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Arsenic (III) oxidation of water applying a combination of hydrogen peroxide and UVC radiation

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Arsenic is toxic to both plants and animals and inorganic arsenicals are proven carcinogens in humans. The oxidation of As(III) to As(V) is desirable for enhancing the immobilization of arsenic and is required for most arsenic removal technologies. The main objective of this research is to apply an Advanced Oxidation Process that combines ultraviolet radiation and hydrogen peroxide (UVC/H_2O_2) for oxidizing aqueous solutions of As(III). For that purpose, a discontinuous photochemical reactor (laboratory scale) was built with two 40 W tubular germicidal lamps ($\lambda = 253.7$ nm) operating inside a recycling system. The study was made beginning with a concentration of 200 µg L^{-1} of As(III), changing the H_2O_2 concentration and the spectral fluence rate on the reactor windows. Based on references in the literature on the photolysis of hydrogen peroxide, arsenic oxidation and our experimental results, a complete reaction scheme, apt for reaction kinetics mathematical modelling, is proposed. In addition, the effectiveness of arsenic oxidation was evaluated using a raw groundwater sample. It is concluded that the photochemical treatment of As(III) using H_2O_2 and UVC radiation is a simple and feasible technique for the oxidation of As(III) to As(V).

1. Introduction

The concentration of arsenic in the earth's crust ranges from 2 to 5 mg kg^{-1}. The median natural soil concentration being 6 mg kg^{-1} and it ranges from 0.1 to 40 mg kg^{-1}. Water-soluble arsenites and arsenates are most common in the environment. Arsenic (especially arsenites) can have a rather high mobility and in the interstitial water it can be estimated to be 10 to 200 times higher than other typical components and concentrations associated with soil particles. Bacteria, fungi, and some plants methylate inorganic arsenic, which converts it to organic arsenic. Some of these compounds are volatile and can be incorporated into the air.[1] Arsenic-polluted groundwater and other types of arsenic impurities are serious threats in Bangladesh, India and also in parts of Argentina, Cambodia, Chile, China, Mexico, Nepal, Pakistan, Taiwan and the United States. Exposure to arsenic can result in a variety of health problems in human, including various forms of cancer (*e.g.* skin, lung and bladder), cardiovascular and peripheral vascular disease and diabetes.[2] Due to the high toxicity of this metalloid, the World Health Organization (WHO) has set a maximum limiting guideline of 10 µg L^{-1} as the drinking water standard.[3]

The high arsenite mobility makes its removal more difficult using traditional physical and chemical processes, such as adsorption, coagulation/precipitation or ion-exchange. This phenomenon is related to the known effect of pH on arsenic speciation. At pH ranges encountered in most surface waters and groundwater (from acidic to weakly alkaline), As(III) exists mainly as the nonionic form (H_3AsO_3), whereas the dominant forms of As(V) species are the anionic $H_2AsO_4^-$ and $HAsO_4^{2-}$. Consequently, most of the remediation methods tend to convert As(III) into As(V). The negatively charged As(V) has higher affinity to the surfaces of various adsorbents and to some of the most widely used flocculants, such as iron- or aluminium-hydroxides, used in post oxidation processes.[4]

Removal of As(III) has been the subject of many studies with a large variety of technologies. The problem of aquatic arsenic has been recently reviewed by Sharma and Sohn.[5] Considering the existence of this valuable report, only a few typical representative chemical processes will be commented on here. Oxidation can be obtained by using oxygen under acidic conditions, a reaction that can be greatly enhanced by the presence of iron.[6] Similarly, conversion of As(III) to As(V) was also achieved using air, pure oxygen and ozone[7] with very significant differences in the required reaction times for each of these treatments. The *in situ* electrolytically generated hypochlorite was also applied to convert arsenite into arsenate.[8] Hexacyanoferrate with and without using iridium(III) as a catalyst was also studied for this purpose.[9] Even sonochemical methods of oxidation have been investigated to achieve the transformation of arsenite into arsenate,[10] a fast reaction that is produced by the generation of hydroxyl radicals by acoustic cavitation. Direct arsenite oxidation employing just hydrogen peroxide was investigated by Pettine

