CHEMICAL ENGINEERING TRANSACTIONS

VOL. 73, 2019

A publication of AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Andrea D'Anna, Paolo Ciambelli, Carmelo Sunseri
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ISBN 978-88-95608-70-9; **ISSN** 2283-9216

DOI: 10.3303/CET1973043

Photocatalytic Oxidation of Arsenite to Arsenate Using a Continuous Packed Bed Photoreactor

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The aim of this work was to evaluate the effectiveness of TiO_2 pellets for the photocatalytic oxidation of As(III) to As(V) under UV light with simultaneous adsorption of As(V) in a continuous packed bed photoreactor. In particular commercial cylindrical pellets of TiO_2 were used as photocatalyst. Experimental photocatalytic tests were carried out in a cylindrical pyrex photoreactor (irradiated by UV-LEDs) which operates in continuous mode in order to treat aqueous solution contaminated with arsenic at different initial As(III) concentration. Preliminary tests conducted in a batch configuration showed that TiO_2 pellets adsorb As(V) produced from the photoreaction, without leading to a deactivation of the active sites and evidencing that the As(V) produced is completely released into the solution. Moreover, TiO_2 pellets maintained an excellent photoactivity and durability after several cycles making it a very promising catalyst to be employed in continuous reactors for the photocatalytic treatment of water polluted by arsenic, obtaining 98% As(III) oxidation yield after only 15 min of UV-LEDs irradiation. Moreover, the use of a continuous packed bed reactor filled with the stable TiO_2 catalyst pellets irradiated by UV light allows to reach a steady state As(III) concentration without any deactivation phenomena. Finally, with 1 mg L^{-1} As(III) initial concentration, no As(V) release was observed from TiO_2 surface during the irradiation time evidencing that the total arsenic removal could be achieved thanks to the photocatalytic properties and adsorption ability of the TiO_2 pellets.

1. Introduction

In many countries, such as Bangladesh, United States, Vietnam and Italy, the contamination of groundwater from arsenic has become a major problem because of the toxicity of this element (Wang and Wai, 2004). The contamination is mainly natural, of geological origin, but also anthropic activities such as the use of pesticides and the presence of industries can result in groundwater contamination. People are exposed to high levels of inorganic arsenic (i) through contaminated drinking water, (ii) by using contaminated water in food preparation as well as (iii) for food crops irrigation, (iv) by eating contaminated food and (v) smoking tobacco. Long-term exposure to inorganic arsenic can lead to chronic arsenic poisoning. Skin lesions and skin cancer are the most characteristic effects. For these reason and in order to minimize arsenic related health risks, the World Health Organization (WHO) set the limit of maximum arsenic concentration in drinking water as low as 10 µg L^{-1} (Sun et al., 2017). The prevalent forms of inorganic arsenic naturally occurring in drinking water are As(III) and As(V). The concentrations and the ratios between As(III) and As(V) are highly variable and depend on the redox conditions present in the water and in the geological context (Cullen and Reimer, 1989). In groundwater As(III) is the predominant form of arsenic, which is more toxic and mobile than As(V) (Sharma and Sohn, 2009). As(III) has low affinity with mineral surfaces, while As(V) adsorbs easily to solid surfaces. Accordingly, a pre-oxidation step to transform As(III) to As(V) is necessary to achieve an optimal As(V) adsorption (Gómez Pastora et al., 2016). In the literature several methods have been reported for the oxidation of As(III) in As(V). They are mainly based on the use of conventional oxidants, such as chlorine, chlorine dioxide (ClO_2), chloramine (NH_2Cl), permanganate (MnO_4^-) (Önnby et al., 2014). However, to avoid the formation of dangerous oxidation by-products and the presence of residuals in the treated water, photocatalysis can be a valid alternative. Recently, several studies have been performed on the application of photocatalysis for the

