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Technical Note

Arsenic removal from water employing heterogeneous photocatalysis with TiO_2 immobilized in PET bottles

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Abstract

Arsenic oxidation (As(III) to As(V)) and As(V) removal from water were assessed by using TiO_2 immobilized in PET (polyethylene terephthalate) bottles in the presence of natural sunlight and iron salts. The effect of many parameters was sequentially studied: TiO_2 concentration of the coating solution, Fe(II) concentration, pH, solar irradiation time; dissolved organic carbon concentration. The final conditions (TiO_2 concentration of the coating solution: 10%; Fe(II): 7.0 mg l^{-1}; solar exposure time: 120 min) were applied to natural water samples spiked with 500 μg l^{-1} As(III) in order to verify the influence of natural water matrix. After treatment, As(III) and total As concentrations were lower than the limit of quantitation (2 μg l^{-1}) of the voltammetric method used, showing a removal over 99%, and giving evidence that As(III) was effectively oxidized to As(V). The results obtained demonstrated that TiO_2 can be easily immobilized on a PET surface in order to perform As(III) oxidation in water and that this TiO_2 immobilization, combined with coprecipitation of arsenic on Fe(III) hydroxides(oxides) could be an efficient way for inorganic arsenic removal from groundwaters.

Keywords: Arsenic; Photocatalysis; Oxidation; Water treatment

1. Introduction

Coprecipitation of arsenic with Fe(III) hydroxides(oxides) and subsequent filtration of the generated precipitates are practical and effective treatment processes commonly used for removing As from water. Nevertheless, iron oxides adsorb As(V) more effectively than As(III) at low to neutral pH values (e.g. pH 4–7) (Impellitteri and Scheckel, 2006). Consequently As(III) has to be oxidized to As(V) prior to the removal with iron hydroxides. Although the oxidation can be achieved by many oxidants (e.g. ozone, Fenton's reagent, chlorine, etc.), recent studies show heterogeneous photocatalysis (HP) in aqueous TiO_2 suspensions to be an efficient and interesting way to promote oxidation of arsenite to arsenate (Bissen et al., 2001; Lee and Choi, 2002; Jayaweera et al., 2003). However it is difficult to simultaneously remove the arsenate from contaminated water, since the TiO_2 usually used has a low surface area and low adsorption capability and, moreover, the separation and reuse of the TiO_2 powder from treated water also limit its application (Zhang and Itoh, 2006). In order to overcome this problem, TiO_2 immobilization appears as a possible alternative. Fergusson and Hering (2006) have previously applied immobilized TiO_2 to oxidize As(III) in a fixed-bed, flow-through reactor. Although they showed that fixed-bed TiO_2 photocatalysis could be a viable option for the preoxidation of As(III) to As(V), the effluent should still be treated to remove As(V).

PET (polyethylene terephthalate) bottles have been successfully used to expose drinking water to sunlight for solar desinfection (Wegelin, 2000) and also for solar

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oxidation and removal of arsenic (Hugh et al., 2001). These bottles appear to be an interesting support for reduced cost technologies for *in situ* water treatment for isolated populations in developing countries without access to municipal water networks (Wegelin, 2000). With the same aim, TiO_2 heterogeneous photocatalysis presents various advantages: solar light may be used and TiO_2 is a relatively cheap, reusable and non toxic material (Meichtry et al., 2007).

Therefore, the aim of this work was to assess the potential of a system including simultaneous As(III) oxidation and As removal from waters when using TiO_2 immobilized in PET bottles in the presence of natural sunlight and iron salts. The process was applied to some water samples naturally contaminated with As(V) and also spiked with As(III), collected in the cities of Ouro Preto and Mariana, Minas Gerais State-Brazil.

2. Experimental

2.1. Procedure

The aim of the first experiments was to optimize the conditions of As(III) oxidation and As removal with immobilized TiO_2. Experiments were carried out in transparent 330 ml PET bottles. TiO_2 immobilization on the internal surface of the bottles was performed based on Meichtry et al. (2007), by shaking ~115 ml of a TiO_2 suspension at pH 2.5 ($HClO_4$) for about 30 s. After removing the excess suspension, the bottles were oven-dried for 20 min at 55 °C to promote TiO_2 adhesion. After cooling, internal washing was performed with distilled water in order to remove unfixed TiO_2.

