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RESEARCH NOTES

Studies on the Oxidation of As(III) to As(V) by In-Situ-Generated Hypochlorite

Subramanyan Vasudevan,* Swaminathan Mohan, Ganapathy Sozhan,
Nenmeni Subbarao Raghavendran, and Chellapa Vadivel Murugan

Central Electrochemical Research Institute (CSIR), Karaikudi 630 006, India

The objective of this study is to oxidize arsenite, which is denoted as As(III), into arsenate, which is denoted as As(V), with an in-situ-generated hypochlorite, using metal-oxide-coated titanium and stainless steel as the insoluble anode and cathode, respectively. The cells were operated at different pH values (pH 3−8), temperatures (300−333 K), concentrations of chloride (50−500 mg/L), and current densities (0.02−0.22 mA/dm^2). The oxidation of As(III) (3 mg/L) to As(V) with in-situ-generated hypochlorite proceeds efficiently (by achieving a oxidation efficiency of 100%) when 125 mg/L of chloride (pH 7.00) is electrolyzed at a current density of 0.04 mA/dm^2 and a temperature of 300 K. It is proven that oxidation by electrolytically formed hypochlorite is a more convenient method/process than dosing the solution with other oxidants.

Introduction

Arsenic is a contaminant of well-known toxicity and carcinogenicity in the drinking water in many parts of the world, including the Bengal delta (in Bangladesh and West Bengal, India). As a water contaminant, arsenite (As(III)) is more toxic and mobile than arsenate (As(V)). Unlike the arsenate anions ($H_2AsO_4^-$ and $HasO_4^{2-}$), the dominant As(III) species, up to pH 8.0, is the nonionic (H_3AsO_3), which does not adsorb as strongly to mineral surfaces as As(V).[1] Thus, As(III) is more mobile in groundwater and is also more difficult to remove in arsenic removal treatments.[2] Therefore, many conventional arsenic removal procedures involves the oxidation of As(III), followed by the adsorption or coprecipitation of the As(V) formed using adsorbents or coagulants, such as metal oxyhydroxides.

Much research has focused on methods for the oxidation of As(III) (including studies that involve oxidation by air and pure oxygen, ozone, activated carbon, iron, and manganese compounds; microbiological oxidation; H_2O_2, Fenton's reagent and photochemical oxidation. It is observed that only a few percent of As(III) were oxidized within 7 days in the presence of air,[3] and 8% of As(III) was oxidized within 60 min in solutions that have been purged with oxygen.[4] The oxidation rate of As(III) increases in the presence of oxidants such as ozone and chlorine dioxide, and it is observed that[5] the oxidation of As(III) with ozone is too expensive for use in developing countries, because of the high energy input. As(III) can be oxidized catalytically in the presence of activated carbon and oxygen, and 90% of the As(III) was oxidized with 5−10 g $^{-1}$ activated carbon within 20−30 min in water that initially contained 40 ppb As(III). Manganese oxides[6−11] and $KMnO_4$[12] is also used to oxidize arsenite to arsenate. If Fe(II) and Mn(II) are present in groundwater, As(III) is often oxidized, because of the presence of bacteria.[6] Hambsch et al.[13] showed that bacteria could oxidize As(III) in the presence of 1 mg/L of oxygen. The oxidation of As(III) in the presence of H_2O_2 was investigated,[14] and it is determined that[15] the oxidation of As(III) by H_2O_2 is a highly pH-dependent reaction. It is reported that[14] arsenite is photocatalytically oxidized under alkaline conditions (pH 9) in the presence of oxygen.

The oxidation of As(III) has also been studied by other researchers, using a variety of techniques, including oxidation by electrogenerated iodine,[16] oxidation by peroxodisulfate,[17] oxidation by perchloric acid,[18] oxidation by chromic acid,[19] and oxidation by hexacyanoferrate(III).[20]

Although many oxidants are available for the oxidation of As(III) to As(V), ozone, hypochlorite, permanganate, chlorine dioxide, hydrogen peroxide, etc., are the effective oxidants that are used in the oxidation of As(III) to As(V) in drinking water. Because of the disadvantages such as higher cost of production, poor oxidation efficiency, and color formation in the case of oxidants such as ozone, chlorine dioxide, and permanganate, respectively, hypochlorite is observed to be the best oxidant for the oxidation of As(III) and not much work was conducted for the in situ generation of hypochlorite to oxidize As(III) to As(V) in drinking water.

