

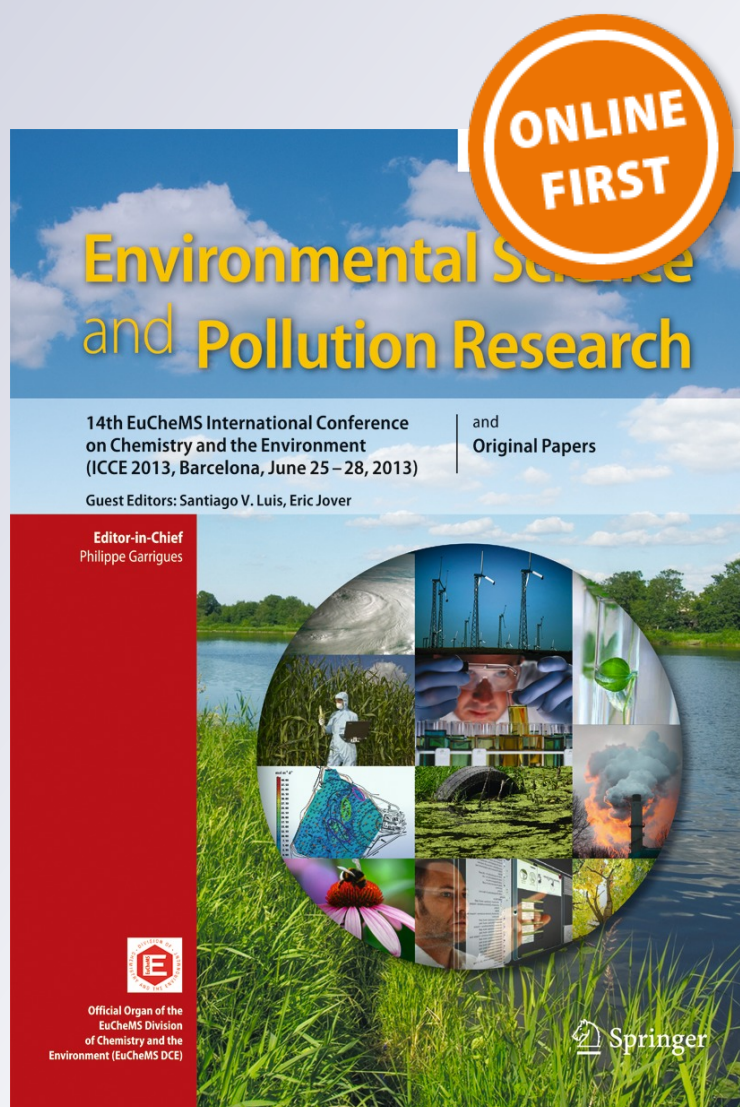
Arsenic removal from water employing a combined system: photooxidation and adsorption

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Arsenic removal from water employing a combined system: photooxidation and adsorption

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Abstract A combined system employing photochemical oxidation (UV/H₂O₂) and adsorption for arsenic removal from water was designed and evaluated. In this work, a bench-scale photochemical annular reactor was developed being connected alternately to a pair of adsorption columns filled with titanium dioxide (TiO₂) and granular ferric hydroxide (GFH). The experiences were performed by varying the relation of As concentration (As (III)/As (V) weight ratio) at constant hydrogen peroxide concentration and incident radiation. Experimental oxidation results were compared with theoretical predictions using an intrinsic kinetic model previously obtained. In addition, the effectiveness of the process was evaluated using a groundwater sample. The mathematical model of the entire system was developed. It could be used as an effective tool for the design and prediction of the behaviour of these types of systems. The combined technology is efficient and promising for arsenic removal to small and medium scale.

Keywords Adsorption · Arsenic · Combined technology · Granular ferric hydroxide · Titanium dioxide · UV/H₂O₂ process · Water treatment

Nomenclature

A_t	Cross-section area, cm ²
C_i	Concentration of the species, mol cm ⁻³
$e_{P,\lambda}^a$	Local volumetric rate of photon absorption (LVRPA), Einstein cm ⁻³ s ⁻¹
$E_{P,o}^\lambda$	Spectral fluence rate, Einstein cm ⁻² s ⁻¹

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$E_{P,o,W}^\lambda$	Spectral fluence rate at the inner wall, Einstein cm ⁻² s ⁻¹
EBRT	Empty bed residence time, s
K_{27}	Kinetic parameter
L_R	Reactor length, cm
L_L	Lamp length, cm
Q	Flow rate, cm ³ s ⁻¹
Q_r	Recirculation flow rate, cm ³ s ⁻¹
Q_R	Reactor flow rate, cm ³ s ⁻¹
R	Reaction rate, mol cm ⁻³ s ⁻¹
r	Weight concentration ratio; also radial coordinate, cm
r_L	Lamp radius, cm
r_i	Inner radius, cm
r_o	Outer radius, cm
r_r	Recycle ratio
s	Lineal coordinate in Ω direction, cm
t	Time, s
X_i	Conversion, %
Y_w	Medium value of the transmittance for the reactor wall
z	Axial coordinate, cm
Z	Column height, cm

Greek letters

$\alpha_{\lambda,P}$	Spectral linear naperian absorption coefficient of the hydrogen peroxide, cm ⁻¹
$K_{P,\lambda}$	Molar naperian absorption coefficient, cm ² mol ⁻¹
λ	Wavelength, nm
v_z	Axial fluid velocity inside the reactor, cm s ⁻¹
θ	Spherical coordinate, rad
Φ_p	Primary quantum yield
φ	Spherical coordinate, rad
$\underline{\Omega}$	Unit vector in the direction of radiation propagation
Ψ	Geometric factor

Special symbols

$\langle \rangle$ Averaged value over a defined space

Introduction

Arsenic pollution is a worldwide problem being one of the most important environmental issues in the last years and has been extensively reported by literature (Mohan and Pittman 2007; Armienta and Segovia 2008; Litter et al. 2010). There are recent reviews that deals with environmental origin, occurrence of arsenic and also with relevant technical and societal options employed for mitigation, relieving and preventing high human exposure of this metalloid through water and food in different regions of the world (Bundschuh et al. 2012; He and Charlet 2013; Mondal et al. 2013; Sharma et al. 2014; Rahman et al. 2014). Chronic exposures, mainly by ingestion of contaminated water, lead to a variety of health effects. Reviews of findings to date suggest the adverse effects of arsenic exposure on the risk of skin lesions (palmer and plantar hyperkeratosis, hypo and hyper pigmentation), high blood pressure, diabetes mellitus, bladder, lung and liver diseases and various types of cancer (UNESCO 2006; Celik et al. 2008; Yunus et al. 2011; Bhattacharjee et al. 2013; Hong-Jie et al. 2014). Due to this fact, the World Health Organization (WHO) has set a limiting guideline of 10 $\mu\text{g/L}$ as the drinking water standard (WHO 2011).

