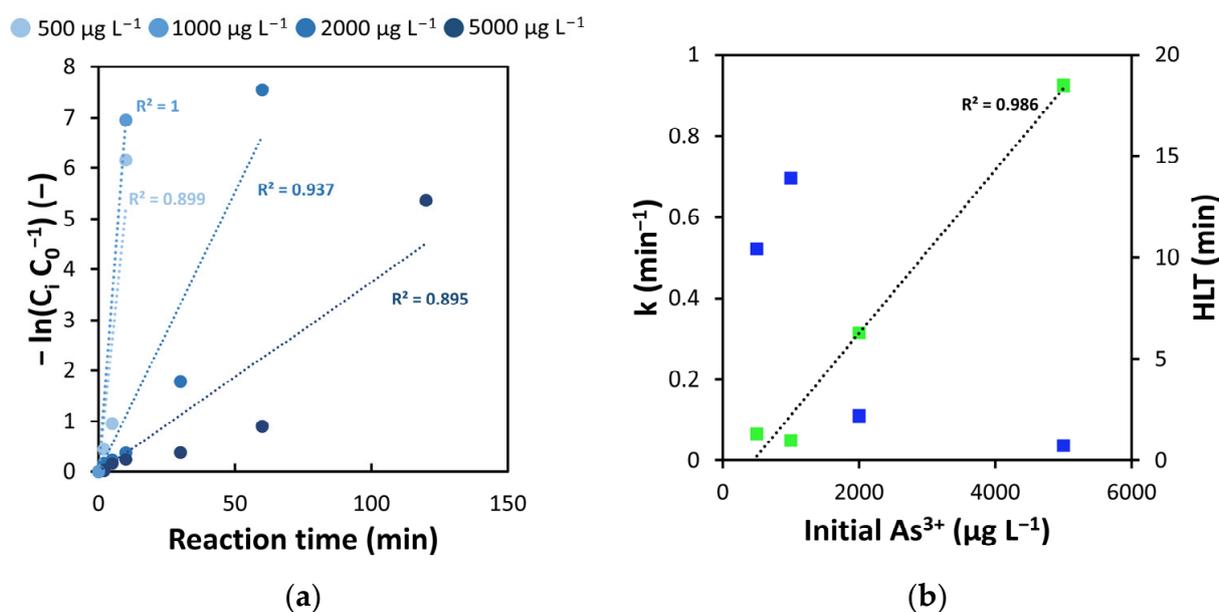


Figure 2. (a) Effect of initial As^{3+} concentration on the electrochemical oxidation of arsenic. pH = 8; conductivity = $780 \mu\text{S cm}^{-1}$. (b) Pseudo first-order kinetic constants k (blue) and HLT (green) as a function of initial As^{3+} concentration.

To describe the kinetic of the arsenic oxidation, a pseudo first-order kinetic was assumed (Equations (1) and (2)):

$$\ln(C_i/C_0) = -k \times t, \quad (1)$$

$$\text{HLT} = \ln(2) k^{-1}, \quad (2)$$

where C_0 and C_i represent the As^{3+} concentration in the initial and i -th samples, respectively. k represents the pseudo-first order kinetic constant of the reaction, while HLT is the half-lifetime of the pollutant.

The pseudo-first order kinetic constant (k) strongly decreased from 0.521 to 0.038 min^{-1} , enhancing the initial As^{3+} concentration from $500 \mu\text{g L}^{-1}$ to $5000 \mu\text{g L}^{-1}$, respectively, and after 10 min only 21.3% of As^{3+} was oxidized (vs. 99.9% in the case of As^{3+} equal to $500 \mu\text{g L}^{-1}$) (Figure 2b). The HLT was 20 times higher in the case of the initial As^{3+} concentration of $5000 \mu\text{g L}^{-1}$ (18.48 min) with respect to $1000 \mu\text{g L}^{-1}$ (1 min).

The literature is contrasting on this point. This result agrees with Lakshmipathiraj et al. [46] that tested the effect of the initial concentration of As^{3+} , up to 100 mg L^{-1} , on its electrochemical removal using iron electrodes. They founded that the partial oxidation and precipitation of As^{3+} when present in high concentration could be attributed to the insufficient generation of iron hydroxide.