Therefore, the main objective of this study is to oxidize arsenite (As(III)) to arsenate (As(V)) with the in-situ-generated hypochlorite, using the oxide-coated titanium and stainless steel as the insoluble anode and cathode, respectively. To optimize the parametric conditions, the cells were operated at different pH, temperatures and current densities.

Materials and Methods

Cell Design and Electrolysis. The electrolytic cell (Figure 1) consisted of a 0.25-L glass vessel that was fitted with a poly(vinyl chloride) (PVC) cell cover with slots to introduce the electrodes, a pH sensor, a thermometer, and the electrolytes. A stainless steel (SS304; SAIL, India) plate with dimensions of 0.009 m^2 was used as a cathode. A noble metal oxide (RuO_2/TiO_2/SnO_2) coated titanium plate (0.009 m^2) of 99.8% purity (Mithani(I) Limited, India) acted as the anode with an interelectrode distance of 0.5 cm. The mixed-oxide electrodes were prepared by the thermal decomposition process, as described in the literature.[21] The coating solution for the preparation of the anodes was prepared from the chlorides of the three metals,

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* To whom correspondence should be addressed. Tel.: 91 4565 227554. Fax: 91 4565 227779. E-mail: vasudevan65@gmail.com, svdevan_2000@yahoo.com.

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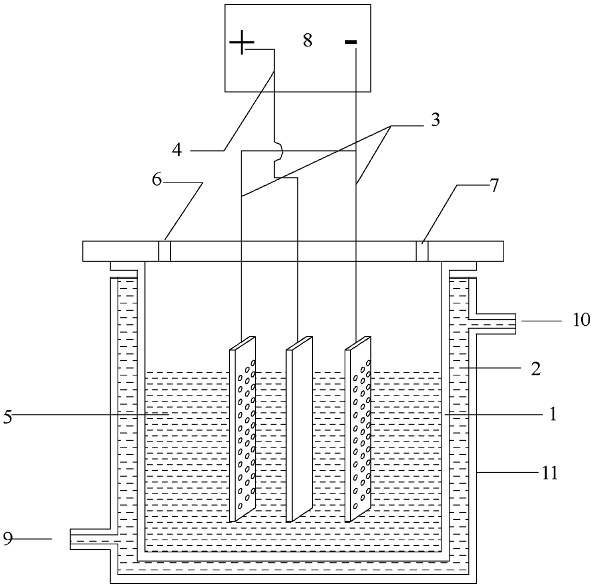

Figure 1. Laboratory-scale cell assembly. Legend is as follows: (1) cell, (2) thermostatic water, (3) stainless steel cathode, (4) anode, (5) electrolyte, (6 & 7) holes to introduce the pH sensor and thermometer, (8) dc source, (9) inlet, (10) outlet, and (11) thermostat.

viz., $RuCl_3{\cdot}xH_2O$ (38.4% ruthenium; Johnson Mathey, U.K.), $TiCl_4$ (25.1% titanium; Riedel De Haan AG) and $SnCl_4{\cdot}5H_2O$ (33.9% tin; J. T. Baker Chemical Co., USA). The salts of the aforementioned three metals were taken in the ratio of 30 RuO_2/50 TiO_2/20 SnO_2, dissolved in 2-propanol (Johnson Mathey, U.K.), and then painted over the pretreated titanium mesh (which was polished, degreased, and etched in a 10% oxalic acid (Johnson Mathey, U.K.) solution at 363 K for 30 min) to produce a uniformly spread layer. The paint layer was dried at 353 K in an air oven for 10 min to evaporate the solvent. The samples were then transferred to a muffle furnace kept at 673 K for 10 min. During this period, the heating zone of the furnace was maintained with a good supply of air from a compressor. The electrode was then removed from the furnace and cooled. The process of brushing the coating solution, drying at 353 K, and then heating in the presence of air at 673 K was repeated six to eight times. After the final coating, the electrode was heated at 723 K for 1 h and allowed to cool in the oven itself over a period of 8 h.