Arsenic in water usually occurs in its two inorganic forms, As (III) and As (V) depending on the prevalent redox conditions, being As (III) more toxic in biological systems than As (V) (Yamamuchi and Fowler 1994). A variety of water treatment technologies for arsenic removal from water have been developed. In the last time, adsorption operations, ion exchange, precipitation and coprecipitation have been extensively studied in order to evaluate its application in arsenic remediation from water containing high levels of this metalloid (Henke 2009).

Different conventional materials have been studied as adsorbents such as different kinds of titanium dioxide, activated carbon, ferric, aluminium, magnesium oxides/hydroxides and manganese oxides (Ouvrard et al. 2002a, b; Bang et al. 2005; Mohan and Pittman 2007; Ma and Tu 2011; Guan et al. 2012). The negatively charged species of As (V) have higher affinity than non-charged As (III) species to the surface of different adsorbents (at natural pH groundwater samples) (Kim et al. 2004; Zhang and Itoh 2006). Because of the neutral charge of As (III), it can be adsorbed on many adsorbents obtaining low removal efficiencies. Due to this fact, a previous oxidation treatment is very important to reach high performance and efficiency for arsenic removal. Also, arsenate sorption in some oxides, for example manganese oxides, may be due to surface complexation mechanisms (Ouvrard et al. 2002a).

There are many technologies to oxidize arsenic in water either by traditional oxidants such as Cl_2 , ClNH_2 , ClO_2 , H_2O_2 ,

KMnO_4 (Frank and Clifford 1986; Pettine et al. 1999; Kim and Nriagu 2000; Dodd et al. 2006; Vasudevan et al. 2006; Lee et al. 2011) or advanced oxidation process (AOP) such as UV/ TiO_2 , UV/ H_2O_2 and UV/ $\text{Fe (III)}/\text{H}_2\text{O}_2$ (Balarama Krishna et al. 2001; Bissen et al. 2001; Lee and Choi 2002; Sorlini et al. 2010, 2014). The above-mentioned works show that AOPs are more convenient for arsenic oxidation in water because they do not generate undesirable by-products. According to the literature found, the UV/ H_2O_2 is the least AOPs studied to transform As (III) into As (V) and can be suitable to apply when pollutants are in low concentrations, such as arsenic, since in this case, it is not necessary to use high concentrations of hydrogen peroxide. Due to this fact, first of all, the authors have been studying the efficiency and kinetics of the UV/ H_2O_2 process for arsenic oxidation (Lescano et al. 2011, 2012). Then, the adsorption process was studied because of its simple operation and relative low cost for arsenic removal. Three different adsorbents were tested by batch and column assays in order to find the best material to carry out the process, being titanium dioxide and granular ferric hydroxide the most suitable ones (Lescano 2013). On the basis of the above, the study of the two processes in a combined continuous system represents the logical next step in our study, and it will be very important in order to design a complete treatment technology for arsenic removal from water. In few publications, a combination of oxidation and adsorption processes for arsenic removal from water was discussed. These works proposed combined systems employing Fenton's techniques with zero-valent iron (Balarama Krishna et al. 2001), UV/ TiO_2 with activated alumina and activated carbon (Nakajima et al. 2005), UV/ TiO_2 and photo-Fenton processes employing activated alumina (Yoon and Lee 2007), photooxidation with TiO_2 and adsorption onto its surface (Nguyen et al. 2008). These publications are only experimental works that show the efficiency of the different systems and the influence of the operation conditions (pH, presence of other ions) but do not study the kinetic and design parameters of the combined system. These lines of processes result to be attractive because of the high oxidative capacity of advanced oxidation technologies and the adsorption as an efficient low-cost technology.

The aim of this work is to evaluate and study the effectiveness of the combination of UV/ H_2O_2 process for As (III) oxidation with an adsorption technology, employing titanium dioxide and granular ferric hydroxide as adsorbent materials. In order to achieve this objective, a combined system was designed (oxidation reactor-adsorption column). Theoretical predictions obtained from the representation of the reactor performance are compared with experimental data furnished by experiments in the prototype. Also, an experimental assay using a groundwater sample is performed in order to test the feasibility of the combined system.

Material and methods

Chemicals and materials

All chemicals were analytical grade, and all stock solutions were prepared with ultrapure water ($0.055 \mu\text{S cm}^{-1}$) obtained from an OSMOIONTM purification system. Arsenic stock solutions containing 1000 mg L^{-1} of As (III) and As (V) were prepared employing sodium (meta) arsenite (AsNaO_2 , $\geq 99\%$, Sigma-Aldrich p.a.) and sodium arsenate dibasic heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, $99\text{--}102\%$, Sigma-Aldrich, ACS reagent), respectively. Also, a stock solution of 500 mg L^{-1} of H_2O_2 was prepared from hydrogen peroxide ($30\% \text{ w/v}$, Cicarelli p.a.). These stock solutions were further diluted for experimental use with ultrapure water. Also, the system was applied using a raw groundwater sample taken from San Genaro village, Santa Fe, Argentina (domiciliary hole, perforation 15 m, water table at above 7 m), by adding known quantities of As (III) and As (V) solutions in order to evaluate the combined system in a real water matrix. The main physicochemical characteristics of the groundwater sample are detailed in Table 1.

Catalase from bovine liver (Fluka, $2,195 \text{ units mg}^{-1}$) was used in the oxidation process to decompose the remnant H_2O_2 (1 unit decompose 1 mmol min^{-1} of H_2O_2 at pH 7.0 and 25°C). For the speciation process, 1 N of hydrochloric acid and methanol (Sintorgan, HPLC grade) were used.

Two commercially available adsorbents for arsenic removal based on titanium dioxide (Adsorbisia[®] As500) and granular ferric hydroxide (GFH) were purchased from Dow Chemical and Pro H_2O companies, respectively. The particle size of TiO_2 and GFH were $0.25\text{--}1.19$ and $0.32\text{--}2 \text{ mm}$, while the specific surfaces of those materials were 200 and $280 \text{ m}^2 \text{ g}^{-1}$, respectively.

Table 1 Physicochemical characteristics of groundwater

Parameter	Value
pH	8.2
Temperature	21.9°C
Dissolved O_2	2.8 mg L^{-1}
Turbidity	1.34 UNT
Total dissolved solids (180°C)	$1,659 \text{ mg L}^{-1}$
Conductivity	2.53 mS cm^{-1}
Total alkalinity (CaCO_3)	762 mg L^{-1}
Chlorines (Cl^-)	198.5 mg L^{-1}
Sulphates (SO_4^{2-})	342.9 mg L^{-1}
Phosphates (PO_4^{3-})	0.88 mg L^{-1}
Total hardness (CaCO_3)	221 mg L^{-1}
Nitrates (NO_3^-)	4.8 mg L^{-1}
Total arsenic (As)	$50 \mu\text{g L}^{-1}$

Experimental device and operation conditions

A combined system including a photochemical reactor connected to an adsorption column for arsenic removal from water was designed and built at bench scale.

