

## Visible Light Active Fe-doped TiO<sub>2</sub> for the Oxidation of Arsenite to Arsenate in Drinking Water

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The aim of this work was to study photocatalysts based on Titania doped with Fe, active in the presence of visible light and effective in the oxidation of As(III) to As(V). Fe-doped TiO<sub>2</sub> photocatalysts were prepared using sol-gel method and characterized by different techniques, such as XRD, UV-Vis DRS and Raman spectroscopy. Photocatalytic experiments were carried out using a cylindrical photoreactor irradiated with a strip of visible-LEDs (nominal power: 10W) with emission in the range 400 - 600 nm. Aqueous samples containing 6 mg L<sup>-1</sup> of As(III) were used in photocatalytic experiments. Chemical-physical characterization results evidenced that the doping of TiO<sub>2</sub> with Fe induced a decrease of band gap value from 3.2 eV to 2.9 eV, thus making the photocatalyst active under visible light. Consistently with the characterization results, the semiconductor Fe-doped TiO<sub>2</sub> exhibited good photoactivity in the visible light driven tests: the complete oxidation of As(III) to As(V) took place after only 30 min of irradiation in distilled water and after 60 min in drinking water.

### 1. Introduction

Arsenic is a toxic element that can be found in many forms in the environment due to the numerous anthropogenic and natural sources. Its presence at concentrations exceeding the limit (10 µg L<sup>-1</sup>) set by WHO (2001) has been documented in waters and soils in many areas of the world. It is estimated that the arsenic contamination of drinking water affects over 144 million people around the world (Shankar et al., 2014). Arsenic (As) contamination in groundwater and soil is widely recognized as a global health problem (Qin et al., 2016). In particular, arsenic typically occurs in the environment in different oxidation states (-III, 0, +III and +V). The distribution of As(III) and As(V) in natural water depends on the redox potential and pH of water (Smedley and Kinniburgh, 2002). Compared with As(V), As(III) is generally reported to have a low affinity to the surface of various minerals, because it mainly exists as non-ionic H<sub>3</sub>AsO<sub>3</sub> in natural water when pH < 9 (Qin et al., 2016). Nevertheless, As(V) adsorbs easily to solid surfaces, so it is easier to be removed. Since As(III) is more toxic and more difficult to remove than As(V), a pre-oxidation process transforming As(III) to As(V) is highly desirable to remove arsenic from water (Zhang et al., 2014). Different methods have been reported in literature about the oxidation of As(III) to As(V), including biological oxidation, chemical oxidation with conventional oxidants, such as chlorine, chlorine dioxide (ClO<sub>2</sub>), chloramine (NH<sub>2</sub>Cl), permanganate (MnO<sub>4</sub><sup>-</sup>), manganese oxides, and hydrogen peroxide (Oennby et al., 2014), and photo-oxidation (Xu and Meng, 2009). Interesting results have already been published in the literature concerning the oxidation of As(III) in As(V) using the photocatalytic process (Vaiano et al., 2016a). In particular, in literature it is reported the effectiveness of this process even in a short time and in presence of a real drinking water matrix (Iervolino et al., 2016). Due to its chemical and biological stability, availability, non-toxicity and high efficiency in water treatment TiO<sub>2</sub> is the most investigated semiconductor (Xu et al., 2010). However, TiO<sub>2</sub> has high band gap energy (3.2 eV) and it can only be activated by the UV fraction of the solar light. For efficient photocatalytic activity, it is necessary to extend the photoresponse of the TiO<sub>2</sub> from the UV to the visible region by modification of its optical properties. Recently, the scientific community is working on studying visible active photocatalysts (Vaiano et al., 2016b), which can also be applied in the photocatalytic oxidation of arsenic present in drinking water (Qin et al., 2017). The most popular transition metals dopants used for the modification of the TiO<sub>2</sub> optical properties are Cr, Fe, Ni, V, Mn, and Cu (Hou et al., 2009). Fe doping has found to enhance the photocatalytic activity of the TiO<sub>2</sub> (Sacco et al.,

2015) for the degradation of dye under visible light (Moradi et al., 2016). Still scarce is the literature about the photocatalytic oxidation of As(III) to As(V) under visible light. Accordingly, the aim of this work was to investigate the photocatalytic oxidation of As(III) into As(V) through a Fe-doped TiO<sub>2</sub> photocatalyst, synthesized by a facile method, active under visible light irradiation.