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et al.,[11] a study that included the catalytic enhancement produced by the presence of cationic components, such as Fe^{2+} and Cu^{2+}. In competition with these methods, new technologies have entered into the scene with the generic denomination of Advanced Oxidation Technologies (AOTs), such as UVC/H_2O_2, UVA/Fe(III) complexes, Fe(II)/H_2O_2, UVA/TiO_2. These processes seem to be more efficient and convenient for the oxidation of arsenic in water than traditional methods, because they do not generate toxic or undesirable by-products. They are based on physicochemical processes capable of producing deep changes in the chemical structure of pollutants. Highly reactive intermediate species are generated, the most relevant being the hydroxyl radical ($OH^{\bullet}$).

The degradation of organic pollutants using AOTs was reported in several previous research articles.[12–15] The same has not occurred with the study of the transformation of metallic ions into species with minor toxicity or that are more easily removable. The metals or metalloids like arsenic have a life-time close to infinite, and the chemical or biological methods for its treatment show severe restrictions or are prohibitive due to their high cost.[16]

As it should be expected, photocatalytic oxidation of arsenite employing titanium dioxide (UVA/TiO_2) has been investigated under different operating conditions leading to a very large number of contributions. Some representative examples of the evolution of this technique to improve the quality of waters polluted with arsenic are shown in previous studies.[17–21] Some of them are important because they provide suggestions about some aspects of the intervening mechanism in the oxidation reaction. The UVA/Fe(III) complexes process was studied using ferrioxalate solutions and the mechanisms involved at different pHs were investigated.[22] The Fenton reaction (Fe(II)/H_2O_2) was also an additional technology that was examined in detail by Hug and Leupin,[23] including the proposal of a very complete kinetic model. An additional significant contribution to the oxidation mechanism was published by Yoon *et al.*,[4] employing vacuum UV lamp irradiation and comparing its efficiency with other processes, such as UVC/H_2O_2/O_2, UVA/Fe(III)/H_2O_2 and UVA/TiO_2.

The relatively simple H_2O_2/UVC process has been shown to be efficient to carry out the arsenic oxidation reaction.[24,25] However, currently, it is one of the least studied technologies for metal and metalloid treatments. Based on an extensive survey of the published literature, we decided to explore in more detail the H_2O_2 approach because of two very attractive characteristics: simplicity and efficiency. These advantages, without excluding other applications, could render a manageable solution, particularly for groundwater sources in areas having a relatively small population. Thus, the main objective of this research is to study arsenic oxidation in water in the presence of hydrogen peroxide and UVC radiation. The first step is to investigate the behaviour of the reaction employing UVC radiation alone (direct photolysis) and hydrogen peroxide alone. Then, the effects of hydrogen peroxide initial concentration and spectral fluence rate on the reactor windows for the combined process will be studied. In addition, resorting to previous investigations and our own experimental results, a general, tentative reaction scheme will be proposed in order to provide a solid basis for further kinetic studies. Furthermore, the method was applied to a raw groundwater sample from the West Region of Santa Fe Province (Argentina) in order to assess the efficiency and feasibility of the process operating under actual conditions.

2. Material and methods

2.1 Reagents

A 1000 mg L^{-1} stock solution of As(III) was prepared by dissolving sodium arsenite (≥ 99%, Sigma–Aldrich p.a.) in ultra pure water. A 500 mg L^{-1} stock solution of H_2O_2 was prepared from hydrogen peroxide (30% w/v, Ciccarelli p.a). Accurately diluted solutions of As(III) and H_2O_2 were prepared daily using standard stock solutions. Fluka Catalase from bovine liver (2195 units mg^{-1}) was used (1 unit decompose 1 μmol min^{-1} of H_2O_2 at pH 7.0 and 25 °C). For the speciation process, 1 N HCl and methanol (Sintorgan, HPLC grade) were used. Ultra pure water (0.055 μS cm^{-1}) was used for all dilutions. This water was obtained from an OSMOION™ purification system. Laboratory glassware was kept overnight in a 10% v/v HNO_3 solution and then rinsed three times with ultra pure water as it was recommended in several publications.[26,27]

2.2 Equipment

The experiences were carried out in a cylindrical reactor made of Teflon®, closed in both extremes with two demountable, flat, circular windows made of quartz Suprasil quality. The reactor length was 5.2 cm and the inner diameter 5.2 cm. (Reactor volume = 110 cm^3).