Sodium arsenite (Analar Reagent) was dissolved in water for the required concentration; a 0.20 L portion of solution was used for each experiment, which was used as the electrolyte. The concentration of chloride present in the water is in the range of 125−150 mg/L. Different concentrations such as 1, 3 and 5 mg/L of the sodium arsenite were simulated and it was oxidized. Oxidation efficiency was calculated as a function of experimental variations, such as pH, concentration of hypochlorite, temperature, etc. The concentration of arsenite, and hypochlorite were all analyzed before and after oxidation of As (III) with standard analytical procedure. Regulated direct current was supplied from a rectifier (25 A, 0−25 V, Aplab Model).

Analysis. Chloride was estimated using a standard silver nitrate (Analar Grade, Ranbaxy, India) solution.[22] Hypochlorite was estimated using standard thiosulfate (Analar Grade, Ranbaxy, India) solution and Starch (Analar Grade, Ranbaxy, India) as an indicator.[22] The presence of arsenite and arsenate was determined by ion chromatography (Metrohm, Ltd.).

Results and Discussion

Hypochlorite ions are generated during the electrolysis of chloride ions present in the water (electrolyte) itself. The reactions involved during the electrolysis of chloride ions are given as follows.

The chloride ions are converted to chloride at the anodic surface,

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad (1)$$

while water is ionized at the cathode to give the hydroxyl ion and hydrogen:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (2)$$

In the bulk, the liberated chlorine reacts with water to produce hypochlorous acid:

$$Cl^- + H_2O \rightarrow HOCl + H^+ + 2e \qquad (3)$$

The generated hypochlorous acid further dissociates to give a hypochlorite ion and a hydrogen ion.

$$HOCl \rightarrow OCl^- + H^+ \qquad (4)$$

The hydroxyl ion reacts with hydrogen to form a water molecule:

$$H^+ + OH^- \rightarrow H_2O \qquad (5)$$

Reactions 1−5 give the mechanism for the generation of the hypochlorite ion. As mentioned previously, the generated hypochlorite ion acts as the main oxidizing species in the oxidation of As(III) present in the water.

The As(III) present in the water reacts with the OCl^- species, according to the reaction

$$H_3AsO_3 + HOCl \rightarrow H_2AsO_4{}^- + 2H^+ + Cl^- \qquad (6)$$

and becomes oxidized.

Effect of pH of the Electrolyte. Increasing the pH from 3 to 8 resulted in an increase in the amount of hypochlorite (from 2.2 mg/L to 6 mg/L; see Table 1). Chlorine was generated from Cl^- ions at the anode surface and diffused to the bulk solution hydrolyzed to hypochlorite. As indicated by reactions 3 and 4, the hydrolysis of chlorine in the bulk phase is inhibited under acidic conditions. From reactions 3 and 4, the hydrolysis of chlorine increases when the concentration of OH^- ions increases.[23] The maximum hypochlorite generation by the anodic oxidation of chloride ions was determined when the pH exceeded 7.0. Thus, the pH was maintained at ≥7.0. These results favor the practical use of As(III) oxidation, because the pH of the groundwater in most of the places is near neutral pH values.