## 2. Experimental

### 2.1 Photocatalysts synthesis and characterization

The photocatalysts were prepared by sol gel method. In particular 50 mg of iron acetylacetonate Fe(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub> (Sigma-Aldrich) was dissolved in 25 mL of titanium isopropoxide (Sigma-Aldrich). This solution was sonicated until complete solubilization of iron acetylacetonate. Then, 100 mL of distilled water were added to obtain a precipitate which was separated from the liquid phase by centrifugation for 5 min at 5,000 rpm. The sample was washed with distilled water to remove any impurities and it was calcined at 450°C for 30 min. In addition, a sample of undoped Titania was prepared following the same procedure. All the samples were characterized using different techniques. The Raman spectra of the samples were recorded with a Dispersive MicroRaman system (Invia, Renishaw), equipped with 514 nm laser, in the range 100 - 2,000 cm<sup>-1</sup> Raman shift. X-ray diffraction patterns were obtained with an X-ray diffractometer (Assing), using Cu-K $\alpha$  radiation. UV-vis reflectance spectra of powder catalysts were recorded by a Perkin Elmer spectrometer Lambda 35 using an RSA-PE-20 reflectance spectroscopy accessory (Labsphere Inc., North Sutton, NH). All spectra were obtained using an 8° sample positioning holder, giving total reflectance relative to a calibrated standard SRS-010-99 (Labsphere Inc., North Sutton, NH). Equivalent band gap determinations of the photocatalysts were obtained from Kubelka-Munk function  $F(R^\infty)$  by plotting  $[F(R^\infty) \times h\nu]^2$  vs.  $h\nu$  (Iervolino et al., 2018).

### 2.2 Photocatalytic activity tests

Photocatalytic tests were carried out in a pyrex cylindrical reactor (ID = 2.5 cm; height = 18 cm) equipped with an air distributor device ( $Q_{\text{air}} = 150 \text{ cm}^3 \text{ min}^{-1}$  under standard temperature and pressure conditions), a magnetic stirrer (to maintain the photocatalyst suspended in the aqueous solution), and a temperature controller. The photoreactor was irradiated by a strip of visible LEDs with wavelength emission range 400-600 nm positioned around the external surface of the reactor so that the light source uniformly irradiated the reaction volume. The suspension was left in dark conditions for 1 hour and then the reaction was started under visible light up to 3 hours. Different catalysts dosage (in the range 1.5 - 4.5 g L<sup>-1</sup>) were tested in 100 mL of aqueous solution containing 6 mg L<sup>-1</sup> of As(III). Photocatalytic tests were carried out in both distilled and real drinking water. During the photocatalytic test, the liquid samples were collected at fixed time and analyzed. In particular, the As(V) concentration was analyzed by a spectrophotometric method based on the formation of molybdenum blue permitting the evaluation of the As(V) concentration at  $\lambda = 880 \text{ nm}$  through a Perkin Elmer UV-Vis spectrophotometer (Iervolino et al., 2016). The concentration of the total arsenic was analyzed by preliminary oxidizing As(III) fraction through the addition of KMnO<sub>4</sub> aqueous solution (0.01 M). In this way As(III) was totally oxidized to As(V) and then analyzed with the molybdenum blue method in both untreated and treated solutions (Vaiano et al., 2016a).

## 3. Results

### 3.1 Photocatalysts characterization

The crystalline structure of the photocatalysts characterized by X-ray diffraction analysis (Figure 1) showed only patterns related to anatase Titania for both samples (Fe-TiO<sub>2</sub> and TiO<sub>2</sub>) (Vaiano et al., 2016a). No signals due to iron oxides appear in the figure. The average size of photocatalysts crystallites was calculated using the Scherrer equation on diffraction plane (1 0 1) (Dai et al., 2010). The results in terms of crystallite size for undoped TiO<sub>2</sub> and Fe-doped TiO<sub>2</sub> are quite similar, being about 8 nm for both samples (Table 1).