Reactor

A continuous annular photochemical reactor was built to perform the oxidation process (Fig. 1). It was formed by an inner cylinder made of quartz and an external glass cylinder closed in both sides with heads of Teflon[®]. The fluid gets in and out from the bottom to the top of the reactor. The source of radiation was supplied by one Philips 15 W (output power of 4.6 W) tubular germicidal lamp. The wavelength emission of the lamp was 254 nm . All the accessories were made of Teflon[®] and stainless steel. The main characteristics of the reactor are detailed in Table 2.

Adsorption column

The reactor is a part of the combined system that includes two filled columns with TiO_2 and GFH, where the adsorption of As (V) will be produced. The columns are cylinders made of acrylic closed in both sides with Teflon[®] heads. They were designed taking into account the oxidation process previously

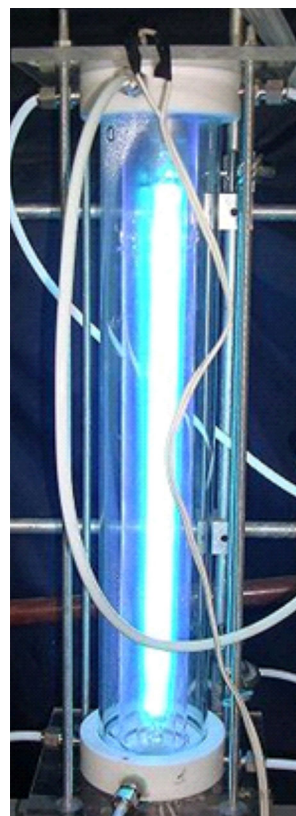


Fig. 1 Photography of the reactor

Table 2 Reactor characteristics

Characteristics	Value
Volume (cm ³)	870
Height (cm)	41
Cross-section area (cm ²)	21.13
Inner radius of the annulus (cm)	2.35
Outer radius of the annulus (cm)	3.5

studied (Lescano et al. 2011) and the experiences performed by mini fixed column assays (Lescano 2013). More details can be found in the “Adsorption column” section.

Combined system

The system consists of a 10 L glass tank containing arsenic-contaminated water that was pumped to the inlet of the reactor at a high flow rate by a multi-stage centrifugal pump (Tonkaflo, model: SS508X, body of stainless still and impeller made of bronze teflon coated) to asses good mixing conditions. At the outlet of the reactor, part of the solution was recirculated to the same reactor while the other portion was forced to let into the adsorption columns. The whole system was operated in a continuous mode. The photochemical reaction is relatively fast, and in order to increase or enhance the reactor efficiency, an open system with recycle was adopted. Due to this fact, the flow inside the reactor was the maximum that could be supplied for the pump avoiding back mixing, reaching as fast as possible the steady-state operation. On this basis, the maximum flow according to the capacity of the pump was set (Q_r). Also, employing an open recycle, the most common flow values for adsorption systems can be used. However, this situation does not mean that the flow relation in this or other similar systems could be optimized.

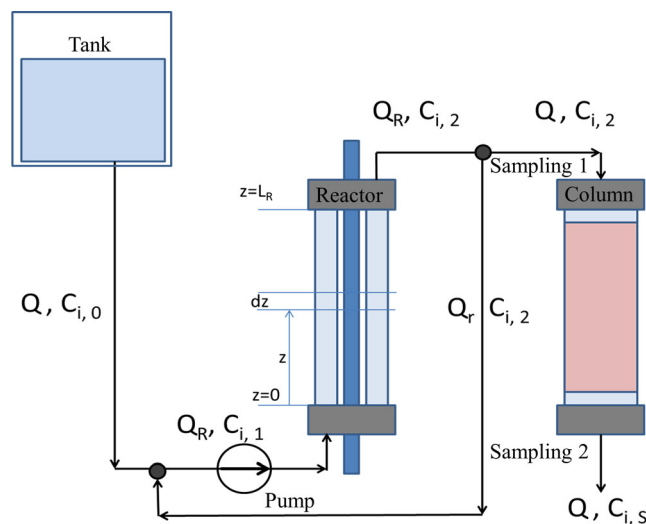
A scheme of the combined system is shown in Fig. 2.

Experimental procedure

Experiments were performed by varying the concentration ratio of As (V)/As (III) at the same total arsenic concentration and at constant spectral fluence rate at the inner wall of the reactor. The dosage of hydrogen peroxide employed for all the experiences were adopted according to a previous work, which includes the study of the optimal H₂O₂ concentration for this process (Lescano et al. 2011). Each experiment was repeated two times. We do not find significant differences between the obtained values (arsenic and hydrogen peroxide concentration), so the averaged values were informed.

The experimental conditions are detailed in Table 3.

The inlet As (III) and As (V) concentrations were measured at $t=0$ from the tank and then sampled (25 mL) at regular time intervals at the outlet of the reactor (UV/H₂O₂ process) in

**Fig. 2** Scheme of the combined system

order to evaluate the steady state of the system and the percentage of As (III) oxidation reached (sampling 1) and also at the outlet of the column to evaluate the percentage of arsenic removal and to ensure that the breakthrough point is not reached (sampling 2).

From the extracted volume of different time intervals in each experiment, the following sequence was performed:

- Sampling 1: 1–15 mL for H₂O₂ determination, (ii) 5 mL for As (III)/As (V) speciation followed by As (III) determination.
- Sampling 2: 1–15 mL for H₂O₂ determination, (ii) 5 mL for As determination.

At the end of the process, the system was carefully washed.

Analysis

Arsenic concentration was measured by atomic absorption spectroscopy (AAS) employing Perkin Elmer

Table 3 Experimental conditions

Variable and units	Value
Arsenic inlet concentration ($\mu\text{g L}^{-1}$)	200
As (III)/As (V) weight ratio	25/175, 50/150, 75/125, 100/100
Hydrogen peroxide inlet concentration (mg L^{-1})	3
Spectral fluence rate at the inner wall of the reactor ($E_{P_{o,W}}^\lambda$) (Einstein $\text{cm}^{-2} \text{s}^{-1}$) $\times 10^8$:	2.17
Initial pH	5.9
Recirculation flow rate ($\text{cm}^3 \text{s}^{-1}$)	133
Flow rate at the outlet of the column ($\text{cm}^3 \text{s}^{-1}$)	6

AAAnalyst 800 equipment with a TGHA graphite furnace. The analytical procedure for arsenic determination was conducted according to EPA Method 200.9 (EPA Protection Agency 1994). 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 %. Prior to the As (III) determination, a speciation process was performed employing solid phase extraction (SPE) in order to separate As (III) and As (V) species. The technique was applied and detailed in a previous work (Lescano et al. 2011). Thus, the concentration of As (V) was calculated from the difference between the As (III) concentration at time t and As (III) initial concentration (measured at $t=0$).