Effect of Temperature of the Electrolyte. Table 2 shows the variation of hypochlorite concentration and the oxidation of As(III) with temperature. The table reveals that the concentration of hypochlorite was steady in the temperature range of 300−313 K and decreased beyond 313 K. Correspondingly, the oxidation efficiency for the oxidation of As (III) also decreased beyond 313 K. Nevertheless, it is always necessary to operate the cell at lower temperatures to prevent the formation of chlorate,[24] per reactions 7 and 8, given below:

$$2HOCl + ClO^- \rightarrow ClO_3{}^- + 2H^+ + 2Cl^- \qquad (7)$$

$$6ClO^- + 3H_2O \rightarrow 2ClO_3{}^- + 6H^+ + 4Cl^- + 1.5O_2 + 6e \qquad (8)$$

$$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^- \qquad (9)$$

Table 1. Effect of pH for the In Situ Generation of Hypochlorite with Oxidation Efficiency of As(III)^a

sample number	pH	Initial Concentration (mg/L)		Final Concentration (mg/L)		oxidation efficiency^b (%)
		hypochlorite	As(III)	hypochlorite	As(III)	
1	3.0	2.2	3	0	0.8	40 (95)
2	5.5	3.5	3	0.5	0	100 (95)
3	6.0	5.0	3	2	0	100 (95)
4	7.0	5.0	3	2	0	100 (95)
5	8.0	6.0	3	3	0	100 (95)

[a] Conditions: concentration of chloride in the electrolyte, 125 mg/L; temperature, 300 ± 1 K; current density, 0.04 mA/dm^2; and duration, 10 min. [b] Values given in parentheses show the time required for oxidation (in seconds).

Table 2. Effect of Temperature for the In Situ Generation of Hypochlorite with Oxidation Efficiency of As(III)^a

sample number	temperature (±1 K)	Initial Concentration (mg/L)		Final Concentration (mg/L)		oxidation efficiency^b (%)
		hypochlorite	As(III)	hypochlorite	As(III)	
1	300	5.0	3	2	0	100 (95)
2	313	4.5	3	1.5	0	100 (95)
3	323	2.2	3	0	0.8	40 (95)
4	333	1.0	3	0	2	33 (95)

[a] Conditions: concentration of chloride in the electrolyte, 125 mg/L; electrolyte pH, 7.0; current density, 0.04 mA/dm^2; and duration, 10 min. [b] Values given in parentheses show the time required for oxidation (in seconds).

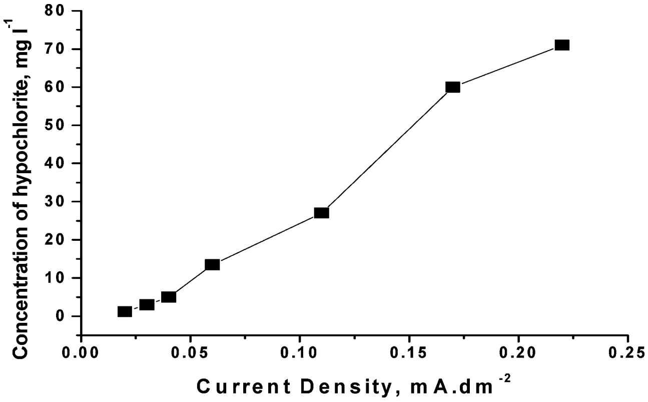

Figure 2. Effect of current density on the generation of hypochlorite. Conditions: concentration of chloride in the electrolyte, 125 mg/L; electrolyte pH, 7.0; electrolyte temperature, 300 ± 1 K; and duration, 10 min.

If the available hypochlorite is converted to chlorate, the oxidation efficiency will be decreased. In addition to the formation of chlorate, higher temperatures would favor the cathodic reduction, as per reaction 9, and self-decomposition of hypochlorite. Therefore, to avoid the formation of chlorate, the reduction of hypochlorite at the cathode, and the self-decomposition of hypochlorite, the cell should be operated below 313 K for better generation of hypochlorite and As(III) oxidation.

Effect of Current Density. Figure 2 depicts the dependence of the hypochlorite production on current density at 300 K with a chloride concentration of 125 mg/L. There is an increase in the generation rate with increasing current density.[24] In the practical use of the oxidation of As(III), this linear increase in the hypochlorite production rate with current density could be used to adjust the hypochlorite production rate, in relation to different concentrations of As(III) (i.e., changing the hypochlorite demand). Table 3 shows the effect of current density relative to the production of hypochlorite and As(III) oxidation efficiency.