Table 1: Photocatalysts and their characteristics

Photocatalysts	Crystallite size (nm)	Equivalent band gap energy (eV)
TiO <sub>2</sub>	8.4	3.2
Fe-doped TiO <sub>2</sub>	7.9	2.9

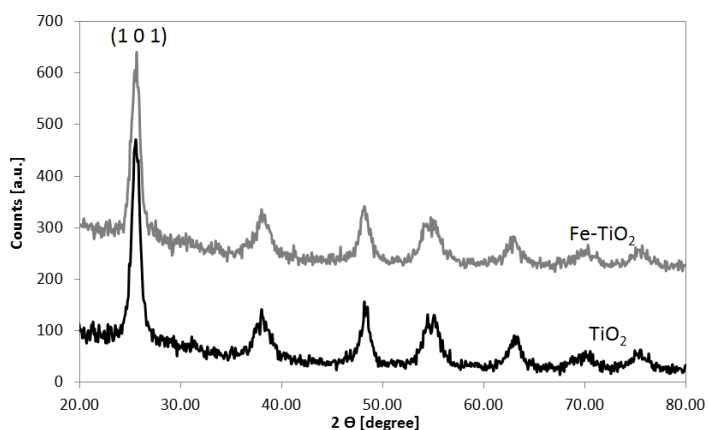


Figure 1: XRD spectra of the photocatalysts

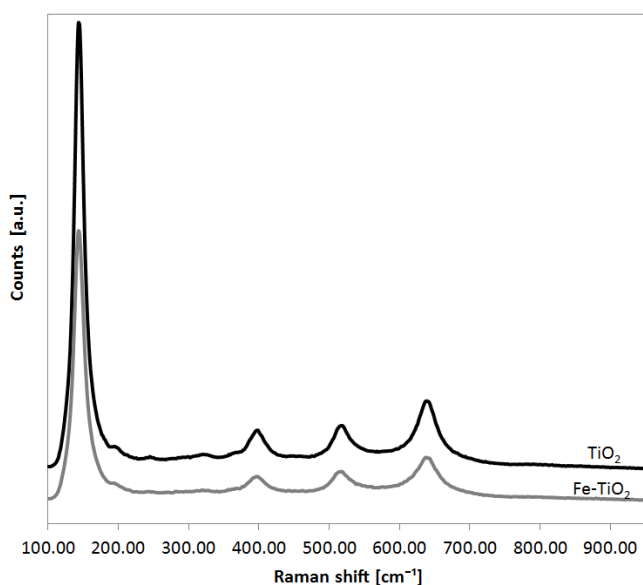


Figure 2: Raman spectra

The Raman spectra of photocatalysts show the common peaks at 144, 396, 514 637  $\text{cm}^{-1}$  and a weak shoulder at 195  $\text{cm}^{-1}$  due to the anatase form of  $\text{TiO}_2$  (Gao et al., 2013) (Figure 2). The signals reported for all photocatalysts are only due to Titania in the anatase crystalline form and there are no signals due to iron oxides. Therefore, these results confirm that  $\text{TiO}_2$  doping process was correctly finalized.

The data obtained from UV–Vis reflectance spectra were used for evaluating the band-gap energy of  $\text{TiO}_2$  and of Fe-doped  $\text{TiO}_2$  photocatalysts, respectively. The doping of  $\text{TiO}_2$  with iron significantly affected the band-gap energy, decreasing from 3.2 eV (for undoped  $\text{TiO}_2$ ) to 2.9 eV for Fe-doped  $\text{TiO}_2$  (Table 1).

### 3.2 Photocatalytic activity results

The efficiency of the prepared and characterized photocatalysts was evaluated in the photocatalytic oxidation of As(III) in As(V) under visible light. In particular, control tests were carried out in the presence of As(III) and irradiating the photoreactor with visible LEDs in the absence of photocatalyst (photolysis reaction), respectively. The behaviour of the As(III) relative concentration (a) and As(V) produced (b) as a function of irradiation time are shown in Figure 3. The photolysis control test did not result in any oxidation activity. An important decrease of the As(III) concentration (Figure 3a) was obtained in presence of Fe-doped photocatalyst. In particular, in the case of undoped  $\text{TiO}_2$  photocatalyst, the concentration of As(III) decreased up to 30 min of irradiation, reaching a As(III) conversion as low as 2%. After 30 min, As(III)/As(III)<sub>0</sub> remained almost constant indicating the  $\text{TiO}_2$  is