Paper Received: 11 June 2018; Revised: 05 August 2018; Accepted: 03 January 2019

Please cite this article as: Iervolino G., Vaiano V., Matarangolo M., Rizzo L., 2019, Photocatalytic Oxidation of Arsenite to Arsenate Using a Continuous Packed Bed Photoreactor , Chemical Engineering Transactions, 73, 253-258 DOI:10.3303/CET1973043

removal of arsenic from drinking water mainly using UV light active TiO_2 or other semiconductors, such as Fe_3O_4 (Sun et al., 2017). In another paper, MoO_x/TiO_2 photocatalytst allowed to achieve the total oxidation of As(III) to As(V) in water without TiO_2 deactivation (Vaiano et al., 2016). TiO_2 and zero-valent iron under simulated sunlight (Xe lamp) were also investigated and photocatalytic oxidation of As(III) to As(V) was found to be strongly affected by pH, being the optimal result observed at pH=3 (Dutta et al., 2005). Also photocatalytic oxidation of As(III) to As(V) under visible light using Fe doped TiO_2 semiconductor was investigated and a complete oxidation was observed after only 30 min of irradiation time (Iervolino et al., 2018). Therefore, according to the literature, photocatalysis with TiO_2 based photocatalyst is effective in the oxidation of As(III) to As(V) (Zhang and Itoh, 2006). However, most of the studies available in scientific literature, deal with slurry reactors (Dutta et al., 2004), but. this experimental set-up would be quite hard to upscale. Therefore, to treat high flow rates and to make the photocatalyst easily removable at the end of the process, the synthesis of structured catalysts is becoming increasingly interesting research area for the scientific community. Accordingly, in this work the use of TiO_2 pellets was proposed for the removal of arsenic from drinking water. However, another limitation of the application of the photocatalytic process is represented by the absence of a proper reactor design and optimization because of the most studied photoreactors are in batch configuration (Sacco et al., 2018). Due to a more easy scale-up process, an interesting alternative is represented by reactors that can be operated in continuous mode (McCullagh et al., 2010). In particular, the use of micro-reactors allows the uniform irradiation of the whole solution volume and consequently the photocatalytic reactions can be substantially accelerated (from h/days for batch process to seconds/mins in continuous-flow) (Cambié et al., 2016). Moreover, micro-reactors can also improve mass transfer, due to the formation of a thin film of the aqueous solution over the catalyst surface, thus enabling an efficient penetration of UV radiation inside the core of the reactor (Sengupta et al., 2001). In this work a solution about the problem of drinking water contaminated by arsenic is proposed, using a continuous mode operated photoreactor, as well as exploiting the photocatalytic efficiency of TiO_2 pellets.

2. Experimental

2.1 Photocatalytic activity tests using batch reactor

The photocatalytic oxidation of As(III) to As(V) was preliminarily studied in a cylindrical batch photoreactor. TiO_2 commercial cylindrical pellets (size equal to 10 x 2.8 mm; anatase crystalline form, Sigma-Aldrich) were used during the photocatalytic tests. The amount of TiO_2 sample, used in the experimental tests, was equal to 4 g. UV-LEDs strip (*LED*s nominal power: 12 W m^{-2}; main emission: 365 nm) was used as light source and positioned around the external surface of the photoreactor. The system was left in dark conditions for 1 hour and then the reaction was started under UV light up to 3 h. The initial As(III) concentration was 5 mg L^{-1} while the solution volume was 100 mL. During the photocatalytic test, 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, which allows the evaluation of As(V) concentration at λ = 880 nm (Perkin Elmer UV-Vis spectrophotometer) (Vaiano et al., 2014). The concentration of the total arsenic was analyzed by preliminary oxidizing As(III) fraction through the addition of a $KMnO_4$ aqueous solution. 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., 2016). In particular the As(III) and As(V) concentrations were calculated using the following equations:

$As_{tot} = As_{oxidized} - As_{reduced}$;

$As(III) = As_{oxidized} - As_{untreated}$;

$As(V) = As_{untreated} - As_{reduced}$;

2.2 Experimental tests using the continuous flow micro-reactor

A cylindrical pyrex reactor (ID = 1.3 cm, L_{TOT} = 10 cm and V_{TOT} = 7 mL), operating in continuous mode, was used for photocatalytic tests (Figure 1). The stock solutions containing the As(III) (at 5 and 1 mg L^{-1} initial concentration) were prepared and collected in the feed tank (3 L). The feed tank was equipped with a magnetic stirrer to assure the complete homogenization of the stock solution. The arsenic solution was pumped from the feed tank to the continuous flow photo-reactor using a peristaltic pump (Watson Marlowe 120 s). The overall liquid stream is fed from the bottom of the reactor at 0.5 mL min^{-1} flow rate. Then it passes through the catalytic bed and finally comes out from the top of the reactor, being conveyed in a tank where the treated solution was collected. The liquid samples to be analyzed were taken at the outlet of the continuous flow reactor. The total amount of TiO_2 pellets used in the experimental tests accounted for 4 g. The micro-reactor was irradiated with a UV-LEDs strip (nominal power: 12 W m^{-2}; wavelength emission peak: 365 nm) positioned on the external surface of the cylindrical reactor.