H₂O₂ concentration was analysed with a spectrophotometric method at 350 nm according to Allen et al. (1952), employing a Cary 100 Bio UV-visible instrument (the standard deviation value ranged from 0.05–0.08 for the calibration range studied), and pH was controlled with HI 98127 Hanna pH metre (accuracy ±0.1). The spectral fluence rate at the inner wall of the reactor was experimentally measured by ferrioxalate actinometry according to Murov et al. (1993).

The parameters pH, dissolved oxygen, conductivity and turbidity tested for the groundwater sample were performed by a multiparametric equipment (Horiba 10). Total alkalinity, total hardness, total dissolved solids, chlorides, sulphate nitrates and phosphates were analysed according to AWWA (2005).

Results and discussions

Predictive models

Reactor

Mass balance Considering cylindrical geometry, being the annular reactor operated in a steady state and neglecting axial diffusive term (axial diffusion can be neglected over to the convective flow due to the high recirculation flow inside the reactor), the mass balance averaged in the cross-sectional area can be written as follows for the i species:

$$\langle v_z \rangle_{At} \frac{d \langle C_i^R \rangle_{At}}{dz} = \langle R_i \rangle_{At} ; \quad \langle C_i^R \rangle_{At} = \frac{1}{At \langle v_z \rangle_{At}} \int_{At} C_i^R v_z dA \quad (1)$$

Where $i = \text{As (III), H}_2\text{O}_2$

The applied model is one-dimensional (1-D), so radial variations of concentration and radiation are considered in the integration of the cross-section area for each axial position.

In order to better understand and easily read the equations, the parenthesis that represents averaged concentration values were avoided from this section up to the end.

Taking into account that dark reactions can be neglected, kinetic expressions from the simplified model developed in our previous work will be used (Lescano et al. 2012), being the final expressions of the mass balances of each species as follows:

$$\langle v_z \rangle_{At} \frac{dC_{As(III)}^R(z)}{dz} = \frac{-2\Phi_p \langle e_{P,\lambda}^a \rangle_{At}}{(rK_{27} + 1)} \quad (2)$$

$$\langle v_z \rangle_{At} \frac{dC_P^R(z)}{dz} = \frac{-2\Phi_p \langle e_{P,\lambda}^a \rangle_{At} r K_{27}}{(rK_{27} + 1)} \quad (3)$$

Where the upper case R represents that the mass balance is applied inside the reactor.

The boundary conditions of Eqs. 2 and 3 are (see Fig. 2) the following:

$$\begin{aligned} C_{As(III)}^R(z=0) &= C_{As(III),1} \\ C_P^R(z=0) &= C_{P,1} \end{aligned} \quad (4)$$

On the other hand, once the profile of the concentrations inside the reactor is obtained, outlet concentrations of the reactor can be evaluated by the following:

$$\begin{aligned} C_{As(III)}^R(z=L_R) &= C_{As(III),2} \\ C_P^R(z=L_R) &= C_{P,2} \end{aligned} \quad (5)$$

Employing the mass balances for each species in the system with recycle, taking into account the concentration in the tank (C_0) and the outlet concentration (C_2), the inlet concentration in the reactor can be obtained (C_1) (see Fig. 2):

$$\begin{aligned} C_{As(III),1} &= (1-r_r)C_{As(III),0} + r_r C_{As(III),2} \\ C_{P,1} &= (1-r_r)C_{P,0} + r_r C_{P,2} \end{aligned} \quad (6)$$

Where r_r is the recycle ratio ($r_r = Q_r/Q_0$) and $Q_R = Q + Q_r$.

In order to obtain the outlet concentrations of the reactor, the system reactor–recycle must be solved iteratively: (1) initially, it will be considered that the inlet concentration of the reactor is the tank concentration, (2) Eqs. 2 and 3 should be solved with its corresponding boundary conditions (Eq. 4) employing Runge Kutta method, (3) the outlet concentration is obtained by Eq. 5, (4) the inlet concentration is recalculated

employing Eq. 6, (5) the cycle is repeated from stage (2) until the outlet concentration converges to a value.

Equations 2 and 3 required the evaluation of the local volumetric rate of photon adsorption (LVRPA) $e_{P,\lambda}^a$ in the cross-section area of the annulus. Therefore, a radiation balance is needed.

Radiation balance The $e_{P,\lambda}^a$ value can be obtained from the spectral fluence rate ($E_{P,o}^\lambda$), the inlet concentration of H_2O_2 and its spectral linear naperian absorption coefficient ($\alpha_{\lambda,P}$)

To obtain the spectral fluence rate, the radiative transfer equation for the reactor must be solved. For a pseudo homogeneous medium in a three-dimensional space, for any particular direction of radiation propagation given by the directional coordinate s , the radiative transfer equation takes the following form:

$$\frac{dL_{\lambda,\underline{\Omega}}(s,t)}{ds} + \alpha_\lambda(s,t)L_{\lambda,\underline{\Omega}}(s,t) = 0 \tag{7}$$

In Eq. 7, $L_{\lambda,\underline{\Omega}}$ is the spectral radiance, valid for the monochromatic radiation (λ) and a given direction of propagation $\underline{\Omega}$. From this equation, one can derive a relevant property for a photochemical system that is the fluence rate:

$$E_{P,o}^\lambda(\underline{x},t) = \int_\Omega L_{\lambda,\underline{\Omega}}(\underline{x},t)d\Omega \tag{8}$$

The radiation field inside the reactor was formulated using the three-dimensional source with volumetric emission model. Upon the integration of Eq. 7 and considering Eq. 8, we have

$$E_{P,o}^\lambda(r,z,t) = \int_{\phi_1}^{\phi_2} \int_{\theta_1}^{\theta_2} d\theta \sin\theta L^0(\theta,\phi) \exp\left[-\int_{S_R}^{S_I} \alpha(s,t)ds\right] \tag{9}$$

As it was demonstrated in Labas et al. (2009), fluence rate can be written in terms of the value of the fluence rate at the inner wall of the annular reactor:

$$E_{P,o}^\lambda(r,z,t) = \frac{E_{P,o,W}^{\lambda=273.5}}{\Psi} \int_{\phi_1}^{\phi_2} \int_{\theta_1}^{\theta_2} d\theta 2[r^2(\cos^2\phi-1) + r_L^2]^{1/2} \exp\left[-\int_{S_R}^{S_I} \alpha(s,t)ds\right] \tag{10}$$

where Ψ is a geometric factor defined as

$$\Psi = \frac{1}{L_R} \int_0^{L_R} dz \int_{\phi_1}^{\phi_2} d\phi \int_{\theta_1}^{\theta_2} d\theta 2[r_i^2(\cos^2\phi-1) + r_L^2]^{1/2} \tag{11}$$

The limiting angles corresponding to the boundary conditions of Eq. 10 are as follows:

$$\begin{aligned} \theta_1(\phi) &= \tan^{-1} \left\{ \frac{r \cos\phi - [r^2(\cos^2\phi-1) + r_L^2]^{1/2}}{L_L - z} \right\} \\ \theta_2(\phi) &= \tan^{-1} \left\{ \frac{r \cos\phi - [r^2(\cos^2\phi-1) + r_L^2]^{1/2}}{-z} \right\} \\ -\phi_1 &= \phi_2 = \cos^{-1} \left[\frac{(r^2 - r_L^2)^{1/2}}{-r} \right] \end{aligned} \tag{12}$$

The value of the fluence rate at the inner wall of the annular reactor $E_{P,o,W}^{\lambda=273.5}$ can be obtained by an actinometrical technique based on the publication of Murov et al. (1993): $E_{P,o,W}^{\lambda=273.5} = 2.17 \times 10^{-8}$ Einstein/cm² s⁻¹.