Radiant energy was supplied by two Heraeus tubular UVC lamps placed at the focal axis of their respective parabolic reflectors made of aluminium, mirror polished, with Alzac® coating. The lamps have a radiant power (P) of 40 W each (that render a radiant output power equal to 16 W = 3.4×10^{-5} einstein s^{-1}). They are germicidal lamps with one single significant emission wavelength at 253.7 nm. Each window permitted the interposing of: one shutter to impede the light passage when desired and neutral density filters to carry out experiments at different irradiation rates. The filters used permitted the transmission of 18% and 43% of the originally received spectral fluence rate. The reactor was part of a recycling batch system that included: a large volume glass tank (2000 cm^3) with strong mechanical stirring and provisions for sampling and pH control and an all glass and Teflon centrifugal recirculation pump (QVF ST 16 3 HS), as described in Fig. 1. The reactor was operated at a high recirculation flow rate, thus good mixing in the reactor was surely achieved. Also, included in the circuit there was a cooling system to keep the temperature constant (20 °C). The whole equipment was protected from extraneous light.

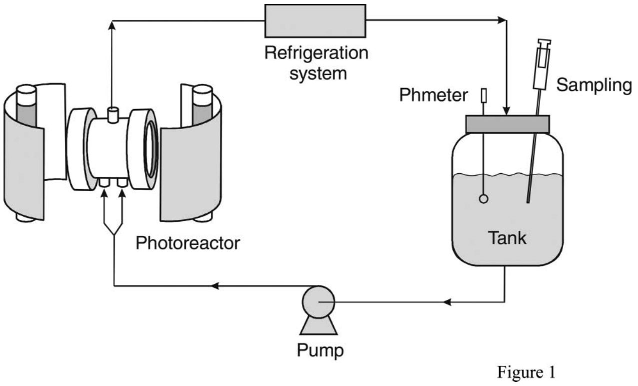

Figure 1

Fig. 1 Experimental setup.

Table 1 Experimental conditions

Variable and units	Value
Arsenic(III) initial concentration (μg L^{-1})	200
Hydrogen peroxide initial concentration (mg L^{-1})	0–30
Spectral fluence rate at the reactor windows:	
$E_{p,o,W}^{\lambda=253.7\,nm}$ (einstein cm^{-2} s^{-1}) $\times 10^9$:	
Heraeus 40 W lamp (100%)	22.4
Heraeus 40 W lamp (with filter) (43%)	9.8
Heraeus 40 W lamp (with filter) (18%)	4.1
Reaction Time (min)	5, 15, 30
Initial pH	5.6–6.7
T/°C	20

2.3 Operation

Experiments were performed by varying the concentration of hydrogen peroxide and the spectral fluence rate at the reactor windows at constant pollutant concentration. Details of the operating conditions are described in Table 1.

Each run was performed as follows: the working solution was added to the reactor with the desired concentration of arsenite and hydrogen peroxide. The germicidal lamps were turned on while the shutters were on and recirculation of the fluid was set in motion. Once the concentration, temperature and lamp operation reached steady state, the shutters were removed and the reaction started indicating the time $t = 0$. The initial concentration of the mixture was measured and sampling (25 mL) was made at regular time intervals. After every run the equipment was carefully washed. It must be noted that due to the type of equipment used in this work (a recycler with a tank) the total reaction time does not represent the one effectively corresponding to the irradiation time of the reaction volume. Thus, the actual exposure to radiation must take into account the ratio given by the Photoreactor Volume over the Total Volume ($V_R / V_T = 0.055$).