not able to oxidize the As(III) present in the solution. On the contrary, in presence of Fe-doped TiO<sub>2</sub> photocatalyst, the complete oxidation of As(III) to As(V) was achieved after only 30 min of visible light irradiation. This result clearly shows that iron doping induces a photocatalytic activity in the presence of visible irradiation. In order to confirm this result, in addition to the analysis of the As(III), the analysis of the As(V) released in solution during the run time was also performed (Figure 3b). After 180 min of irradiation time, As(V) concentration in solution was equal to 6 mg L<sup>-1</sup> (i.e. equal to the As(III) initial value). This last results is very important because clearly shows that As(V) produced by the photo-oxidation of As(III) was completely released into the solution, thus not occupying the active sites of the catalyst, avoiding its deactivation and enhancing its stability (Vaiano et al., 2014). Moreover, the As(III) conversion, achieved after 30 min of irradiation time, using Fe-doped TiO<sub>2</sub> photocatalyst at different dosages (in the range 1.5 - 4.5 g L<sup>-1</sup>), increased as catalyst loading was increased to 3 g L<sup>-1</sup>. But, a further increase of catalyst dosage to 4.5 g L<sup>-1</sup>, resulted in a decrease of As(III) oxidation. This result may be explained by the increased opacity of the water solution due to the increase of the catalyst loading, which possibly made light penetration through the solution more difficult (Vaiano et al., 2014). Accordingly, 3 g L<sup>-1</sup> of photocatalyst loading was considered the optimum dosage.

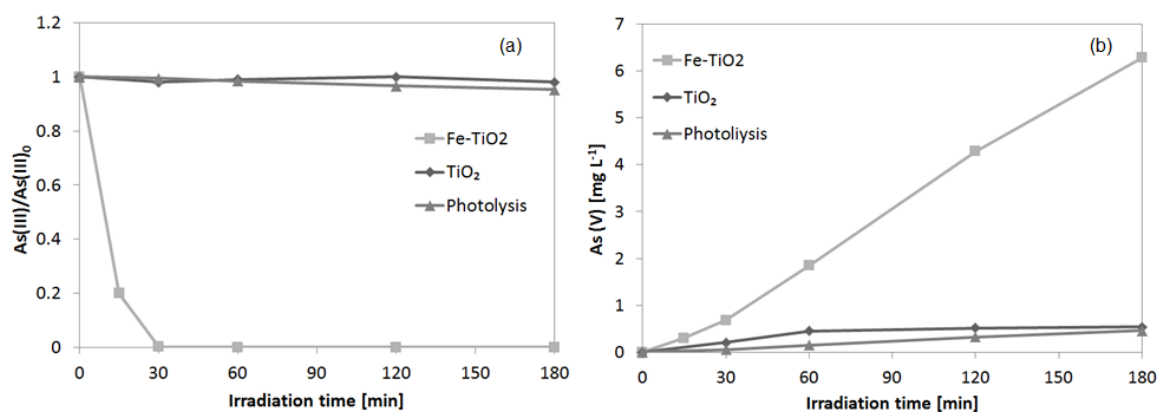


Figure 3: Behaviour of As(III) relative concentration in solution (a) and behaviour of As(V) concentration in solution (b) as a function of visible light irradiation time for both undoped TiO<sub>2</sub> and Fe-doped TiO<sub>2</sub> photocatalysts.

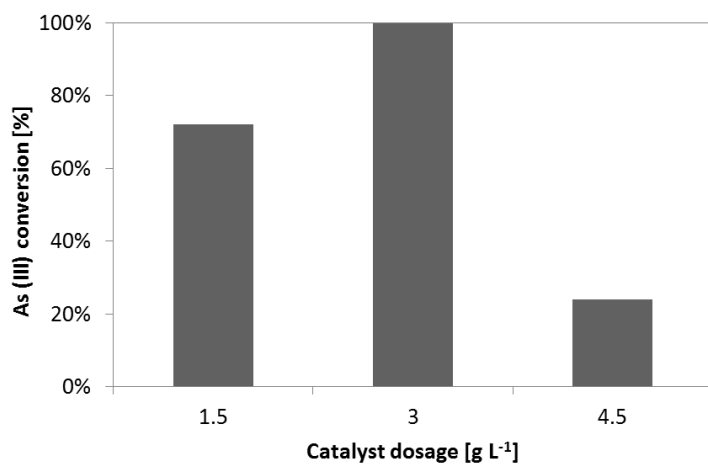


Figure 4: Influence of Fe-doped TiO<sub>2</sub> dosage on the As(III) conversion after 30 min of visible light of irradiation time.