In order to apply Eqs. 2 and 3, the value of $E_{P,o}^\lambda$ volume averaged in the cross section must be obtained. The result is:

$$\begin{aligned} \langle E_{P,o}^\lambda \rangle_{At} &= \frac{2}{r_o^2 - r_i^2} \left(\frac{E_{P,o,W}^\lambda}{\Psi} \right) \int_{r_i}^{r_o} r dr \int_{\phi_1}^{\phi_2} d\phi \int_{\theta_1}^{\theta_2} d\theta 2[r^2(\cos^2\phi-1) + r_L^2]^{1/2} \\ &\quad \exp\left[-\int_{S_R}^{S_I} \alpha(s,t)ds\right] \end{aligned} \tag{13}$$

Therefore, the final expression to calculate the LVRPA is given by:

$$\begin{aligned} \langle e_{P,\lambda}^a \rangle_{At} &= \frac{2\alpha_{P,\lambda}}{r_o^2 - r_i^2} \left(\frac{E_{P,o,W}^\lambda}{\Psi} \right) \int_{r_i}^{r_o} r dr \int_{\phi_1}^{\phi_2} d\phi \int_{\theta_1}^{\theta_2} d\theta 2[r^2(\cos^2\phi-1) + r_L^2]^{1/2} \\ &\quad \exp\left[-\int_{S_R}^{S_I} \alpha(s,t)ds\right] \end{aligned} \tag{14}$$

Once the value of $e_{P,\lambda}^a$ is obtained by the numeric integration of Eq. 14 inside the reactor as a subroutine of a computer programme taking into account the value of K_{27} previously estimated (Lescano et al. 2012), Eqs. 2 and 3 can be solved iteratively (including Eqs. 4, 5 and 6) as it was explained before (system reactor-recycle). Finally, hydrogen peroxide and As (III) concentrations in the reactor are obtained.

Adsorption column

Taking into account the oxidation process previously studied (Lescano et al. 2011) and the experiences performed by mini fixed column assays (Lescano 2013), an adsorption column is designed in order to be connected to the annular reactor above

described. The dimensions of the column and the employed flow rate were calculated from the empty bed residence time (EBRT) and the bed volume desired. Also, a typical fluid velocity for this kind of process was set.

A summary of the column adsorption parameters is presented in Table 4.

According to the breakthrough curves obtained in the experiences carried out by mini fixed columns, an operational time can be estimated and evaluated under the conditions described above to assess an outlet concentration of As from the designed column under the guideline limit set by OMS. These results are shown in Table 5. The initial concentration of As (III) or As (V) employed for these experiments was $200 \mu\text{g L}^{-1}$.

Experimental results

Photochemical oxidation of As (III)

First of all, steady-state conditions for the oxidation process were studied. Concentrations lower than 4 and $7 \mu\text{g L}^{-1}$ were reached in 20 min (steady state) for As(III)/As(V) weight ratios: 25/125–50/150 and 75/125–100/100, respectively. Also, conversions of hydrogen peroxide varied between 8.47 and 9.3 %. Lower conversions of H_2O_2 were obtained for those weight ratios with lower As (III) concentration.

Model and experimental results Experimental results for the conversion (X) of As (III) oxidation at the outlet of the annular system reactor–recycle were compared with the results of the model (Table 6).

The values corresponding to the model were found through modelling the reactor detailed in the “Reactor” section taking into account the kinetic parameters obtained in a previous work (Lescano et al. 2012).

Experimental conversions (%) of As (III) and H_2O_2 (X_{Exp}) and the ones obtained from the model (X_{Mod}) are defined as follows:

$$X_{\text{Exp/Mod}} = \left[\frac{(\text{Inlet Concentration} - \text{Outlet Concentration})}{\text{Inlet Concentration}} \right] \times 100 \tag{15}$$

Table 4 Design parameters of the adsorption column

Parameter and units	Value
EBRT (s)	145.2
Fluid velocity (cm s^{-1})	0.28
Volume (cm^3)	870
Height (cm)	41
Flow rate (cm^3s^{-1})	6
Diameter (cm)	5.2

Table 5 Operational conditions of the designed columns

	GFH		TiO ₂	
	As(V)	As(III)	As(V)	As(III)
Treatment time (h)	25.9	23.9	60.9	52.1
Treated volume (L)	560	518	1,318	1,128

The calculated error is the difference between the experimental value and the value obtained from the model, assuming that the real value is the experimental one:

$$\text{Error}(\%) = \left(\frac{X_{\text{Exp}} - X_{\text{Mod}}}{X_{\text{Exp}}} \right) \times 100 \tag{16}$$

A very good prediction can be noticed for the experimental data, obtaining values of error lower than 4 and 5.3 % for all the estimated As (III) and H_2O_2 conversions, respectively. In fact, these values prove the predictive capacity of the proposed model.

Based on the result of this study, it can be observed how the modelling of a photochemical reactor can be used, in simulation mode, for a given system and a set of known variables (flow, initial concentrations) to figure out its efficiency (values of the outlet conversions or concentrations).

Removal of arsenic by UV/H₂O₂–TiO₂/GFH system

Arsenic concentration was measured at the outlet of the adsorption column reaching a complete removal of the contaminant for every ratio studied after 20 min of reaction for both TiO₂ and GFH (As concentration lower than $4 \mu\text{g L}^{-1}$). This result is reasonable according to the values obtained in Table 5 previously shown related to the design of the adsorption column. The predicted times according to the breakthrough curves for bed saturation for As (V) employing TiO₂ and GFH as adsorbents are 60.9 and 25.9 h. On this basis, after all the experiences carried out in the system (total time=1.3 h.), the

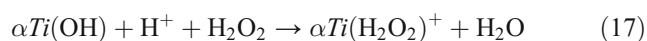
Table 6 Experimental and predicted data from the model for the oxidation reaction in the annular reactor

$C_{\text{As(III)}}/C_{\text{As(V)}}$	As(III)			H ₂ O ₂		
	X_{Exp}	X_{Mod}	Error %	X_{Exp}	X_{Mod}	Error %
50/150	93.0	94.0	1.2	9.3	9.5	2.5
25/175	93.6	93.9	0.4	9.8	9.3	5.3
75/125	90.0	93.7	4.0	8.9	9.0	0.6
100/100	91.3	93.6	2.5	8.5	8.8	4.4

percentage of bed saturations are approximately 2.1 and 5 % employing TiO_2 and GFH, respectively.