In contrast, these results seem to be different from the previous literature findings which highlighted higher removal with lower initial concentrations of As^{3+} , although in diverse operational conditions. For instance, Li et al. [47] carried out the electrocatalytic oxidation of arsenite using electrodes made from reduced graphene oxide. They highlighted that enhancing the initial As^{3+} concentration from 10 to 50 mg L^{-1} , the kinetic of the reaction clearly decreased [47].

3.2. Influence of Initial PH

The influence of pH on the kinetics of As^{3+} electrochemical oxidation was investigated. The results highlighted that acid and alkaline conditions scavenged the electrochemical reactions of oxidation which, in contrast, seemed to be stimulated with almost neutral pH (equal to 8) (Figure 3a). In the best conditions, the oxidation process was accelerated and

completed within 10 min. In the case of higher alkaline and acid conditions, a longer time (from 30 to 60 min) was required to complete the oxidation of As^{3+} into As^{5+} .

These results were also confirmed looking at pseudo first-order kinetic constants. In the case of pH equal to 8, k assumed the value of 0.461 min^{-1} , more than seven times higher than in other tested conditions ($0.064 \pm 0.001 \text{ min}^{-1}$) (Figure 3b). Slightly alkaline conditions (pH = 8) also reduced the HLT from 10.85 ± 0.25 (as in other alkaline and acidic tested conditions) to 1.51 min.

The detrimental effect of alkaline conditions in electrochemical treatments is confirmed by the literature [48,49]. For instance, Ün et al. [50], who studied the electrochemical treatment of fluoride in drinking water, pointed out that acidic pH represented the best conditions for pollutant removal. In addition, Lebik-Elhadi et al. [51] focused on the electrochemical oxidation of thiamethoxam on a boron-doped diamond anode and highlighted that the increase in pH from 3 to 11 badly affect the degradation of the pollutant with a drop in the kinetic constant from 2.13 to 0.017 min^{-1} . Studying the removal of paracetamol in water using a graphite anode, Periyasamy et al. [52] found that the effect of initial pH was a crucial parameter with lower removal efficiencies in alkaline conditions.

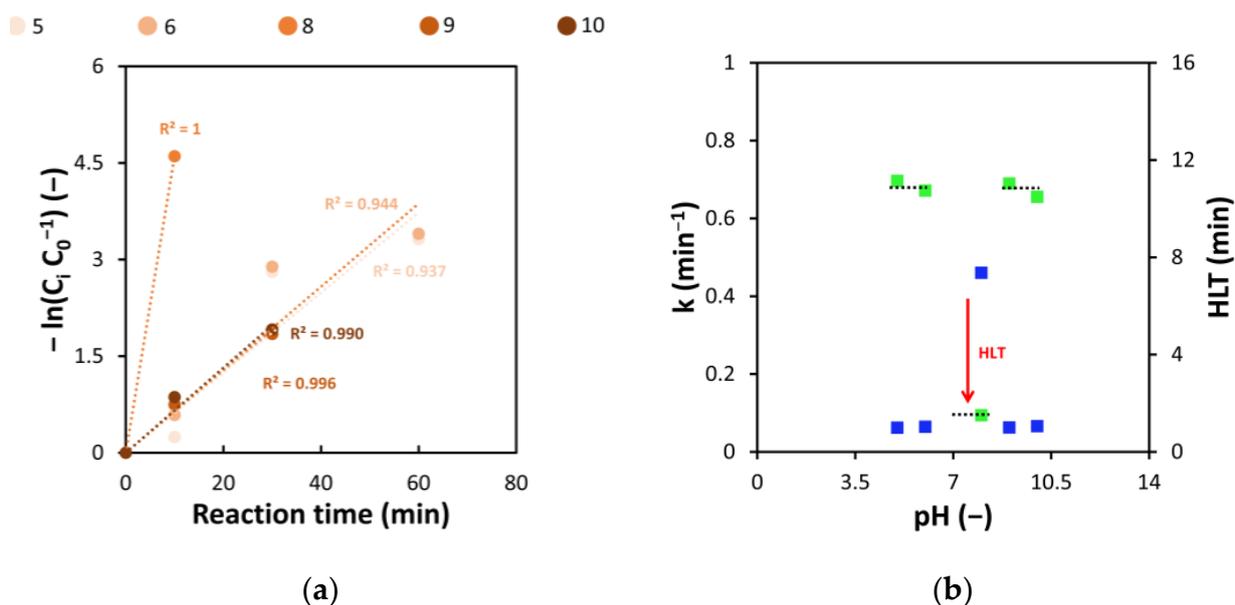


Figure 3. (a) Effect of initial pH on the electrochemical oxidation of arsenic. Initial $\text{As}^{3+} = 1000 \mu\text{g L}^{-1}$; conductivity = $780 \mu\text{S cm}^{-1}$. (b) Pseudo first-order kinetic constants k (blue) and HLT (green) as a function of initial pH.