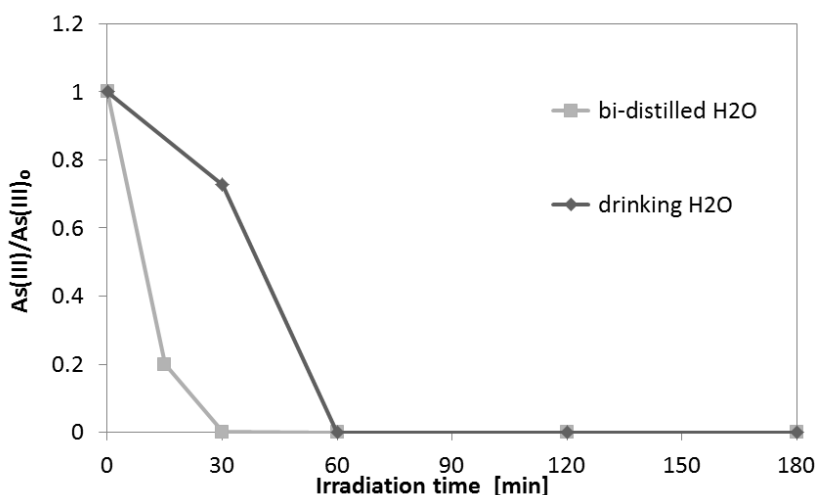


Figure 5: Comparison between the photocatalytic test performed on the solution of As(III) in bi-distilled water and on the solution of As(III) in real drinking water under visible light irradiation with Fe-doped TiO<sub>2</sub>.

Once the optimal photocatalyst dosage has been established (3 g L<sup>-1</sup>), its effectiveness has also been tested on a drinking water matrix. Figure 5 shows the comparison between the photocatalytic test performed on the solution of As(III) in bi-distilled water with an initial concentration of As(III) of 6 mg L<sup>-1</sup> and the photocatalytic test carried out on the solution of As(III) in real drinking water with the same As(III) initial concentration. It is possible to observe that the efficiency of the photocatalytic oxidation of As(III) in real drinking water was lower than that one observed in bi-distilled water. As matter of fact, after 30 minutes of irradiation, the percentage of As(III) oxidized to As(V) was as low as 27 % compared to 100 % in bi-distilled water. It is well known that ionic species like bicarbonates, sulfates and chlorides, generally present in drinking water, act as radical scavengers in photocatalytic processes (Iervolino et al., 2016), worsening the photocatalytic activity. However, it is worth noting that, the Fe-doped TiO<sub>2</sub> photocatalyst was able to completely oxidize As(III) after 60 minutes of visible light irradiation in real drinking water.

#### 4. Conclusions

Photocatalytic oxidation of As(III) into As(V) in mild conditions and under visible light was investigated in the presence of Fe-doped TiO<sub>2</sub> catalyst. Characterization results evidenced that the doping of TiO<sub>2</sub> with Fe induced a decrease of band gap value from 3.2 eV to 2.9 eV. The Raman and XRD analysis evidenced the presence of only signals related to the Titania in the anatase crystalline form and the absence of signals due to iron oxides. Photocatalytic experiments were carried out under visible-LEDs irradiation with emission in the range 400 - 600 nm. The obtained results showed that Fe-doped TiO<sub>2</sub> exhibited good performances in presence of visible light, achieving the complete oxidation of As(III) to As(V) after only 30 min of irradiation time. Moreover, As(V) produced by the photo-oxidation of As(III) was completely released into the solution, thus not occupying the active sites of the catalyst, avoiding its deactivation and enhancing its stability. Finally, the synthesized visible light active photocatalyst was also able to completely oxidize As(III) into As(V) in drinking water matrix in 60 min of irradiation light. The Fe-doped TiO<sub>2</sub> catalyst can be considered an interesting semiconductor to be used in the photocatalytic oxidation of As(III) into As(V) in presence of the direct sunlight, making this process ecofriendly and with low energy consumption. In fact, the photocatalytic tests have shown its effectiveness in a short time in the presence of visible light. The formulated photocatalyst makes the oxidation phase very fast, allowing to reach the complete arsenic removal by means the use of an adsorption process after the photocatalytic oxidation. However, further studies should be focused on the formulation of visible light active structured photocatalysts in order to avoid the recovery of catalyst particles after the photocatalytic process.

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