As it was said in the “**Experimental procedure**” section, H_2O_2 concentration was also measured at the outlet of the adsorption columns. The presence of H_2O_2 was not detected at the outlet of both columns assuming the adsorption or decomposition of hydrogen peroxide employing this combined technology. This finding adds an advantage to the designed system because it removes arsenic and also the H_2O_2 remnant of the UV/ H_2O_2 process in one step. The UV/ H_2O_2 processes become more expensive at a higher H_2O_2 concentration. Also, the remnant H_2O_2 must be treated before desanting. So, employing this combined system, a very low concentration of H_2O_2 is used (3 mg L^{-1}) obtaining a complete removal of arsenic and hydrogen peroxide at the outlet of the equipment. This behaviour will be discussed in more detail in the next section.

Behaviour of H_2O_2 in the system A yellow colour can be observed in the column filled with TiO_2 after the experiences. There are some publications that study hydrogen peroxide adsorption onto titanium-based compounds and could explain this behaviour (Muhlebach et al. 1970; Boonstra and Mutsaers 1975; Kubota et al. 1995; Gonçalves et al. 2007). These works report the interaction of hydrogen peroxide in the surface of titanium. Gonçalves et al. (2007) state that Ti (IV) may react with H_2O_2 forming a yellow-coloured complex according to the reaction



Being $\alpha\text{Ti}(\text{OH})$ the hydroxyl group attached to titanium onto the matrix surface and $\alpha\text{Ti}(\text{H}_2\text{O}_2)^+$ the complex titanium-peroxide form in the oxide surface.

In this way, it can be seen that the adsorption of hydrogen peroxide is possible through the formation of the complex with the titanium.

Conversely, H_2O_2 adsorption onto ferric base compounds is not well known. There are few publications that study this phenomenon and the mechanism of H_2O_2 adsorption onto these kinds of materials is not clearly established. The absence of H_2O_2 at the outlet of the column filled with GFH suggests the decomposition of hydrogen peroxide. This situation may be due to that the decomposition of hydrogen peroxide is more likely to occur than adsorption since this chemical species is very unstable, especially with iron.

In order to experimentally demonstrate the adsorption produced by H_2O_2 onto TiO_2 surface and calculate how the useful lifetime of the column will be reduced because of this phenomenon, two breakthrough curves were built on mini fixed bed columns. One experience was performed by passing through the column a concentration of $200 \mu\text{g L}^{-1}$ of As

(V), and the other experience was performed employing the same concentration of As (V) but adding a concentration of H_2O_2 of 3 mg L^{-1} .

From the obtained results (Fig. 3), a shift of the breakthrough point between both curves can be seen, rendering a clear proof of the adsorption of H_2O_2 onto the TiO_2 (because hydrogen peroxide will be competing with As (V) for the adsorption sites of TiO_2 , and the system As(V) + H_2O_2 will reach the saturation condition earlier).

From these analyses, it can be concluded that the useful lifetime of the column will be reduced, but this percentage of reduction will be very low and assess the removal of the remnant H_2O_2 that comes from the process (about 20 %).

Arsenic desorption/sorbent regeneration Once the sorbent becomes exhausted, the metals must be recovered and the sorbent regenerated. In most of arsenic sorption studies, desorption/regeneration was not discussed (Mohan and Pittman 2007). Furthermore, once arsenic is recovered in the concentrated form, the problem of how to dispose this concentrated arsenic product must be addressed. According to some publications encountered in literature, granular ferric hydroxide can be regenerated by an alkaline solution (e.g. NaOH) because Na^+ does not adsorb onto ferric hydroxides (Mohan and Pittman 2007; Manna et al. 2003). Regarding the issue of the final disposal of the concentrated arsenic product, there are recent publications dealing with this problem. For example, Tresintia et al. (2014) design a continuous recirculation configuration, with a NaOH solution flowing sequentially through the saturated adsorbent (leaching step) and the MgO (adsorption step) column beds.

It can be inferred from the experiences carried out in this work and from the related literature that even though iron- and titanium-based materials seem to be efficient for arsenic removal, GFH has the advantage that it could be regenerated. This possibility for titanium dioxide is not well known and needs more study to be elucidated.

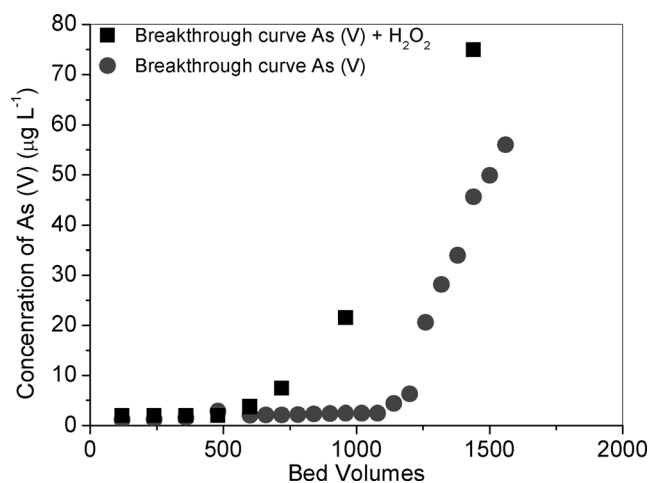


Fig. 3 As (V) breakthrough curves with and without H_2O_2

Groundwater assays

In order to evaluate, as a first approach, the feasibility of the combined system, the process was carried out employing a real groundwater sample (taken from San Genaro village, Santa Fe, Argentina). The main physicochemical characteristics of the sample are detailed in Table 1. The sample contained a concentration of As (V) of $50 \mu\text{g L}^{-1}$. Microlitres of stock solutions of As (III) and As (V) were added in order to obtain a final concentration in the work solution (10 L) of 150 and $50 \mu\text{g L}^{-1}$ of As (V) and As (III) respectively.

Experimental conditions were as follows: H_2O_2 concentration = 3 mg L^{-1} , $E_{P,o,W}^\lambda = 2.17 \times 10^{-8} \text{ Einstein cm}^{-2} \text{ s}^{-1}$, adsorbent: TiO_2 . The procedure carried out for the oxidation/adsorption in the combined equipment was exactly the same as it was described in the “Experimental procedure” section.

Conversions obtained for 11 min from this experiment were compared with the results previously obtained employing ultrapure water (Fig. 4). Arsenic (III) conversions obtained at the outlet of the reactor for groundwater sample and ultrapure water sample were 60 and 93 %, respectively.