In fact, a strong alkaline condition is generally related with the presence of a high amount of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-), which are known for their scavenging properties in hydroxyl radical formation [49]. This explains why k at pH > 8 was lower in respect to that obtained at slightly alkaline conditions.

Therefore, an acidic pH should not limit OH^\bullet production, with positive effects on the performance of the oxidation, in contrast to our results.

However, the influence of pH strongly depends on several factors, such as the type of pollutants and the electrode materials [53]. For instance, Can et al. [48] tested pH from 2 to 8 to evaluate the influence on arsenite oxidation and removal by electrocoagulation through iron electrodes. They found that the optimal pH was 4 with lower values in both more acid and alkaline conditions. However, they evaluated the influence on the entire electrocoagulation process, not focusing only on the oxidation of the compounds and operated with diverse operational conditions (conductivity, initial As^{3+} concentration, and voltage).

Therefore, a direct comparison with previous results which generally adopted different operational conditions is not simple, and other studies on the mechanism which bring acidic pH to reduce the pseudo first-order kinetic constants of arsenite oxidation are required. It should be also considered that the pH influence on electrochemical processes can be quite complex depending also on the ionization state of the pollutant and its interactions with the electrode [51].

3.3. Influence of Initial Conductivity

The influence of initial conductivity on the kinetics of As^{3+} electrochemical oxidation was investigated. Water conductivity seemed to influence the oxidation of As^{3+} into As^{5+} (Figure 4a).

In the case of water with low conductivity ($700\text{--}1000\ \mu\text{S cm}^{-1}$), the pseudo first-order kinetic constant was lower than in the case of higher conductivity conditions ($1500\text{--}2000\ \mu\text{S cm}^{-1}$) (Figure 4b). After 10 min, 95 and 99.9% of As^{3+} was oxidized in the case of conductivity of 700 and $2000\ \mu\text{S cm}^{-1}$, respectively. However, in both cases, 1.5–5.8 min was enough to oxidize half of the As^{3+} concentration.

Higher conductivity generally determines advantages in electrochemical processes as, for instance, lower energy requirements due to the higher concentration of the electrolyte [54]. In addition, several studies highlighted that the presence of a higher amount of electrolyte also stimulates the electrochemical oxidation of pollutants [49]. In our work, the use of NaCl to simulate high-salinity water allowed the indirect generation of more chlorine and hypochlorite [55], promoting the oxidation of As^{3+} into As^{5+} , but, especially in the case of real applications, the presence of chloride ions represents a severe risk for production of toxic precursors [31].