After TiO_2 coating, bottles containing 200 ml of an As(III) and Fe(II) solution were exposed to solar light in the horizontal position. At the end of each experiment, the bottles were maintained in the vertical position for 12 h, in the dark, for precipitation of colloidal material. Determination of As(III) and As(V) concentrations was performed after filtration through quantitative filter-paper (J. Prolab, Brazil). The effects of many parameters were studied: TiO_2 concentration, Fe(II) concentration, pH, solar irradiation time and dissolved organic carbon concentration.

2.2. Application to As contaminated water samples

In order to verify the influence of natural water matrix, the optimized process was applied to As contaminated natural water samples collected in two subterranean gold mines, two water-pipes and one river located in Ouro Preto and Mariana cities, Iron Quadrangle, MG, Brazil. At each point, 2 l were collected in polyethylene bottles for arsenic removal studies. Collected samples were spiked with 500 $\mu g\,l^{-1}$ As(III) and submitted to the removal process. As(III) and As(V) concentrations were determined before and after the As removal treatment.

2.3. Analysis

As(III) and As(V) concentrations were determined by differential pulse cathodic stripping voltammetry, according to Pereira et al. (2007). Briefly, the voltammetric measurements were carried out using a potentiostat–galvanostat AUTOLAB PGSTAT30 (Eco Chemie, B.V. The Netherlands) coupled to a microcomputer. A graphite electrode was used as counter electrode and all potentials were recorded against an Ag/AgCl, KCl_{sat} reference electrode. A hanging mercury drop electrode was used as working electrode. All As(III) determinations were performed in 2.0 M $HCl + 3.15 \times 10^{-4}$ M Cu(II) supporting electrolyte. Total As (As_{Tot}) concentration was determined after reduction of As(V) to As(III) with sodium thiosulphate and the As(V) concentration was calculated by the difference between As_{Tot} and As(III). The detection and quantitation limits were 0.5 and 2 $\mu g\,l^{-1}$, respectively, for both species. Solar irradiation was measured with a Cole-Parmer radiometer, at 365 nm. The concentration of some anions in the water samples was determined by ion chromatography (Dionex, DX-500).

2.4. Reagents and solutions

Reagents used for the preparation of solutions were analytical grade and distilled water was purified in a Milli-Q system (18.2 MΩ cm) from Millipore (USA). A standard stock solution of 1000 $mg\,l^{-1}$ As(III) was prepared by dissolving As_2O_3 (Merck, Germany) (previously dried in an oven at 110 °C for 2 h) in 0.4% (w/v) NaOH (Merck, Germany); the solution was then acidified to pH 2 by adding HCl. A standard stock solution of 1000 $mg\,l^{-1}$ As(V) was prepared by dissolution of $Na_2HAsO_4 \cdot 7H_2O$ (Aldrich, USA) in water. A standard stock solution of 1000 $mg\,l^{-1}$ Fe(II) was prepared from $FeSO_4$. The TiO_2 used in this study was P 25 (Degussa, Germany). The influence of organic matter on As removal was evaluated in presence of humic acid (38.4% C, 4.3% H and 0.28% N) (Aldrich, USA). In all optimization experiments, mineral water (Icuara, Mogi das Cruzes, SP, Brazil) was used.

3. Results

3.1. TiO_2 concentration

TiO_2 suspensions with concentrations varying between 2 and 20% (w/v), at pH 2.5 ($HClO_4$), were tested for internal coating of the PET bottles. In this experiment the other parameters were: initial As(III) concentration: 1 $mg\,l^{-1}$; Fe(II) concentration: 5 $mg\,l^{-1}$; pH: 7.0, exposure time to sunlight: 4 h; mean solar intensity: 1.2 $mW\,cm^{-2}$; all experiments were performed in duplicate. Results are shown in Fig. 1a. As(III) and As(V) final concentrations decreased when the TiO_2 concentration of the coating solution was increased up to 10%, when As removal reached a maximum value (98%); with a 20% TiO_2 concentration, the result was