In the same way, this phenomenon was commented and explained in a previous publication (Lescano et al. 2011), some components in the employed groundwater sample affect the activity of hydroxyl radicals resulting in a decrease of the oxidation rate (especially because of the presence of carbonates and bicarbonate ions evidenced by the high alkalinity value encountered: 762 mg L^{-1}). Also, in this case, the presence of nitrate ions should produce a reduction in the As (III) oxidation rate due to the fact that these ions strongly absorb UV light at a wavelength of 254 nm (Glaze et al. 1995).

On the other hand, the concentration of arsenic was also measured at the outlet of the adsorption column reaching a complete removal of the contaminant (concentration lower than $4 \mu\text{g L}^{-1}$). This result shows that even there is an As (III) remnant concentration at the outlet of the reactor, the

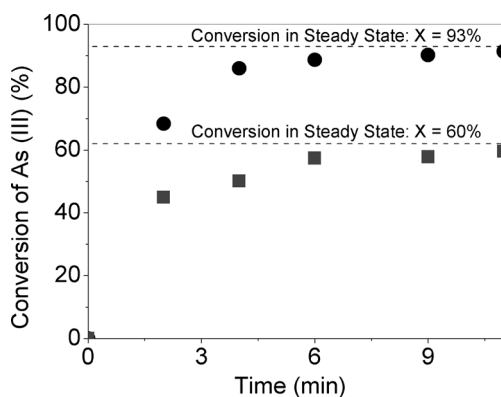


Fig. 4 Comparison of As (III) conversions employing ultrapure (filled circle) and groundwater samples (filled square)

lowest concentration obtained ($18 \mu\text{g L}^{-1}$) could be easily adsorbed by the solid adsorbent, and the useful lifetime of the column will be surely shorter.

Therefore, the steady state, when real waters are treated, should be determined taking into account the particular physicochemical composition in each case. In these studies, for this kind of water, 20 min would be probably enough to reach an As (III) concentration lower than $4 \mu\text{g L}^{-1}$ after the oxidation process.

Conclusions

In this work, a combined process employing a photochemical reactor connected to an adsorption column was studied. A bench-scale photochemical reactor for oxidation process and an adsorption column filled with the adsorbents TiO_2 and GFH were designed, modelled and simulated. A fixed concentration of total arsenic was used, varying the species weight ratio As (III)/As (V). These rates were chosen taking into account media values of arsenic species concentrations present in groundwater samples of America.

From the obtained results, it can be concluded that the combined process UV/ H_2O_2 -adsorption onto TiO_2 /GFH could be a feasible and efficient technique for complete arsenic removal from water (both III and V species) at small and middle scale. Applying this combined technology up to 500 and 1000 L of water contaminated with arsenic ($200 \mu\text{g/L}$) can be treated employing GFH and TiO_2 as adsorbents, respectively, in a few hours. Although the titanium-based material can treat larger volumes of water, GFH seems to be more efficient than TiO_2 due to the feasibility of its regeneration. As a first approach regarding to arsenic remediation in real groundwater samples, it can be concluded from the obtained results that the application of this combined system could be a feasible solution to treat water in real situations. However, more experiences should be conducted in a future work in order to evaluate the effect on the system of the different ions present in groundwater samples.

Also, experimental oxidation results were satisfactorily compared with those predicted by the model employing kinetics parameters estimated in a previous work with a small reactor. A good concordance was obtained between the theoretic predictions and experimental values proving and showing the usefulness of getting intrinsic kinetic parameters and its application for the design and scaling up purposes of photochemical reactors.