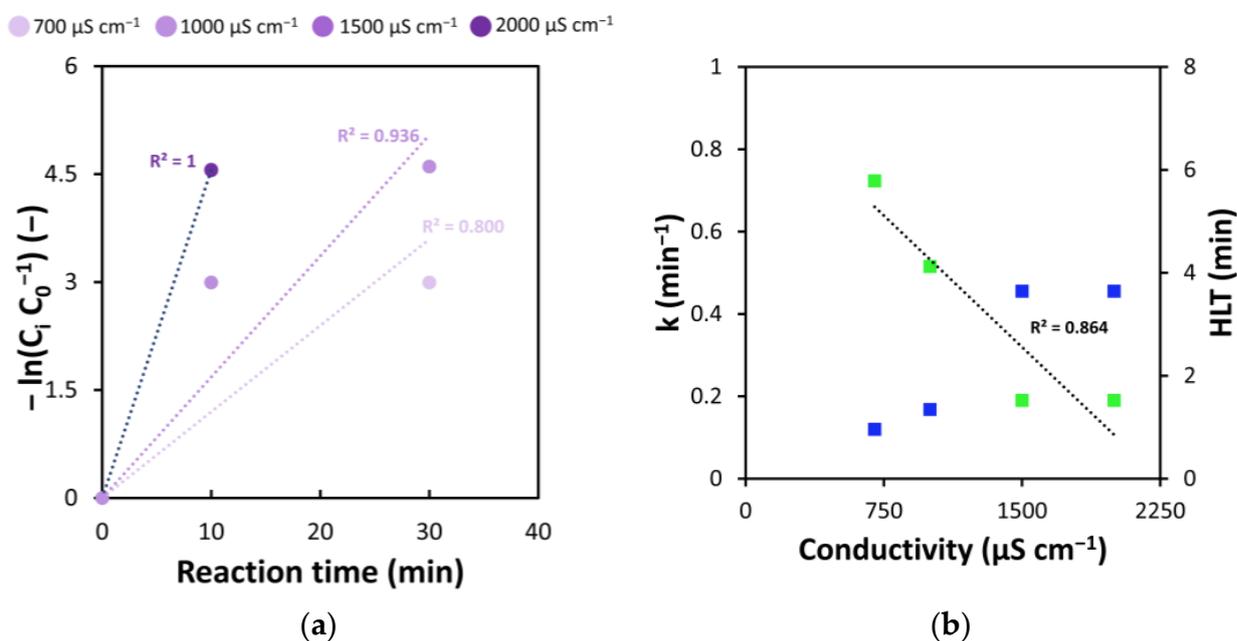


Figure 4. (a) Effect of initial conductivity on the electrochemical oxidation of arsenic. Initial $\text{As}^{3+} = 1000\ \mu\text{g L}^{-1}$; pH = 8. (b) Pseudo first-order kinetic constants k (blue) and HLT (green) as a function of initial conductivity.

This means that this process can be optimal for drinking water initially characterized by high salt concentrations, but at the same time, good results in terms of the oxidation of As^{3+} into As^{5+} can also be obtained with drinking water characterized by low salinity without adding any salt.

3.4. Limitations of the Study and Tips for Future Research

In this study, three main limitations can be highlighted. Firstly, the influence of other operational factors, such as voltage and current density, and other pollutants have not been taken into consideration. Although this work mainly focused on the influence of characteristics typical of drinking water (initial As^{3+} concentration, pH, and conductivity) on the effectiveness of electrochemical oxidation, the knowledge of optimal operational factors represents an important step, especially in the case of application of this treatment at full scale.

Moreover, the impact on As^{3+} oxidation of concomitant pollutant species in drinking water should be investigated. This aspect has not been investigated in our study but could be very significant in deciding when the electrochemical oxidation of arsenite can be applied in different real case studies, depending on the characteristics of the untreated drinking water.

Finally, another possible limitation of this study could be represented by the amount of data, which is not yet sufficient to perform a study on the statistical influence of different parameters on the effectiveness of the electrochemical process. Although the optimal conditions for initial As^{3+} concentration, pH, and conductivity have been studied, the authors also encourage the weight with which these parameters influence the electrochemical oxidation to be statistically evaluated.

This work provides helpful information about the optimal initial As^{3+} concentration, pH, and conductivity of drinking water for the effective electrochemical oxidation of arsenite, but further studies are needed to fully clarify all the factors influencing the electrochemical process, especially before application in a full-scale plant.

4. Conclusions

The tests showed that the electrochemical oxidation of As^{3+} represents a very fast and efficient process. The effect of the initial arsenite concentration, pH, and conductivity of drinking water on the oxidation of As^{3+} into As^{5+} was investigated. The results showed that the initial As^{3+} concentration strongly directly influences the oxidation process. Enhancing the initial arsenite concentration up to $5000 \mu\text{g L}^{-1}$, the pseudo-first order kinetic constant (k) strongly decreases to 0.038 min^{-1} (voltage: 10 V; current: 1.7 A). The electrochemical oxidation into As^{5+} was favored by slightly alkaline conditions (pH equal to 8). The increase in conductivity up to $2000 \mu\text{S cm}^{-1}$ enhanced the kinetic of the oxidation, although the HLT remained on the same order of magnitude as in the case of conductivity equal to $700 \mu\text{S cm}^{-1}$ (1.5 min vs. 5.8 min, respectively). It is the opinion of the authors that the influence of other operational factors, such as voltage and current density, and other pollutants should be deeply studied in order to optimize the treatment especially in the case of an application at full scale. In addition, when a consistent amount of data is reached, a statistical evaluation can be helpful to understand the different weight with which these parameters influence the electrochemical process. However, these results provide helpful indications to future research having highlighted the influence of the initial As^{3+} concentration, pH, and conductivity on the electrochemical oxidation of arsenic.

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