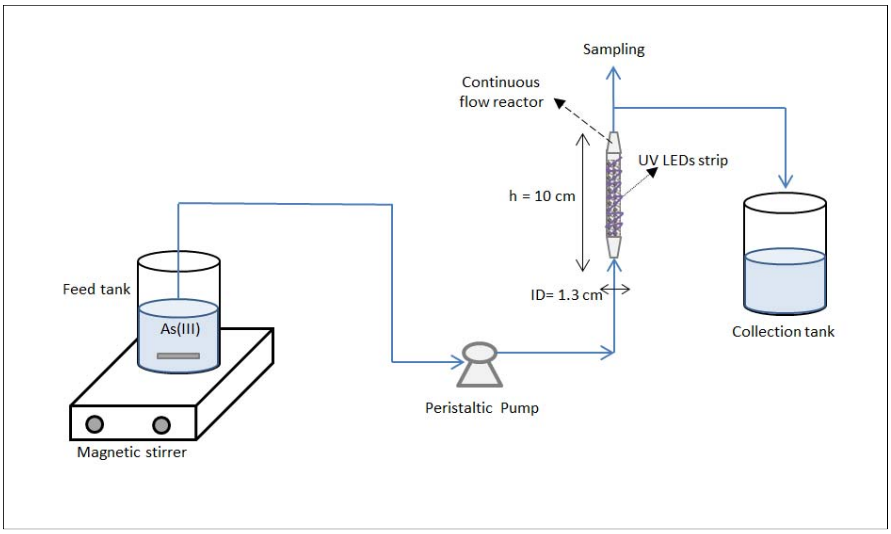

Figure 1: Experimental set-up apparatus using continuous flow reactor.

3. Results

3.1 Photocatalytic tests in batch

In order to evaluate the efficiency of TiO_2 pellets photocatalysts in batch conditions, the photocatalytic oxidation of As(III) to As(V) under UV light was evaluated. In particular, control tests were carried out in the presence of As(III) and irradiating the photoreactor with UV LEDs in the absence of the photocatalyst (photolysis reaction). Subsequently, this result was compared with the photocatalytic test. The behavior of the As(III) relative concentration (Figure 2a) and As(V) produced (Figure 2b) as a function of irradiation time is shown in Figure 2. The photolysis control test did not result in any oxidation activity. In presence of TiO_2 pellets an important decrease of the As(III) concentration was obtained. In particular, it is possible to observe that, after only 15 min of irradiation, 90% of As(III) was removed. The total As(III) removal was obtained after about 1 hour of treatment. It is important to underline that this result remains constant after 5 cycles of photocatalytic activity (Figure 2a). Figure 2b shows the formation of As(V) during the photocatalytic test. During the early minutes of irradiation, the As(V) was released in the solution. However, after 15 min, the As(V) obtained from the oxidation of the As(III) started to decrease due to the adsorption on TiO_2 pellets, thus ensuring the complete removal of the As(III) and As(V) present in solution after 120 min of treatment. Accordingly, TiO_2 pellets photocatalyst was effective in the simultaneous removal of As(III) and As(V) formed during the photocatalytic oxidation of As(III), and it was also proven to be reusable for several cycles, keeping its activity constant. In order to confirm the adsorption ability of TiO_2 pellets, experimental tests were carried out in the presence of only As(V) solution (initial concentration equal to 5 mg L^{-1}), in dark condition (Figure 3). In this case, TiO_2 pellets showed an important adsorbing property for As(V), being it removed by 87% after 60 min of treatment and 100% after 180 min, so confirming the literature results about the affinity of As(V) with the adsorbent materials (Pena et al., 2005). In addition, TiO_2 pellets were used for several cycles (without regeneration steps) and it was possible to note that, after 180 min, their activity remains constant also after four reuse cycles. These results demonstrate that the use of TiO_2 pellets allows to obtain two processes in a single step, the oxidation of As(III) in As (V) (Figure 2b) and the adsorption of As(V) to the photocatalyst, avoiding subsequent adsorption step, typically necessary for the complete removal of the As(V) from water (Iervolino et al., 2016).

