



## Comparison of photocatalysis and photolysis processes for arsenic oxidation in water



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### ABSTRACT

The oxidation of As(III) to As(V) in aqueous solution was evaluated using heterogeneous photocatalysis and photolysis. The influence of TiO<sub>2</sub> as catalyst in different crystalline (rutile, anatase) and commercial forms was evaluated in a batch reactor and an insignificant difference was observed between them. The process by photocatalysis reached up to 97% As(III) oxidation and no significant difference was observed comparing to results obtained by photolysis. The photolysis experiments (UV radiation only), also carried out in a batch system, showed a high oxidation rate of As(III) (90% in 20 min). The influence of different matrices (well water, river water and public water supply) were evaluated. Additionally, the effect of As(V) concentration, generated during the oxidation process, was studied. Continuous photolysis experiments using only UV radiation were performed, resulting in a high As(III) oxidation rate. Using a flow rate of 5 mL min<sup>-1</sup> and an initial concentration of As(III) 200 µg L<sup>-1</sup>, gave an oxidation percentage of As(III) of up to 72%, showing a simple and economical alternative to the oxidation step of As(III) to As(V) in the treatment of water contaminated with arsenic.

### 1. Introduction

Arsenic (As) is a potentially toxic element that can be found in different states of oxidation in the environment. However, the inorganic forms of trivalent arsenite (As(III)) and/or pentavalent arsenate (As(V)) are generally found in natural water (Nguyen et al., 2008). Arsenic contamination is currently considered a global problem and can occur from natural or anthropic sources, such as wood industry, agricultural pesticides, mining and metallurgy activities. The contamination of drinking water by As is a problem that can be observed around the world. As exposure is a global concern that can be related to the increase in several kinds of cancer, including urinary bladder cancer, as well as blackfoot disease (Nguyen et al., 2008; Lee et al., 2015; Tsimas et al., 2009; Guana et al., 2012). Currently, the maximum concentration of arsenic in drinking water recommended by the World Health Organization is 10 µg L<sup>-1</sup> (Lee et al., 2015; Guana et al., 2012).

The toxicity of As is dependent on its oxidation state. Compared to As(V), As(III) is more toxic, mobile, and hard to remove using conventional treatment processes. However, As(V) can easily be removed using adsorption, precipitation, or ion exchange processes. Thus, for the removal of As(III), a previous oxidation process is generally applied, facilitating the removal of this contaminant as As(V) (Guana et al., 2012; Kim et al., 2015). Several techniques are used for oxidation of As(III); however, some need large amounts of oxidants, while in others the

oxidation process is slow.

In this context, heterogeneous photocatalysis presents as an excellent alternative for the oxidation process of As(III) to As(V). Heterogeneous photocatalysis is a process that is able to destroy or transform a variety of potentially toxic compounds by oxidative or reductive mechanisms. In addition to being very efficient, it is an environmentally friendly technology (Zhang and Itoh, 2006; Murrini et al., 2008). During the photocatalytic process, catalyst irradiation results in electron-hole pair generation, providing energy equal to, or greater than, the band-gap. The photo-generated electrons can react with electron acceptors, such as oxygen and/or metal cations (photo-reduction), while the photo-generated holes may react with electron donors such as organic materials (photo-oxidation) (Kosera et al., 2017; Kumordzi et al., 2016).

Titanium dioxide (TiO<sub>2</sub>) is one of the most widely used semiconductors in photocatalysis and has been employed in various fields such as fuel generation, chemical conversion, green synthesis, biomass degradation, industrial effluent treatment, smart surface coating, antimicrobial surfaces, and self-cleansing materials (Raja et al., 2016; Erjavec et al., 2016; Nitoi et al., 2015). The main advantages of a TiO<sub>2</sub> catalyst are its high photocatalytic activity, low cost, low toxicity and high stability to light illumination, as well as the capacity to regenerate several times without significantly losing its activity (Valari et al., 2015; Expósito et al., 2017). Titanium dioxide exists in three polymorphic

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forms: anatase, rutile and brookite and photocatalytic efficiency depends on the crystalline morphology and the interfacial contact (Bojinova et al., 2007; Pelaez et al., 2012). The anatase and rutile forms have demonstrated efficiency for the degradation of organic and inorganic compounds. However, compared to the rutile form, the anatase form of  $\text{TiO}_2$  has shown much higher photocatalytic activity (Nguyen et al., 2005).

The present work evaluated the oxidation of As(III) to As(V), using the heterogeneous photocatalysis process. Different crystalline forms of  $\text{TiO}_2$  catalyst (anatase and rutile), as well as commercial  $\text{TiO}_2$  and commercial calcined  $\text{TiO}_2$  623.15 K, were evaluated for oxidation of As(III). Parameters affecting the process were evaluated, such as pH and catalyst concentration, as well as effects of the influence of the matrix and the concentration of As(V) generated in the process. A comparison between the oxidation efficiency of As(III) by photocatalysis (UV + catalyst) and photolysis (UV radiation only) was realized. Continuous flow experiments, to evaluate the oxidation efficiency of As(III) by photolysis, were also performed.