The adopted constant temperature for our studies (20° C) does not necessarily constitute the optimum operating conditions. Heating the fluid resorting to different means, could lead to higher reaction rates. However, optimization of the reaction operation was not within the scope of this work

2.4 Measurements

The arsenic concentration was measured using a Perkin Elmer AAnalyst 800 atomic absorption spectrometer (ASS) equipped with a TGHA graphite furnace. An electrodeless discharge lamp (EDL) was used as the source of radiation for arsenic determination. The procedure for atomic absorption measurements was followed according to the EPA.[28] Each analysis was repeated three times to obtain the average value and its relative standard deviation (%RSD). The RSD value of the three replicate samples of each analysis was below 2.5%. Immediately after sampling, prior to the analysis of arsenic by ASS, a catalase solution was added to each sample in order to decompose the remaining hydrogen peroxide and avoid further oxidation.

For the arsenic speciation analyses, the samples were allowed to pass through silica based strong anion exchange cartridges (SAX) with bonded group aminopropyl chloride form (Varian). The cartridges retained As(V), while As(III) was collected and analyzed by ASS. To check the reliability of this approach several solutions containing mixtures of both oxidation states were prepared and submitted to the procedure. The results indicate that speciation even at very low levels is possible, obtaining reasonable values of recovery (ranging from 98 to102%). Thus, the concentration of As(V) was calculated from the difference of the total arsenic concentration (before passing the cartridges) and the concentration of As(III) obtained by ASS.

The H_2O_2 concentration was analyzed with a spectrophotometric method at 350 nm according to Allen *et al.*,[29] employing a Cary 100 Bio UV-visible instrument (the standard deviation value ranged from 0.05–0.08 for the calibration range studied). pH was controlled with HI 98127 Hanna pH meter (accuracy: ±0.1).

The spectral fluence rate at the reactor windows was experimentally measured by ferrioxalate actinometry according to Murov *et al.*[30] and Zalazar *et al.*[31]

Raw groundwater parameters analyses were made as follows: pH, salinity, dissolved oxygen; conductivity and turbidity were measured employing Horiba 10 portable equipment. Total organic carbon was measured with a Shimadzu TOC-5000 A instrument. Total alkalinity, total hardness, chlorides, sulphates and phosphates were analyzed according to AWWA.[32]

3. Results and discussion

3.1 Preliminary runs

Preliminary runs were carried out to separately investigate the effect of H_2O_2 and UVC radiation. The first run was performed employing concentrations of As(III) and H_2O_2 of 200 μg L^{-1} and 3 mg L^{-1}, respectively, without UV radiation. After 15 min of recycling under normal operating conditions, an oxidation yield of 13% was reached. A similar run was performed with an As(III) concentration of 200 μg L^{-1} using 40 W Heraeus UVC lamps without H_2O_2. After 15 min, an oxidation yield of 12% was reached. No distinguishable changes in As(III) were observed after 15 min for both experiments. It is curious what happened with UV radiation alone since none of the possible arsenic species absorbs photons at the employed radiation wavelength. A run designed to study this phenomenon was made with only 200 μg L^{-1} of As(III) in the absence of UV radiation and hydrogen peroxide. After 30 min, an oxidation yield of 10% was reached. On the basis of this result, the conversion obtained with UV alone could probably be explained by the effect of dissolved O_2. Therefore, the effect of H_2O_2 alone is too low if dissolved oxygen is able to oxidize 10% of the initial As(III) concentration.

The direct effect of hydrogen peroxide in As(III) oxidation has been previously reported by Yang *et al.*[25] They found that complete oxidation of As(III) can be obtained at pH = 9 but by using a very large excess of hydrogen peroxide with respect to the stoichiometric demand. The reaction was also studied by Pettine *et al.*,[11] observing that the reaction is possible in both alkaline and acidic conditions. They found that the reaction is strongly influenced by the existing pH, which gives rise to different dominant As species that are thermodynamically feasible for undergoing oxidation. However, increasing the pH above 8 shows a remarkable effect on the rate. These two studies provide the explanation of the low oxidation efficiency observed under the operating conditions employed in this work (pH 5.6–6.7). Kim and Nriagu[7] reported that oxidation of As(III) in water with dissolved air is possible even if the efficiency of this process is very low. The reaction may become more important only if oxygen saturated water environments are used for the process.[33,34] Thus, the obtained results in this work are in accordance with former studies.

Hence, even if conversion is not very important in the case of dissolved O_2 and the effect of H_2O_2 is too low (almost nil) in the transformation of As(III) into As(V), they must be part of the reaction mechanism.

