

## **Arsenic in the Iberoamerican region. The IBEROARSEN Network and a possible economic solution for arsenic removal in isolated rural zones**

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*ABSTRACT:* In this work, a short description of the problematic of arsenic in Iberoamerica will be given, indicating the affected geographical regions and their incidence on the quality of life of the populations. In Argentina, Chile, Bolivia, Peru, Ecuador and Mexico, at least 4 million people depend on water sources with toxic concentrations of arsenic. While in these countries the problem is known since decades, in Uruguay, Brazil, Nicaragua, Honduras and El Salvador, the problem has been detected or investigated only in last years, and, in other Latinamerican countries, the studies began only recently. In Spain and Portugal the problem of As is becoming increasingly important. The presence of As in drinking waters, together with poverty and malnutrition, causes the incidence of CERHA (chronic endemic regional hydroarsenicism, HACRE in Spanish), an illness that provokes serious problems like skin lesions and even cancer. The activities of the IBEROARSEN Network of the CYTED Program, an Iberoamerican project that aims at the interconnection of groups devoted to arsenic R&D, trying to find solutions to this problem in the region, will be described. In addition, results of evaluation of the efficiency of two very simple low-cost methods for As removal in plastic bottles using solar light, one of them using heterogeneous photocatalysis with TiO<sub>2</sub> immobilized on the walls followed by iron addition, and another one based on the use of zerovalent iron, which employs very cheap materials, are presented. The study was performed with synthetic and natural waters of rural, isolated, poor populations, not connected to the drinking water network of the provinces of Tucumán and Santiago del Estero, Argentina. For HP tests, synthetic as well as natural samples containing arsenic placed in bottles internally covered by a TiO<sub>2</sub> layer and exposed to solar or artificial UV light followed by an addition of an iron source resulted in As concentration well below the national standards. For ZVI tests, iron wool demonstrated to be a better iron source than packing wire for As removal. Solar irradiation, in synthetic as well as in natural samples, seems to definitively improve As removal, avoiding the use of high amounts of iron. Although both HP and ZVI gave similar results, the use of the first one could be superior due to the ability of removing simultaneously As, organic matter, toxic metals and microbiological contamination.

*KEYWORDS:* arsenic, Iberoamerica, heterogeneous photocatalysis, zerovalent iron.

### **1. INTRODUCTION**

An important amount of rural population in Latin America cannot access to safe water and is particularly affected by hydric diseases. Among the chemical pollutants present in ground and surface waters, especially those used for human drinking, arsenic is relevant due to the problems

associated to it. Although arsenic pollution can be attributed to some human activities (mining, wood preservatives, pesticides), the main causes are natural, due to the dissolution of local minerals in waters.

The presence of arsenic in drinking waters causes the incidence of chronic endemic regional hydroarsenicism (CERHA, HACRE in Spanish), a disease characterised by melanodermy, leucodermy and palmoplantar keratosis, ending in different types of cancer. To reduce the risks of As in drinking water, the European Union and the USA have established the limit for arsenic in drinking water in  $10 \mu\text{g L}^{-1}$ , value that is turning to be adopted in most of the Iberoamerican countries.

Although several regions in the world are affected by CERHA, especially Asiatic countries with low incomes (Bangladesh, India, China, Taiwan) (Hug, 2000), an important part of Iberoamerican countries suffers problems related to As, derived from natural or artificial pollution (figure 1). The most affected populations live in rural areas, where the problems are exacerbated by unfavourable socioeconomic, cultural and sanitary conditions (Sancha et al., 2000; Smedley and Kinniburgh, 2002).



Figure 1 – Map of As distribution in the world (digital elevation model from PIA03388 image; <http://photojournal.jpl.nasa.gov>; courtesy NASA/JPL-Caltech).

In this paper, an overview on the problematic of As in Iberoamerica, the objectives of the IBEROARSEN CYTED Network and the results of novel methods for arsenic removal based on the use of economic materials and solar light will be presented.

## 2. DISTRIBUTION OF ARSENIC IN IBEROAMERICA

In Argentina (figure 2), Chile, Bolivia, Peru, Ecuador and Mexico, at least 4 million people depend on water sources with toxic concentrations of arsenic ( $> 0.05 \text{ mg L}^{-1}$ ), coming mainly from geogenic sources, dissolution or lixiviation of volcanic rocks and metallic sulphur-rich reservoirs. Arsenic pollution is also originated by anthropogenic activities, like those related to mining.

While in these countries the problem is known since decades, in Uruguay, Brazil, Nicaragua, Honduras and El Salvador, the problem has been detected or investigated only in last years, and, in Latinamerican countries with similar geological characteristics, the studies began only recently (Bundschuh and García, 2008).