## 2. Experimental procedure

### 2.1. Materials and chemicals

All chemicals used were of analytical grade ultrapure water with resistivity of  $18 \text{ M}\Omega \text{ cm}$  was purified in a purifier (Master All 2000, Gehaka, Brazil).  $\text{HNO}_3$  (Biotec, Brazil)  $0.1 \text{ mol L}^{-1}$  and NaOH (Neon, Brazil)  $0.1 \text{ mol L}^{-1}$  solutions were used to adjust the pH of the solutions. Standard Arsenic (III) solution (SpecSol, Brazil) was used for the oxidation and preparation of the calibration curve. The following oxides were evaluated as catalysts: Titanium dioxide ( $\text{TiO}_2$ ) in anatase form (Sigma-Aldrich, USA), Titanium dioxide ( $\text{TiO}_2$ ) in rutile form (Sigma-Aldrich, USA), and commercial  $\text{TiO}_2$  (Perquim, Brazil). The following reagents were used in the determination of As(III) in the solution: Sodium borohydride (Neon, Brazil), HCl (Vetec, Brazil), citric acid (Biotec), sodium citrate (Biotec) and KI (Neon). A solution of As(V) ( $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ , Sigma-Aldrich, USA) was used for the adsorption tests of As(V).

### 2.2. Photocatalytic and photolysis batch experiments

To verify the photocatalytic activity, the experiments were performed in a batch reactor (Pyrex glass), with a capacity of  $1000 \text{ cm}^3$  and a cooling system for maintaining the temperature of the medium at  $23 \pm 5^\circ \text{C}$ . The reaction medium was maintained under magnetic stirring and air flow ( $13 \text{ L min}^{-1}$ ). A mercury vapor lamp of 250 W was used as a source of UV radiation. To evaluate the oxidation of As(III) to As(V), samples were taken at regular time intervals. The samples were centrifuged and the concentration in the supernatant was determined. Adsorption tests (in the absence of radiation) and photolysis (in the absence of catalyst) were performed following the same procedure. All experiments were performed at pH 7, with the exception of the pH influence test.

To evaluate the influence of the increase of As(V) concentration generated in the process, experiments were performed on several consecutive cycles of photocatalysis. In these experiments, a solution containing  $200 \mu\text{g L}^{-1}$  of As(III) and  $2 \text{ g L}^{-1}$  of catalyst was subjected to UV radiation for 30 min. After this, As(III) was again added to this solution to restore the initial concentration of  $200 \mu\text{g L}^{-1}$ , which was then subjected to UV radiation again. This procedure was performed for four consecutive cycles. The influence of As(V) present in the reaction medium was also evaluated in the four-cycles photolysis process by using the same procedure described for photocatalysis.

To evaluate the matrix effect in the photolysis, three different matrices were used: well water, river water and public water supply. In this study, a concentration of  $200 \mu\text{g L}^{-1}$  of As(III) was added to the three matrices. A control sample containing ultrapure water and

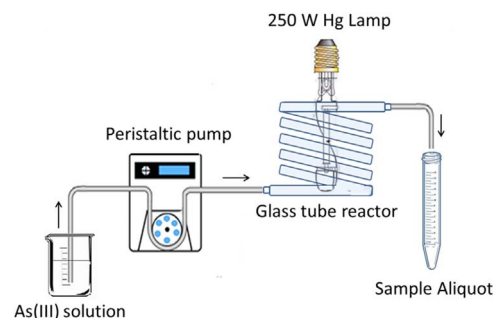


Fig. 1. Illustration of the experimental setup for As(III) oxidation by photolysis continuous flow.

$200 \mu\text{g L}^{-1}$  As(III) was also evaluated. The experiments were performed as described previously.

### 2.3. Photolysis continuous flow experiments

Continuous flow photolysis experiments were performed in a spiral shaped, glass tube reactor with a total length of 3.8 m and an internal diameter of 0.6 cm. For the photolysis tests, flow rates from 5 to  $20 \text{ mL min}^{-1}$  were evaluated, with the 250 W Hg UV lamp being placed in the center and the solution of As(III) pumped with the aid of a peristaltic pump (Watson Marlow 120 S, England). The experimental setup for photolysis continuous flow experiments is illustrated at Fig. 1. The photolysis in continuous flow were performed in absence of air flow. Aliquots were periodically collected triplicates and the As concentration determined.

### 2.4. Determination of arsenic concentration

The concentrations of As(III) and As(V) were determined by hydride generation atomic absorption spectrometry (HG AAS), using a spectrometer (Perkin Elmer AAnalyst 700, Germany) equipped with a hydride generation system (FIAS 100) with atomization in the quartz T-tube cell. A solution of  $\text{NaBH}_4$  0.3% (w/v) in NaOH 0.05% (w/v) was used as the reducing agent. A solution of HCl 10% (v/v) was used as carrier and the volatile species generated were carried into the quartz cell by an argon flow. To determine As(III), 1.0 mL of citric acid/sodium citrate buffer was added, along with 10 mL of ultrapure water. The determinations of As(V) were performed by adding 1.0 mL of the solution KI 20% (w/v) and 1.0 mL of concentrated HCl, with the solutions being allowed to stand for 45 min to pre-reduce the As(V) to As(III). The samples were then added with 10 mL of ultrapure water and analyzed by HG AAS. The limit of detection (LOD) obtained for the method for determination of As(III) was  $0.2 \mu\text{g L}^{-1}$ .

## 3. Results and discussion

### 3.1. Influence of pH

The influence of pH on the As(III) oxidation was verified using rutile as catalyst at a concentration of  $0.1 \text{ g L}^{-1}$ . The obtained results are shown in Fig. 2.

When analyzing Fig. 2, it can be noticed that the solutions with pH adjusted to 3, 7 and 9, after 15 min of exposure to UV radiation, presented a percentage of oxidation higher than 90%. These results indicate that, under the conditions used, there was no significant influence of the pH on the oxidation process from As(III) to As(V).

The effect of pH on water removal was evaluated by Fostier et al. (2008) using  $\text{TiO}_2$  immobilized in PET bottles. In the evaluated pH range of 4–9, influence of the pH was not observed in this process. According to the authors, this fact is due to the stability of  $\text{TiO}_2$  in a wide pH range. In addition, according to Lee and Choi et al. (2002), the

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