Effect of Concentration of Chloride. The effect of the hypochlorite generation rate on the chloride ion concentration

Table 3. Effect of Current Density for the In Situ Generation of Hypochlorite with Oxidation Efficiency of As(III)^a

sample number	current density (mA/dm^2)	Initial Concentration (mg/L)		Final Concentration (mg/L)		oxidation efficiency^b (%)
		hypochlorite	As(III)	hypochlorite	As(III)	
1	0.02	1.2	1	0	0	100 (95)
2	0.02	1.2	3	0	2	34 (95)
3	0.02	1.2	5	0	4	21 (95)
4	0.04	5	1	4	0	100 (95)
5	0.04	5	3	2	0	100 (95)
6	0.04	5	5	0	0	100 (95)
7	0.06	13.5	2	11.5	0	100 (95)
8	0.06	13.5	5	8.5	0	100 (95)
9	0.06	13.5	10	3.5	0	100 (95)

[a] Conditions: concentration of chloride in the electrolyte, 125 mg/L; electrolyte pH, 7.0; electrolyte temperature, 300 ± 1 K; and duration, 10 min. [b] Values given in parentheses show the time required for oxidation (in seconds).

Table 4. Effect of Concentration of Chloride for the In Situ Generation of Hypochlorite with Oxidation Efficiency of As(III)^a

sample number	concentration of chloride (mg/L)	Initial Concentration (mg/L)		Final Concentration (mg/L)		oxidation efficiency^b (%)
		hypochlorite	As (III)	hypochlorite	As (III)	
1	50	1.0	3	0	2	34 (95)
2	125	5.0	3	2	0	100 (95)
3	250	9.0	3	6	0	100 (95)
4	500	13.5	12	1.5	0	100 (95)

[a] Conditions: electrolyte pH, 7.0; electrolyte temperature, 300 ± 1 K; current density, 0.04 mA/dm^2; and duration, 10 min. [b] Values given in parentheses show the time required for oxidation (in seconds).

(ranging from 50 to 500 mg dm^{-3} at 300 K) , relative to the oxidation efficiency of As(III), is presented in Table 4. It can be seen that the hypochlorite generation increases as the chloride concentration increases. As observed in the current density, in the present case also for the practical use of oxidation of As(III), the increase in the hypochlorite generation rate with chloride ion concentration (varies with different places) could easily be used to adjust the hypochlorite generation rate, in relation to the As(III) concentration of a particular area.

Conclusion

The oxidation of As(III) (3 mg/L) to As(V) using in-situ-generated hypochlorite proceeds efficiently (by achieving a oxidation efficiency of 100%) when chloride (125 mg/L, pH 7.00) is electrolyzed at a current density of 0.04 mA/dm^2 and a temperature of 300 K.

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Literature Cited

(1) Kinniburgh, D. G.; Smedley, P. L. Arsenic contamination of groundwater in Bangladesh; Final Report Summary; Bangaladesh Department for Public Health Engineering, British Geological Survey, 2000.

(2) Meng, X. G.; Bang, S.; Korfiatis, G. P. *Water Res.* **2000**, *34*, 1255−1261.

(3) Clifford, D.; Ceber, L.; Chow, S. Arsenic(III)/arsenic(V) separation by chloride-form ion-exchange resins. Presented at the XI American Water Works Association (AWWA) Water Quality Technology Conference, Norfolk, VA, 1983.

(4) Frank, P.; Clifford, D. Arsenic(III) oxidation and removal from drinking water, U.S. Environmental Protection Agency, EPA-600-52-861021, 1986; pp 2−86.

(5) Jiang, J. Q. Removing arsenic from groundwater for the developing world−A review. *Water. Sci. Technol.* **2001**, *44*, 89−98.

(6) Driehaus, W.; Seith, R.; Jekel, M. Oxidation of arsenite (As(III)) with manganese oxides in water treatment. *Water Res.* **1995**, *29*, 297−305.

(7) Borho, M.; Wilderer, P. Optimized removal of arsenate(III) by adaptation of oxidation and precipitation processes to the filtration step. *Water Sci. Technol.* **1996**, *34*, 25−31.