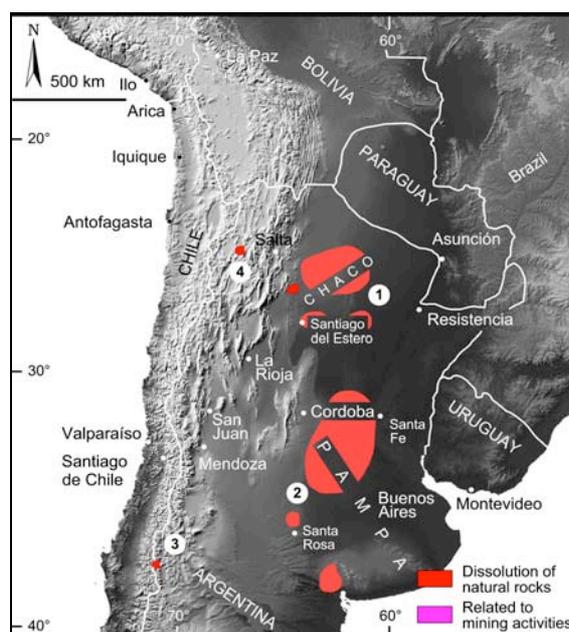


Figure 2 – Distribution of arsenic in Argentina. (1) Chaco, (2) Pampa, (3) Copahue and (4) San Antonio de los Cobres (digital elevation model from PIA03377 image; <http://photojournal.jpl.nasa.gov>; courtesy NASA/JPL-Caltech).

In countries where the problem is less dramatic like Brazil, in the region known as “Cuadrilátero Ferrífero” (Minas Gerais), centuries of gold extraction and exploitation originated a high level of As pollution (Deschamps et al., 2002) (figure 3).

In Spain, the problem of As is considered important in the area nearby the Pyrenees, in Iscar (Valladolid), in Madrid and in the Duero Basin (Segovia) (Herráez et al., 1993, Calvo Revuelta et al., 2003, Carretero Rivera et al., 2004, Aragonés Sanz et al., 2001) (figure 4).

In the North of Portugal, quartz veins with sulphur minerals are quite common; these minerals are easily leached by groundwater and may contain high amounts of As. In some communities (Águas de Tras-os-Montes and Alto Douro, Vila Flor, figure 4), As content in waters reaches hundreds of micrograms per litre (Freixeda, values of As near  $800 \mu\text{g L}^{-1}$  in groundwater and  $60 \mu\text{g L}^{-1}$  in surface water bodies) (Pereira et al., 2005, Pereira and Cordeiro, 2005, Ávila et al., 2006). In many cases, As pollution is closely related to mining activities.

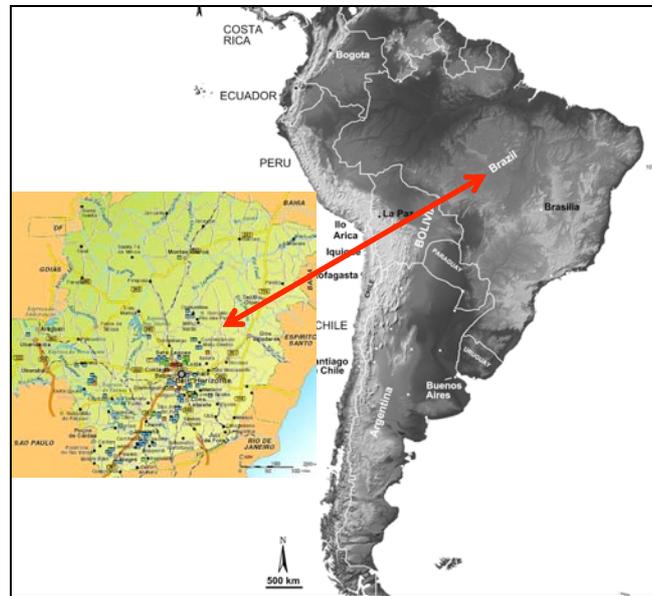


Figure 3 – In Minas Gerais, Brazil, gold extraction resulted in high As concentrations (digital elevation model from PIA03377 image; <http://photojournal.jpl.nasa.gov>; courtesy NASA/JPL-Caltech).



Figure 4 – Areas of Spain and Portugal affected by As pollution.

Although there is good available information about the most affected areas, the distribution of As in the Iberoamerican regions is far of being completely known. Based on the socioeconomic problem, the affected population can be divided in two defined types: the urban one, where the problems can be solved due to the possibility of installing relatively expensive treatment plants (North of Chile, cities of the Chacopampean Plain), and the population from dispersed rural areas, with a high level of isolation and poverty, which is the most affected.