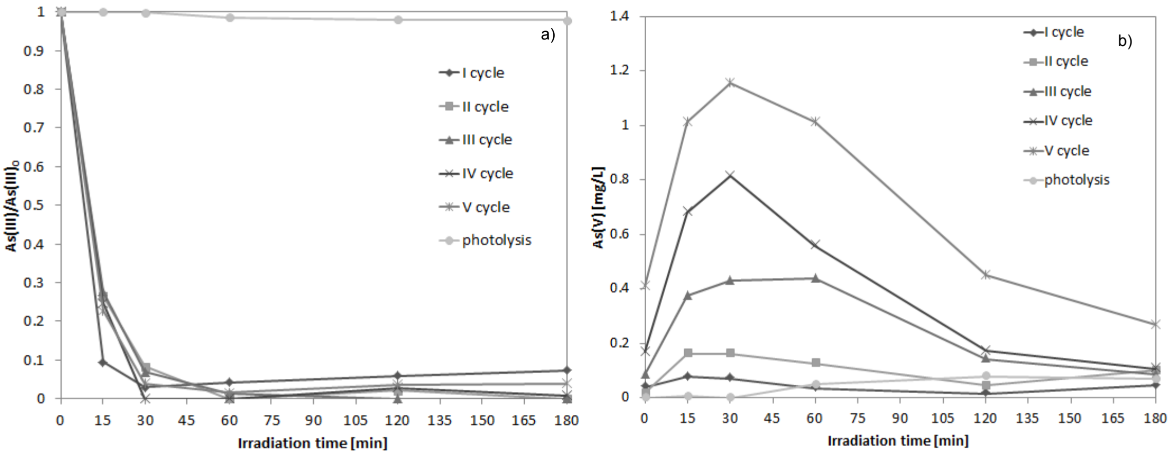

Figure 2: Behaviour of As(III) relative concentration in solution (a) and behaviour of As(V)concentration in solution (b) as a function of UV light irradiation time.

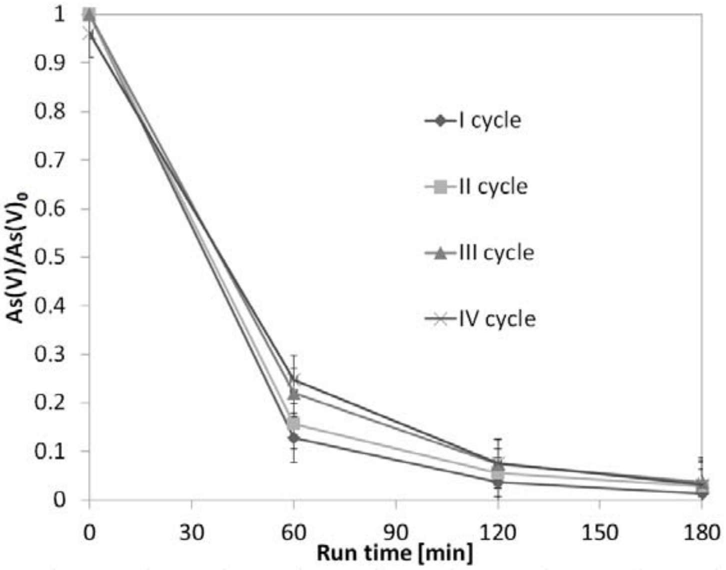

Figure 3: Behaviour of As(V) relative concentration in solution during dark adsorption experiment.

3.2 Photocatalytic tests in the continuous flow reactor

The results of photocatalytic experiments performed in the continuous flow micro-reactor are reported in Figure 4. In particular, the graph shows the oxidation of As(III) to As(V) in the presence of UV LEDs and with an initial concentration of As(III) equal to 5 mg L^{-1}. It is possible to note that during the experiment, the TiO_2 pellets maintained their activity and the As(III) oxidation was equal to 80% in the steady state condition. The formation of As(V) released in solution increased up to about 2.5 mg L^{-1}, a significantly lower amount than the expected value (4 mg L^{-1}). In order to perform a test in almost real conditions, the same photocatalytic experiment was performed at lower initial As(III) concentrations (1 mg L^{-1}) (Figure 5). In this case it was possible to note that the As(III) was totally oxidized without any release of As(V) in the solution, indicating that the obtained As(V) was adsorbed on the TiO_2 pellets surface, confirming the results obtained under batch conditions (Figures 2 and 4) where the As(V) adsorption was observed for different reuse cycles. Therefore, the developed system could be able to guarantee the complete removal of the arsenic from water matrix, especially at very low As(III) initial concentration.