3.2 Effect of H_2O_2 initial concentration

Evaluating the effect of H_2O_2 is essential when this process (H_2O_2/UVC) is studied. It is well known that for organic pollutants, there is an optimum concentration ratio between the hydrogen peroxide and the organic substance.[12,14,35,36] There are no reasons to think that this effect cannot be also present in this process. The oxidation rate increases continuously when the concentration of hydrogen peroxide is raised till a point where it reaches a maximum and then, also in a continuous manner, decreases. The reason for this behavior is known to be produced by the scavenging effect of an excess of hydrogen peroxide on the $OH^{\bullet}$ radicals that are, as commented before, mainly responsible for the oxidation reaction. The maximum depends on the chemical species under consideration and must be determined for each particular case. In addition, the use of high concentrations of H_2O_2 can affect the process economic feasibility and sometimes the oxidant remnant cannot be tolerated in the effluent discharge.

Various experiments were carried out in order to study this effect starting with a concentration of As(III) of 200 μg L^{-1}, varying the above mentioned molar ratio, defined as $r = C_{H_2O_2}/C_{As(III)}$ between $r = 0$ and $r \approx 350$ (0 to 30 mg L^{-1} of H_2O_2 initial concentration) at constant temperature and spectral photon fluence rate at the reactor windows. The results have shown pseudo-first order behaviour for arsenic oxidation (with the consequent appearance of an observed pseudo-first order rate constant). The term "observed" is used here because its value was obtained for the conditions mentioned above. If these conditions change, the observed rate constants will also vary. Experimental results using the observed pseudo-first order rate constants obtained and the molar ratios for each run are shown in Fig. 2. It can be seen that 159–247 is the molar ratio range of the higher reaction rates. These values correspond to H_2O_2 concentrations between 15 and 20 mg L^{-1}. A run made under the best operating conditions (H_2O_2 concentration of 20 mg L^{-1}) is represented in Fig. 3. The progression of As(III) concentration, H_2O_2 concentration and pH can be observed. The arsenic(III) concentration decays, as has been said before, following pseudo-first order kinetics with an observed pseudo-first order rate constant $k = 1.23 \times 10^{-2}$ s^{-1} with a correlation coefficient of 0.998. The concentration of H_2O_2 decays linearly (percentage of conversion in 5 min = 6.4%), while the pH remains relatively constant (5.6–6.0). The oxidation conversion of arsenic was almost 97% after 5 min under these experimental conditions.

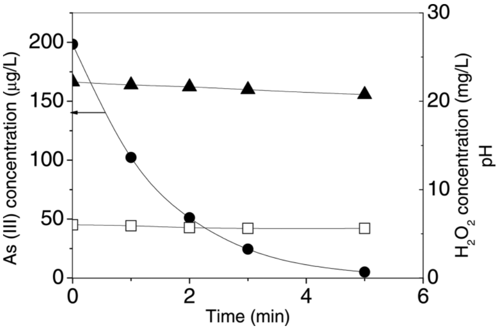

Fig. 3 Oxidation of arsenic. Evolution of As(III) (●), H_2O_2 (▲) and pH (□). $C^0_{As(III)} = 200$ μg L^{-1}; $C^0_{H_2O_2} = 20$ mg L^{-1}.

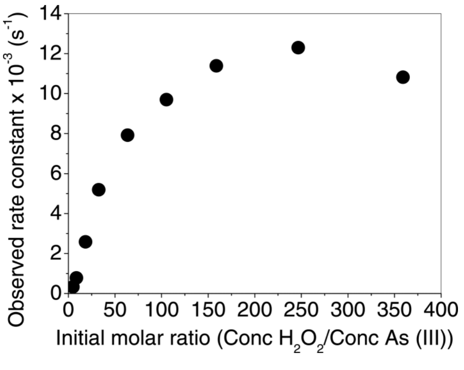

Fig. 2 Observed rate constant for As(III) *vs.* Initial molar ratio (Conc H_2O_2/Conc As(III)). $C^0_{As(III)} = 200$ μg L^{-1}.