### 3. THE IBEROARSEN NETWORK (2006-2009)

The IBEROARSEN Network has been approved by the General Assembly of CYTED in December 2005. CYTED (Iberoamerican Program of Science and Technology for the Development) is an organization that groups the organisms responsible for Science and Technologies of 21 countries of Iberoamerica. IBEROARSEN constitutes an interconnection project carried out by R&D groups working on the problematic of arsenic from the three following aspects: a) origin, transport and distribution of arsenic in water and soils; b) analytical methodologies for the determination and speciation of arsenic in water and soils; c) low-cost technologies for the removal of arsenic in water.

The objectives of IBEROARSEN are:

1. Construction of a map of geographical and geological distribution of As in water and soils of Iberoamerica.
2. Increase and interchange of knowledge and formation of human resources in:
  - As distribution,
  - Analytical methodologies for the determination and speciation of As,
  - Technologies for removal of As in water.
3. Writing of four monographs:
  - I. Geographical and geological distribution of As in Iberoamerica,
  - II. Analytical methodologies for the determination and speciation of As,
  - III. Low-cost technologies for As removal in water,
  - IV. Situation of As in Iberoamerica. Possible articulated and integrated actions for As removal in isolated areas.

The final product of IBEROARSEN is the Network itself: once established, the high interest in the topic will guarantee its continuity and, with it, the existence of an international consulting agency to advice governments, institutions and communities. The immediate products of the Network will be the four monographs mentioned above, the formation of human resources highly trained through courses and stays in laboratories, and the elaboration of didactic and informative material, including the already launched web page (<http://www.cnea.gov.ar/xxi/ambiental/iberoarsen/>). The activities will establish the grounds for precompetitive projects of technological development aimed at solve the dramatic situation caused by arsenic in the region. At present, IBEROARSEN is formed by 43 groups of 17 Iberoamerican countries, and several exchanges among the groups have already been done, with the initiation of some collaborative projects.

### 4. AN ECONOMIC METHOD FOR ARSENIC REMOVAL

#### 4.1. Introduction

Several methods are appropriate to remove As from water. Among them, anionic exchange, reverse osmosis, precipitation, flotation and adsorption have been tested, as large-scale methods of variable costs. Alternatively, low-cost and small-scale technologies for As removal are continuously explored, as for example:

- Solar oxidation processes
- Biomass, clay or lime adsorption
- Fitoremediation

In last years, the attention has been focused on the so-called “Advanced Oxidation Processes” (AOPs) like Heterogeneous Photocatalysis (HP) (Ferguson et al., 2005) and Zerovalent Iron (ZVI) (Su et al., 2001), which can be considered simple and economic technologies to remove As from water. These technologies can be applied in isolated rural areas to reach arsenic concentrations below the established limits of the international legislation and to offer safe drinking water to the population.

HP is based on the use of an innocuous material, the semiconductor  $\text{TiO}_2$ , which under UV irradiation originates chemical reactions leading to the mineralization of organic matter, bacteria destruction and transformation of toxic metals (Litter, 2005).  $\text{TiO}_2$  can be conveniently supported on the internal walls of PET bottles and, by solar irradiation, can bring about the oxidation of As(III) to As(V) (figure 5). In a further or simultaneous step, iron can be added to immobilize As(V) by adsorption or coprecipitation with iron oxides.

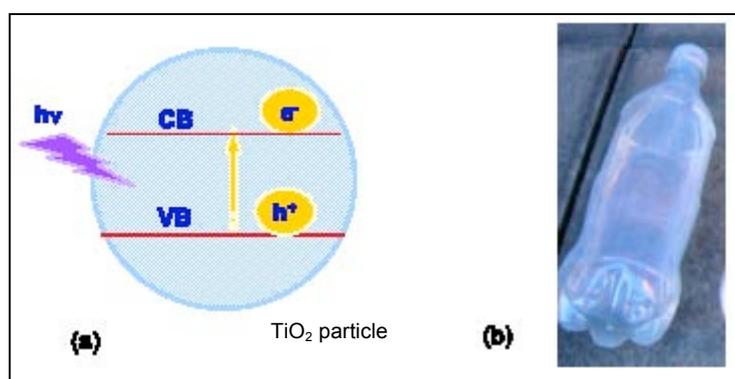


Figure 5 – a:  $\text{TiO}_2$  particle UV-irradiated; b:  $\text{TiO}_2$  supported on a PET plastic bottle.