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References

- Allen A, Hochanadel C, Ghormley J (1952) Decomposition of water and aqueous solutions under mixed fast neutron and gamma radiation. *J Phys Chem* 56:575–586
- Armenta M, Segovia N (2008) Arsenic and fluoride in the groundwater of Mexico. *Environ Geochem Health* 30:345–353
- AWWA (2005) Standard methods for the examination of water and wastewater, 21st edn. American Waters Works Association, USA
- Balarama Krishna M, Chandrasekharan K, Karunasagar D, Arunachalam J (2001) A combined treatment approach using Fentons reagent and zero valent iron for the removal of arsenic from drinking water. *J Hazard Mater B84*:229–240
- Bang S, Patel M, Lippincott L, Meng X (2005) Removal of arsenic from groundwater by granular titanium dioxide adsorbent. *Chemosphere* 60:389–397
- Bhattacharjeea P, Chatterjeea D, Singhb K, Giri A (2013) Systems biology approaches to evaluate arsenic toxicity and carcinogenicity: an overview. *Int J Hyg Environ Health* 216:574–586
- Bissen M, Vieillard-Baron M, Schindelin A, Frimmel F (2001) TiO₂-catalyzed photooxidation of arsenite to arsenate in aqueous samples. *Chemosphere* 44:751–757
- Boonstra A, Mutsaers C (1975) Adsorption of hydrogen peroxide on the surface of titanium dioxide. *J Phys Chem* 79(18):1940–1943
- Bundschuh J, Litter M, Parvez F, Román-Ross G, Nicolli B, Jean JS, Liu CW, López D, Armenta M, Guilherme L, Gomez Cuevas A, Cornejo L, Cumbal L, Toujaguez R (2012) One century of arsenic exposure in Latin America: a review of history and occurrence from 14 countries. *Sci Total Environ* 429:2–35
- Celik I, Gallicchio L, Boyd K, Lam T, Matanoski G, Tao X, Shiels M, Hammond E, Chen L, Robinson K, Caulfield L, Herman J, Guallar E, Alberg A (2008) Arsenic in drinking water and lung cancer: a systematic review. *Environ Res* 108:48–55
- Dodd M, Vu N, Ammann A, Le V, Kissner R, Pham H, Cao T, Berg M, Von Gunten MU (2006) Kinetics and mechanistic aspects of As (III) oxidation by aqueous chlorine, chloramines and ozone: relevance to drinking water treatment. *Environ Sci Technol* 40:3285–3292
- EPA (Environmental Protection Agency) (1994) Methods for the determination of metals in environmental samples. Supplement I-EPA/600/R-94-111. Method 200.9, revision 2.2.—Determination of trace metals by stabilized temperature graphite furnace atomic absorption. Cincinnati, Ohio, USA
- Frank D, Clifford D (1986) Arsenic (III) oxidation and removal from drinking water. U. S. Environmental Protection Agency EPA-600-52/86/021, pp 2–86
- Glaze W, Lay Y, Kang J (1995) Advanced oxidation processes. A kinetic model for the oxidation of 1,2-dibromo-3-chloropropane in water by the combination of hydrogen peroxide and UV radiation. *Ind Eng Chem Res* 34:2314–2323
- Gonçalves JE, Filho UPR, Franco DW, Gushikem Y (2007) Adsorption of hydrogen peroxide on the surface of silica–titania mixed oxide obtained by the sol-gel processing method. *Eclat Quim* 32(2):41–45
- Guan X, Du J, Meng X, Sun Y, Sun B, Hu Q (2012) Application of titanium dioxide in arsenic removal from water: a review. *J Hazard Mater* 215–216:1–16
- He J, Charlet L (2013) A review of arsenic presence in China drinking water. *J Hydrol* 492:79–88
- Henke K (2009) Arsenic. Environmental chemistry, health, threats and waste treatment. University of Kentucky Center for Applied Energy Research. John Wiley, USA
- Hong-Jie S, Bala R, Bing W, Jun L, Li-Ping P, Lena M (2014) Arsenic and selenium toxicity and their interactive effects in humans. *Environ Int* 69:148–158
- Kim M, Nriagu J (2000) Oxidation of arsenite in groundwater using ozone and oxygen. *Sci Total Environ* 247:71–79
- Kim Y, Kim C, Choi I, Rengaraj S, Yi J (2004) Arsenic removal using mesoporous alumina prepared via a templating method. *Environ Sci Technol* 38:924–931
- Kubota L, Gushikem Y, Mansanares A, Vargas H (1995) Sorption of hydrogen peroxide by titanium (IV) oxide grafted on silica gel surface. *J Colloid Interface Sci* 173:372–375
- Labas M, Brandi R, Zalazar C, Cassano A (2009) Water disinfection with UVC radiation and H₂O₂. A comparative study. *Photochem Photobiol Sci* 8:670–676
- Lee H, Choi W (2002) Photocatalytic oxidation of arsenite in TiO₂ suspension: kinetics and mechanism. *Environ Sci Technol* 36:3872–3878
- Lee G, Song K, Bae J (2011) Permanganate oxidation of arsenic (III). Reaction stoichiometry and the characterization of the solid product. *Geochim Cosmochim Acta* 75:4713–4727
- Lescano M (2013) Doctoral thesis “Study of advanced processes for the oxidation and removal of arsenic from water. Application of UV H₂O₂ system”. Faculty of Chemical Engineering (FIQ) National University of Litoral (UNL) (in Spanish)
- Lescano M, Zalazar C, Cassano A, Brandi R (2011) Arsenic (III) oxidation of water applying a combination of hydrogen peroxide and UVC radiation. *Photochem Photobiol Sci* 10:1797–1803
- Lescano M, Zalazar C, Cassano A, Brandi R (2012) Kinetic modelling of arsenic (III) oxidation in water employing the UV/H₂O₂ process. *Chem Eng J* 211–212:360–368
- Litter M, Morgada M, Bundschuh J (2010) Possible treatments for arsenic removal in Latin American waters for human consumption. *Environ Pollut* 158:1105–1118
- Ma L, Tu S (2011) Removal of arsenic from aqueous solution by two types of nano TiO₂ crystals. *Environ Chem Lett* 9(4):465–472
- Manna B, Dey S, Debnath S, Ghosh U (2003) Removal of arsenic from ground-water using crystalline hydrous ferric oxide (CHFO). *Water Qual Res J Can* 38:193–210
- Mohan D, Pittman C Jr (2007) Arsenic removal from water/wastewater using adsorbents—a critical review. *J Hazard Mater* 142:1–53
- Mondal P, Bhowmick S, Chatterjee D, Figoli A, Van der Bruggen B (2013) Remediation of inorganic arsenic in groundwater for safe water supply: a critical assessment of technological solutions. *Chemosphere* 92:157–170
- Muhlebach J, Muller K, Schwarzenbach G (1970) The peroxo complexes of titanium. *Inorg Chem* 9(11):2381–2390
- Murov S, Carmichael I, Hug G (1993) Handbook of photochemistry. 2nd ed. Marcel Dekker, New York
- Nakajima T, Xu Y, Mori Y, Kishita M, Takahashi H, Maeda S, Ohki A (2005) Combined use of photocatalyst and adsorbent for the removal of inorganic arsenic (III) and organoarsenic compounds from aqueous media. *J Hazard Mater B120*:75–80
- Nguyen T, Vigneswaran S, Ngo H, Kandasamy J, Choi H (2008) Arsenic removal by photo-catalysis hybrid system. *Sep Purif Technol* 61:44–50
- Ouvrard S, Simonnot M, de Donato P, Sardin M (2002a) Diffusion controlled adsorption of arsenate on natural manganese oxide. *Ind Eng Chem Res* 41:6194–6199
- Ouvrard S, Simonnot M, Sardin M (2002b) Reactive behavior of natural manganese oxides towards the adsorption of phosphate and arsenate. *Ind Eng Chem Res* 41:2785–2791
- Pettine M, Campanella L, Millero F (1999) Arsenite oxidation by H₂O₂ in aqueous solutions. *Geochim Cosmochim Acta* 63:2727–2735
- Rahman S, Kim K-H, Kumar Saha S, Swaraz A, Kumar Paul, D (2014) Review of remediation techniques for arsenic (As) contamination: a

- novel approach utilizing bio-organisms. *J Environ Manag* 134:175–185
- Sharma A, Tjell J, Sloth J, Holm P (2014) Review of arsenic contamination, exposure through water and food and low cost mitigation options for rural areas. *Appl Geochem* 4:11–33
- Sorlini S, Gialdini F, Stefan M (2010) Arsenic oxidation by UV radiation combined with hydrogen peroxide. *Water Sci Technol* 61:339–344
- Sorlini S, Gialdini F, Stefan M (2014) UV/H₂O₂ oxidation of arsenic and terbuthylazine in drinking water. *Environ Monit Assess* 186(2): 1311–1316
- Tresintia S, Simeonidis K, Katsikinis M, Palourac E, Bantsisa G, Mitrakasa M (2014) A novel approach for arsenic adsorbents regeneration using MgO. *J Hazard Mater* 265:217–225
- UNESCO (United Nations Educational, Scientific, and Cultural Organization) (2006) Bottled water, weekly newsletter of the water portal number 152 http://www.unesco.org/water/news/newsletter/153_es.shtml (in Spanish)
- Vasudevan S, Mohan S, Sozhan G, Raghavendran N, Murugan C (2006) Studies on the oxidation of As (III) to As (V) by in-situ-generated hypochlorite. *Ind Eng Chem Res* 45:7729–7732
- WHO (World Health Organization) (2011) Guidelines for drinking-water quality. 4th ed. WHO Press, Switzerland
- Yamamuchi H, Fowler B (1994) Toxicity and metabolism of inorganic and methylated arsenicals. In: Nriagu JO (ed) *Arsenic in the environment part II. Human health and ecosystem effects*. Wiley, New York, pp 35–53
- Yoon S, Lee J (2007) Combined use of photochemical reaction and activated alumina for the oxidation and removal of As (III). *J Ind Eng Chem* 13(1):97–104
- Yunus M, Sohel N, Kumar Hore S, Rahman M (2011) Arsenic exposure and adverse health effects: a review of recent findings from arsenic and health studies in Matlab, Bangladesh. *Kaohsiung J Med Sci* 27:371–376
- Zhang F, Itoh H (2006) Photocatalytic oxidation and removal of arsenite from water using slag-iron oxide-TiO₂ adsorbent. *Chemosphere* 65: 125–131