3.3 Effect of UVC spectral fluence rate at the reactor windows

As(III) evolution for three different levels of the spectral fluence rate at the reactor windows ($E^{\lambda = 253.7\,nm}_{p,o,W}$) and two different H_2O_2 concentrations is represented in Fig. 4. The runs were made with 200 μg L^{-1} of As(III), 3 mg L^{-1} and 20 mg L^{-1} of H_2O_2. The values of the spectral fluence rate were: 22.4×10^{-9} Einstein cm^{-2} s^{-1} (two 40 W lamps), 9.82×10^{-9} Einstein cm^{-2} s^{-1} and 4.11×10^{-9} Einstein cm^{-2} s^{-1} (with the same lamps but using neutral filters that permitted the passage of 43% and 18%, respectively, of the spectral fluence rate). In Fig. 4, it can be noticed that the observed rate constant for the passage of As(III) to As(V) for both H_2O_2 concentrations increased linearly with the spectral photon fluence rate at the reactor windows. These results are in accordance with publications that study UV/H_2O_2 process for organic compounds.[12,14,36,42] Therefore, this dependence will be considered in the development of the kinetic model.

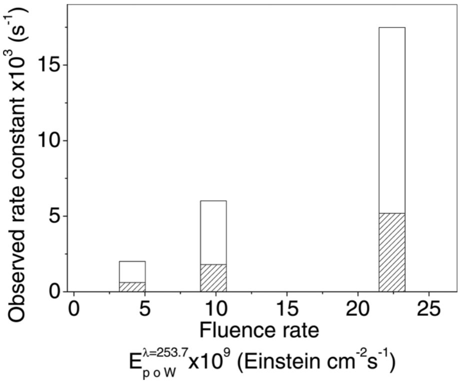

Fig. 4 Effect of the spectral fluence rate at the reactor windows ($E^{\lambda = 253.7\,nm}_{p,o,W}$) on the observed rate constant (s^{-1}). $C^0_{As(III)} = 200$ μg L^{-1}; $C^0_{H_2O_2} = 3$ mg L^{-1} (▨); $C^0_{H_2O_2} = 20$ mg L^{-1} (□).

3.4 Proposal of an oxidation scheme

Arsenious acid (inorganic As(III)) is a weak acid that primarily exists as dissolved $H_3AsO_3^\circ$ at pH conditions below 9.2 and in the form of its dissociated anions under more alkaline conditions ($H_2AsO_3^-$ pK_a = 9.2, $HAsO_3^-$ pK_a = 12.1 and AsO_3^{3-} pK_a = 13.4).[37] Arsenic acid (inorganic As(V)) is also a weak acid, which includes $H_3AsO_4^\circ$ under very acidic conditions (pH < 2.2) and its dissociated anions in less acidic, neutral and alkaline waters ($H_2AsO_4^-$ pK_a = 2.2, $HAsO_4^{2-}$ pK_a = 6.8; and/or AsO_4^{3-} pK_a = 11.6).[37] The existence of As(IV) as a transitory intermediate has been reported in previous research studies.[4,6,17,38–41] Klanning *et al.*,[39] have noted the presence of different species of As(IV) in the pH range 2–13. They have suggested an assignment of $As(OH)_4$, $HAsO_3^-$ (pK_a = 3.64), $As(OH)_3O^-$ (pK_a = 7.26) and AsO_3^{2-} (pK_a = 7.57) to these species.

Since the working pH is between 5.6 and 6.7, the inorganic species that will be considered in our proposal are: $H_3AsO_3^\circ$ to denote As(III), $HAsO_3^-$ to denote As(IV) and $H_2AsO_4^-$ to denote As(V).

The photolytic reactions that occur between UV radiation (wavelength below 300 nm) and H_2O_2 are well-known and will be adopted here.[42,43] However, during some time between 2002 and 2009, in two important advanced oxidation processes, namely UVA/TiO_2 (with and without the addition of sensitizers, for instance, Pt) and UVC/H_2O_2, the role of the main involved oxidant species for As(III) oxidation was a subject of controversy. In both reactions $OH^\bullet$ and superoxides $HO_2^\bullet/O_2^{\bullet-}$ radicals are formed. For this particular reaction, initially it was proposed that superoxides were the main radicals responsible for the conversion of As(III) into As(V).[17,18] Further detailed studies confirmed that the main oxidant species is the $OH^\bullet$ radical and that superoxides have a less significant contribution to the transformation.[19,21,40,44] Nevertheless, in order to provide a complete oxidation scheme, the effect of superoxide ions will also be included here.