The primary advantages of ZVI application include the low cost and availability of iron in rural areas in form of very cheap materials, together with simplicity in the handling and scaling. The mechanism of As removal by ZVI involves the formation of As(III) and As(V) complexes on the iron oxides formed in situ as the result of Fe0 corrosion (Lackovic et al., 1999). The method has been investigated previously by our group (García et al., 2004, d’Hiriart et al., in press, Figure 6).



Figure 6 – PET bottles filled with arsenical solutions and cheap iron materials.

We present here results obtained for the evaluation of the efficiency of HP for As removal in bottles with TiO<sub>2</sub> supported on the walls and iron addition, and of ZVI using very cheap iron materials. This study was carried out with synthetic arsenical solutions and natural groundwater from Los Pereyra, a small settlement of 1000 inhabitants located 70 km SE from San Miguel de Tucumán City, and from Las Hermanas, a very poor area near Santiago del Estero City. Both localities, situated in the Argentine NW, have been chosen due to the unfavourable socioeconomic conditions and the detection of several cases of CERHA. The region belongs to the physiographic unit of the Dulce-Salí River basin.

## 4.2. Material and methods

### Chemicals

All chemicals were reagent grade and used without further purification. As(III) and As(V) stock solutions were prepared from NaAsO<sub>2</sub> and NaH<sub>2</sub>AsO<sub>4</sub>·7H<sub>2</sub>O, respectively, both Baker. Real water samples were obtained from wells of Las Hermanas and Los Pereyra. Synthetic samples of similar composition to that of Los Pereyra well waters were prepared with  $1.3 \times 10^{-4}$  M MgSO<sub>4</sub>,  $2.3 \times 10^{-4}$  M CaCl<sub>2</sub>,  $4.0 \times 10^{-5}$  M NH<sub>4</sub>Cl,  $9.0 \times 10^{-6}$  M FeCl<sub>3</sub> and NaOH to adjust pH to 7.8.

Fe(III) was added as FeCl<sub>3</sub> (Mallinckrodt). Zerovalent iron was introduced in the form of commercial packing wire or iron wool (Virulana®), both non-galvanized. XRD patterns showed that both materials were pure metallic Fe with only traces of Al and CaSiO<sub>3</sub> in the case of packing wire. TiO<sub>2</sub> (Degussa P-25) was provided by Degussa AG Germany and used as received. For analytical determinations, (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O (Stanton), potassium and antimonyl tartrate (Baker), L-ascorbic acid (Sigma-Aldrich) and KMnO<sub>4</sub> (Riedel-de-Häen) were used. Water was purified with a Millipore Milli-Q equipment (resistivity = 18 MΩ.cm).

### Experiments of As removal

Experiments were performed in 600 mL plastic colourless polyethyleneterephthalate (PET) bottles of soft drinks or mineral water. For HP tests, the inner surface of the bottles was covered with a TiO<sub>2</sub> thin film, following an easy technique already reported by this group (Meichtry et al., 2007). Bottles were manually shaken in order to oxygenate solutions previous to the experiment and before each sampling.

Artificial light was provided by a black-light tubular UV lamp (Philips TLD/08, 15 W, maximum emission at 366 nm). The lamp intensity was 800 μW cm<sup>-2</sup>. The intensity of the solar light used in the experiments corresponded to that of the Buenos Aires City Spring (34°38'S, 58°28'W, October 2006) and ranged 1600-2000 μW cm<sup>-2</sup>. Both light intensities were measured with a Spectroline DM-365 XA radiometer.

### Analytical determinations

As(V) was determined through the formation of the arsenomolybdic complex (Lenoble et al., 2003), adding 126 mg KMnO<sub>4</sub>/mg As (contact time 120 minutes), to previously oxidize As(III). As(III) concentration was calculated by difference. In natural water samples, total As was determined by ICP-OES, using a Perkin-Elmer Optima 3100 XL apparatus or by Total Reflection X-Ray Fluorescence (TRXRF), using a PANalytical PW3830 X-ray generator. Before analysis, all samples were filtered through a 0.45 μm Millipore membrane.

## 4.3. Results and discussion

In the case of HP experiments, irradiation under UV light for 6 h, followed by the addition of a piece of iron packing wire resulted in more than 80% of As removal. The semiconductor could

be reused without further modification. The method was validated with real water samples from wells from Las Hermanas, under solar irradiation for more than 4 h, followed by the addition of FeCl<sub>3</sub> (table 1). In this case, more than 94% As removal was obtained, reaching very low As concentrations, in one case below the WHO standard.