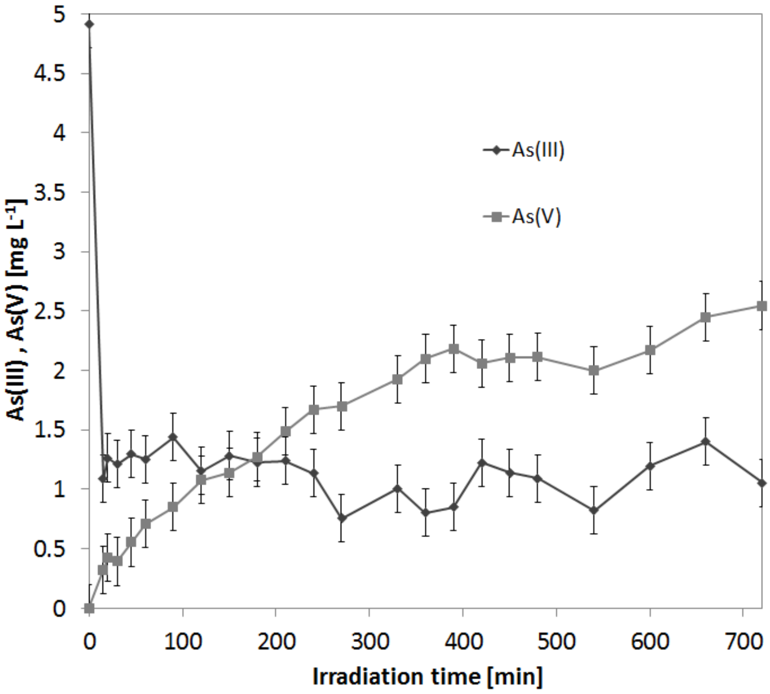

Figure 4: Behaviour of As(III) and As(V) concentration during the photocatalytic test. As(III) initial concentration: 5 mg L^{-1}.

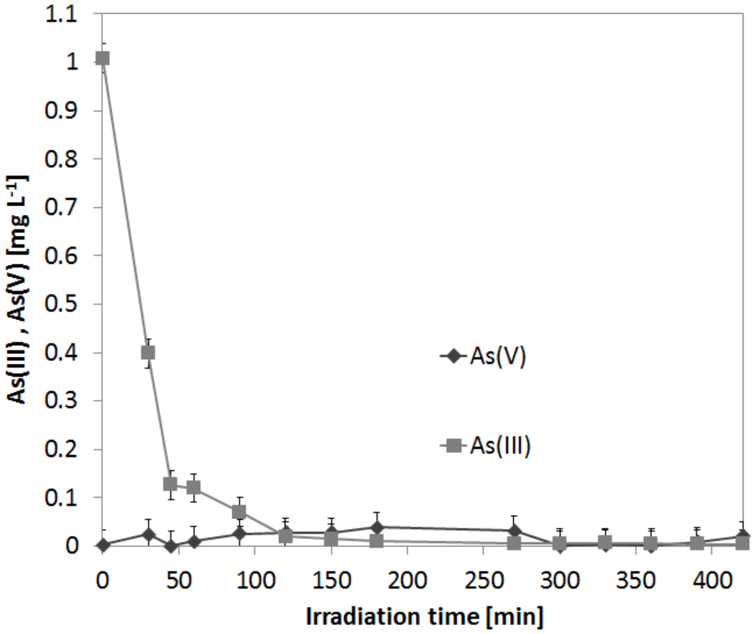

Figure 5: Behaviour of As(III) and As(V) concentration during the photocatalytic test. As(III) initial concentration: 1 mg L^{-1}.

4. Conclusions

The photocatalytic oxidation of As(III) to As(V) in mild conditions was investigated in the presence of TiO_2 pellets. The results from batch condition tests showed 90% of photocatalytic oxidation of As(III) under UV light, after only 15 min of irradiation. During the early minutes of the treatment, the As(V) was released into the solution. Subsequently, adsorption on TiO_2 pellets took place, ensuring the simultaneous and complete removal of the As(III) and As(V) from the aqueous solution. The continuous flow micro-reactor configuration confirmed the performances obtained under batch conditions, highlighting that, even in the presence of low As(III) concentrations (1 mg L^{-1}), the system was effective in the purification of arsenic contaminated water. Moreover, after several reuse cycles, TiO_2 pellets maintained an excellent photoactivity and durability making it a very promising catalyst to be employed in continuous reactors for the photocatalytic treatment of arsenic polluted water. The results showed in this work are extremely interesting and could be considered as a proof of concept for the scale up application of the photocatalytic oxidation systems to be used in the removal of arsenic form drinking water.

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