A plausible, tentative reaction mechanism for the oxidation of As(III) to As(V) using the UV/H_2O_2 process is shown in equations 1–12 of Table 2. The oxidation of As(III) is caused by the highly reactive $OH^\bullet$ radicals (reaction 7)[6,23,41] that were produced by the hydrogen peroxide photolysis (reactions 1–6). Although H_2O_2 by itself is not the important species responsible for the rapid oxidation of As(III) observed in the current study, on the basis of the experimental results and on the support of references from the literature,[11,25] the reaction between As(III) and H_2O_2 should be included (reaction 8). Also, experimental results and reference[45] have shown that the reaction between As(III) and dissolved oxygen could not be neglected, even if low oxidation yields were obtained (reaction 9). For the sake of completeness, as it was mentioned before, the possibility of a minor intervention of the superoxide ion will be also considered (reaction 10).[21,44] The kinetic study that will be conducted after this work will indicate if its effect is of the same order of magnitude as compared with the one produced by the direct oxidation by oxygen and hydrogen peroxide alone or lower. The resulting As(IV) is highly unstable and readily undergoes further oxidation with either another $OH^\bullet$ radical or with dissolved oxygen forming the stable As(V) (reactionz 11 and 12).[4,23,41]

From the previous reaction sequence, it will be possible to derive, in a future work, a mathematical model able to represent the kinetics of arsenic oxidation and validate its predictive quality with the experiments presented in this one. This constitutes the objective of our next study.

Table 2 A proposal of the reaction mechanism

N°	Constants	Reactions
(1)	Φ_p	$H_2O_2 \rightarrow 2OH^\bullet$
(2)	k_2	$H_2O_2 + OH^\bullet \rightarrow HO_2^\bullet + H_2O$
(3)	k_3	$H_2O_2 + HO_2^\bullet \rightarrow OH^\bullet + H_2O + O_2$
(4)	k_4	$2OH^\bullet \rightarrow H_2O_2$
(5)	k_5	$2OH^\bullet \rightarrow H_2O_2 + O_2$
(6)	k_6	$OH^\bullet + HO_2^\bullet \rightarrow H_2O + O_2$
(7)	k_7	$H_3AsO_3 + OH^\bullet \rightarrow H_3AsO_3^- + H^+ + H_2O$
(8)	k_8	$H_3AsO_3 + 1/2H_2O_2 \rightarrow HAsO_3^- + H^+ + H_2O$
(9)	k_9	$2H_3AsO_3 + 1/2O_2 \rightarrow 2HAsO_3^- + 2H^+ + H_2O$
(10)	k_{10}	$H_3AsO_3 + HO_2^\bullet \rightarrow HAsO_3^- + HO_2^- + 2H^+$
(11)	k_{11}	$HAsO_3^- + O_2 + H_2O \rightarrow H_2AsO_4^- + HO_2^\bullet$
(12)	k_{12}	$HAsO_3^- + OH^\bullet \rightarrow H_2AsO_4^-$

3.5 Raw groundwater test

In order to evaluate the effectiveness of the UV/H_2O_2 process, the oxidation of As(III) was carried out employing a raw groundwater sample (obtained from a manual pump located in Angelica village, Santa Fe, Argentina) spiked with 100 µg L^{-1} of sodium arsenite. The experimental conditions were: H_2O_2 concentration = 20 mg L^{-1}; $E_{p,o,W}^{\lambda = 253.7\,nm} = 22.4 \times 10^{-9}$ einstein cm^{-2}s^{-1}; reaction time = 5 min. The procedure was the same as it was described before.

The groundwater characteristics are shown in Table 3.