(8) Bajpai, S.; Chaudhuri, M. Removal of arsenic from groundwater by manganese dioxide-coated sand. *J. Environ. Eng.* **1999**, *8*, 782−784.

(9) Chiu, V. Q.; Hering, J. G. Arsenic adsorption and oxidation of manganite surfaces. Method for simultaneous determination of adsorbed and dissolved arsenic species. *Environ. Sci. Technol.* **2000**, *34*, 2029−2034.

(10) Jourhassat, C.; Charlet, L.; Bosbach, D.; Manceau, A. Arsenic(III) oxidation by birnessite and precipitation of manganese(III) arsenate. *Environ. Sci. Technol.* **2002**, *36*, 493−500.

(11) Manning, B. A.; Fendorf, S. E.; Bostick, B.; Suarez, D. L. Arsenic(III) oxidation and arsenic(V) reactions on synthetic birnessite. *Environ. Sci. Technol.* **2002**, *36*, 976−981.

(12) Jekel, M. Removal of arsenic in drinking water treatment. In *Arsenic in the Environment, Part 1. Cycling and Characterization*; Nriagu, J. O., Ed.; Advances in Environmental Science and Technology, Vols. 26−27; Wiley: New York, 1994; pp 19−132.

(13) Hambsch, B.; Raue, B.; Brauch, H. J. Determination of As(III) for the investigation of the microbial oxidation of arsenic(III) to arsenic(V). *Acta Hydrochim. Hydrobiol.* **1998**, *23*, 166−172.

(14) Yang, H.; Lin, W. Y.; Rajeshwar, K. Homogeneous and heterogeneous photocatalytic reactions involving As(III) and As(V) species in aqueous media. *J. Photochem. Photobiol. A: Chem.* **1999**, *132*, 137−143.

(15) Pettine, M.; Campanella, L.; Millero, F. T. Arsenite Oxidation by H_2O_2 in Aqueous Solutions. *Geochim. Cosmochim. Acta* **1999**, *63*, 2727−2735.

(16) Johnson, D. C.; Bruchenstein, D. C. A study of the kinetics of the oxidation of As(III) by electrogenerated iodine in alkaline media. *J.−Am. Water Works Assoc.* **1968**, *90*, 5692−6596.

(17) Nishida, S.; Kimura, M. Kinetic studies of the oxidation reaction of As(III) to As(V) by peroxodisulphate ion in aqueous alkaline media. *J. Chem. Soc. Dalton Trans*. **1989**, *9*, 357−360.

(18) Everett, K. G.; Skoog, D. A. Study of uncatalysed oxidation of As(III) by Ce(IV) in perchloric acid medium. *Anal. Chem.* **1971**, *43*, 1541−1547.

(19) SenGupta, K. K.; Chakladar, J. K. Kinetics of the chromic acid oxidation of As (III). *J. Chem. Soc., Dalton Trans*. **1989**, *2*, 222−225.

(20) Mohan D. Kinetics and mechanism of the oxidation of As(III) by Hexacyanoferrate(III) in alkaline medium. *Inorg. Chem*. **1977**, *16*, 1020−1029.

(21) Pushpavanam, S.; Narasimham, K. C.; Vasu, K. I. Structural properties of Ru−Ti−Sn mixed oxide coatings. *Bull. Electrochem.* **1988**, *4*, 979−983.

(22) Vogel, A. I. *Quantitative Inorganic Analysis*; Libgnabs Green: London, 1964; pp 259−260.

(23) Kraft, A.; Stadelmann, M.; Blaschke, M.; Kreysig, D.; Sandt, B.; Schroder, F.; Rennau, J. Electrochemical water disinfection. Part I: Hypochlorite production from very dilute chloride solutions. *J. Appl. Electrochem*. **1999**, *29*, 861−868.

(24) Vasudevan, S.; Mohan, S. Electrochemical preparation of barium chlorate from barium chloride. *Ind. Eng. Chem. Res*. **2006**, *45*, 2923−2928.

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