Sample	[As] <sub>i</sub> (µg/l)	[As] <sub>f</sub> (µg/l)	t <sub>irradiation</sub> (h)	pH <sub>i</sub>	pH <sub>f</sub>	[Fe(III)]:[As]	As removal efficiency (%)
W1	961	31	10*	7.36	8.32	162	96.8
W2	1090	13	4.2	7.59	6.2	214	98.8
W3	551	30	4.9	7.98	7.32	424	94.5
W4	1530	14	3.8	-	6.26	152	99.1
W5	1830	25	10*	7.05	8.25	85	98.6
W6	1630	<10	5.1	6.96	5.88	143	>99.4

\*partially cloudy day

Table 1 – As removal from natural groundwater from Las Hermanas using HP + FeCl<sub>3</sub>.

For the ZVI experiments, iron packing wire or iron wool was added to the plastic bottles containing synthetic arsenical solutions. Samples were irradiated with artificial UV light for more than 2 h, and the results were compared with those obtained in the dark. Iron wool resulted to be a better iron source than iron packing wire, reaching a complete removal in 2 h, while using the wire only 30% removal was obtained in the same time; however, in the last case, the removal increased to 75% after 22 h-settlement in the dark (figure 7). The better results with the iron wool can be attributed to a higher oxidizable surface of the material. After the experiments, both materials were analysed by XRD, and signals of maghemite, lepidocrocite and magnetite could be observed. The reaction in the dark was somewhat less efficient.

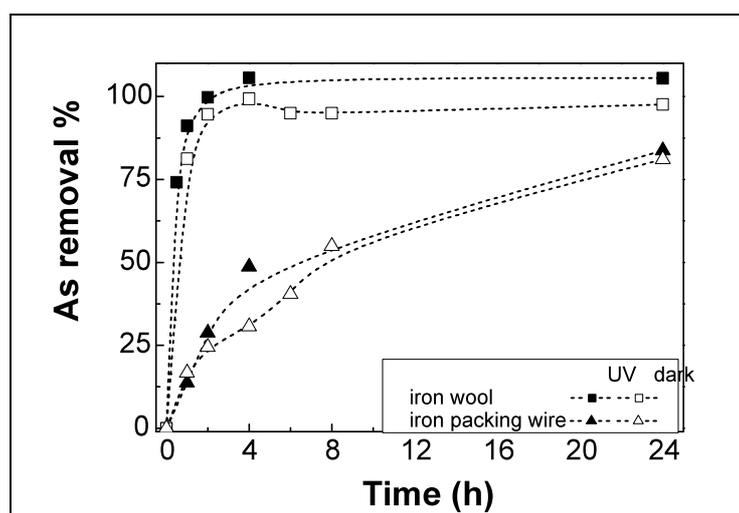


Figure 7 – As removal from synthetic solutions irradiated with UV light (t<sub>irradiation</sub> = 2 h) or kept in the dark, followed by a 22 h-settlement.

A sample from Los Pereyra was exposed to solar light for 6 h in a PET bottle containing a piece of iron packing wire. After 24 h-settlement, As removal was higher than 70%. The reaction was much less efficient in the dark. This result differs from that obtained for the synthetic arsenical samples, where, for the same Fe(0) concentration, no significant differences were

observed under irradiation. The differences were more remarkable when the iron concentration was lower. Different experimental conditions can be responsible for this behaviour in the absence and in the presence of light, such as the presence in natural waters of chemical species that could increase the rate of Fe(0) oxidation under solar light (e.g., organic matter) or that could increase As adsorption on the flocs of ferric oxides. The beneficial effects of solar irradiation could be seen at low iron concentrations; in consequence, a more prolonged irradiation would result in a good As removal, turning the process more economic.

## 5. CONCLUSIONS

A brief description of As content in ground and surface waters of the Iberoamerican region indicates that the problem is becoming increasingly dramatic, especially for poor populations. The IBEROARSEN CYTED Network is a program which intends to offer solutions to this situation connecting groups from the region involved in three aspects: distribution, trace analysis of the element and economic removal technologies. Related to this last point, experiments for arsenic removal using novel low-cost methods, HP and ZVI, which use plastic bottles and very cheap materials, were essayed in synthetic and natural waters of the Chacopampean region of Argentina. Although both technologies gave similar results, the use of the first one could be superior due to the ability of removing simultaneously As, organic matter, toxic metals and microbiological contamination.

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*Received 14 January 2008*  
*Revised 7 February 2008*  
*Published 6 May 2008*

## **Appendices**

Participants of the IBEROARSEN meeting in Buenos Aires, Argentina, December 2006.