The evolution of As(III) concentration, H_2O_2 concentration and pH is represented in Fig. 5. It can be seen that As(III) decays following a pseudo-first order kinetics with an observed rate constant $k = 4.9 \times 10^{-3}$ s^{-1} with a correlation coefficient of 0.997. The concentration of H_2O_2 decays linearly (percentage of conversion in 5 min = 10.9%), while the pH remains constant (pH = 7.9). This behaviour was the same as it was observed for ultra pure water. The conversion of arsenic was almost 77% after 5 min of exposure time. The observed rate constants for different initial concentrations of arsenic and different compositions of water should not be rigorously compared. However, in this case, it is useful to establish a preliminary measure of the efficiency of the process in groundwater samples. The As(III) observed rate constant in groundwater sample was slowed by about 60% compared with ultrapure water (Fig. 6). Apparently, some of the components of the raw water used (*e.g.* carbonate species) affects the activity of the hydroxyl radicals, which is an aspect that has been frequently mentioned in other studies.[4,12,42]

Table 3 Groundwater characteristics

Parameter	Value
pH	7.6
Temperature	20.9 °C
Dissolved O_2	6.7 mg L^{-1}
Turbidity	1
Salinity	0.1%
Conductivity	2.7 mS cm^{-1}
Total Organic Carbon	3.25 mg L^{-1}
Total alkalinity ($CaCO_3$)	920 mg L^{-1}
Chlorides (Cl^-)	137 mg L^{-1}
Sulphates (SO_4^{2-})	307 mg L^{-1}
Phospates (PO_4^{3-})	2.3 mg L^{-1}
Total hardness ($CaCO_3$)	75 mg L^{-1}

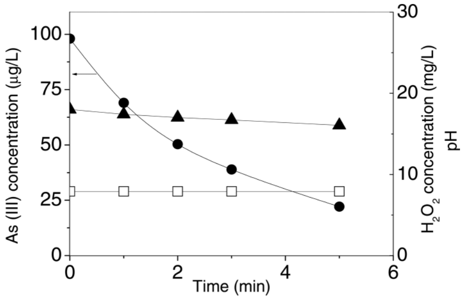

Fig. 5 The oxidation of arsenic in groundwater. Evolution of As(III) (●), H_2O_2 (▲) and pH (☐). $C^0_{As(III)} = 100\ \mu g\ L^{-1}$; $C^0_{H_2O_2} = 20\ mg\ L^{-1}$.

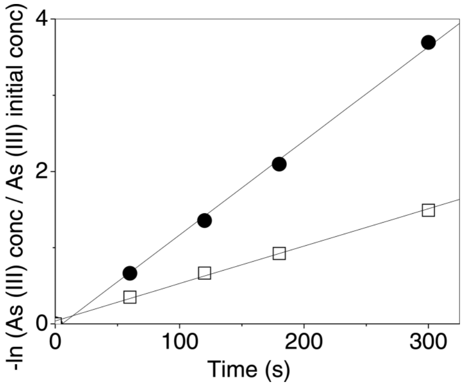

Fig. 6 Kinetics of As(III) oxidation by a UV/H_2O_2 process in ultrapure water (●), $k = 1.23 \times 10^{-2}\ s^{-1}$and groundwater (☐), $k = 4.9 \times 10^{-3}\ s^{-1}$. $C^0_{H_2O_2} = 20\ mg\ L^{-1}$.

The results of this study indicate that UV/H_2O_2 process could be a promising technique for the oxidation of As(III) in surface and groundwater.

4. Conclusions

The application of UV radiation and H_2O_2 separately is not effective for the oxidation of arsenic in water. Conversely, using the combined UV/H_2O_2 process employing low concentrations of H_2O_2, high conversion values in very short reaction times are obtained.

The experimental results have shown that for the usual values of As(III) found in typical raw waters, an initial molar ratio in the range of 159–247 renders higher efficiency to carry out the process.

The spectral photon fluence rate has a significant influence in the reaction rate. The linear dependence (proven at different H_2O_2 concentrations) will be considered in the development of the kinetic model in our next work.

A proposal of an oxidation reaction scheme is presented on the basis of references from previous reports and our own experimental data.

The proposed Advanced Oxidation Process UV/H_2O_2 results in a feasible and effective technology to oxidize arsenic(III) in natural waters.

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