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Photo catalytic activity under visible light to transform As (III) with nitrogen-doped TiO_2 nano particles, using urea as a nitrogen source. Optimization by multivariate analysis

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ABSTRACT

Arsenic (III) is a common by product of mining activity. This contaminant can have a high environmental impact because it might accumulate in the food chain and seriously affect human health. The purpose of this study is to develop a method to remove arsenic (III) using the photo catalyst TiO_2-N activated by visible light. The catalyst TiO_2 Degussa P-25 was doped with nitrogen in order to narrow the energy gap and to work with radiation in the visible range. A multi variable approach was used in order to optimize the removal of arsenic, varying the concentration of the catalyst and the pH, maintaining the initial concentration of As (III) in 3 mg L^{-1}. Two optima were determined, in one of which As (III) was reduced by 96.7% at pH 2, and in the other As was reduced by 80% at pH 7. Furthermore, the toxicity of the As (III) solutions was determined using *Daphnia magna* before and after the photochemical treatment. Mortality in the initial concentration was 87%. After the treatment at pH 2.0, a significant reduction in toxicity was recorded, with a mortality of only 30%.

Keywords: Arsenic; *Daphnia magna*; FTIR; X-ray fluorescence spectrophotometry (XRF); Heterogeneous photo catalysis; TiO2-N; Visible light

1. Introduction

Arsenic is a chemical element that is present in the ground, which might also be found in high concentrations in places close to mining activity. It may pose complex problems for humans, especially when it reaches high concentrations in drinking water [1,2]. A usual water treatment involves systems of coagulation and precipitation [3–5], which does not solve completely the problem, as the residue must be removed through a filtering processes and this byproduct must then be stored in a safe place [6]. Semiconductors that allow oxidation and adsorption have been used for water decontamination, therefore reducing the toxicity [7,8]. For example, TiO_2 Degussa P-25, doped with various elements, has been used, which allows a reduction in the energy gap to be used within the visible radiation spectrum [9–11]. It is known that titanium dioxide (TiO_2) is a suitable material for the removal of arsenic from water, due to its properties of physical and chemical stability, resistance to corrosion, and nontoxicity [12].

However, the use of TiO_2 as a catalyst is restricted due to its high energy gap (+ 3.2 eV), requiring a high energy radiation to produce the electronic jump from valence to conduction band [13,14]. This energy represents a very small fraction of the visible spectrum (3–5%). A way to reduce the energy gap in order to make TiO_2 sensitive to visible light can be achieved by doping the semiconductor with different elements and methods. For example, doping with nitrogen and lanthanum and using sol gel method it was possible reach 97% degradation of organic matter within 9 h under simulated sunlight [15]. In another approach, benzene degradation was observed under visible light using Cl–N-codoped TiO_2 nano crystallites that were prepared through sonication of a solution of tetraisopropyl titanium

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and NH_4Cl in water and isopropyl alcohol at 70°C [16,17]. In general, the sol gel methods are the most frequently used to incorporate nitrogen in the TiO_2 network [18,19].

The aim of this work is to develop a simple and inexpensive arsenic removal method that involves adding nitrogen to TiO_2 and work with radiation in the visible range.

2. Experimental

2.1. Experimental conditions

Sodium arsenite (sigma) was prepared in a stock solution of 3 mg L^{-1}. The reaction was performed using a mercury lamp of 250W (230V-50 Hz). The solution remained with constant agitation and aeration for 60 min. The TiO_2-N was obtained through a thermal process doping TiO_2 Degussa P-25 with nitrogen from urea, characterized by Fourier-transform infrared (FTIR) spectroscopy.

In the TiO_2-N obtained, the mole ratio between N and TiO_2 Degussa P-25 was 0.5. The incorporated nitrogen reached 14%, which was determined by means of elemental analysis with a PE 2400, AUTOSAM, AD-6000.

2.2. Experimental design

In order to optimize the efficiency of the doped TiO_2 in the arsenic removal, an experimental design was used, which considered a pH range from 2 (–1) to 7 (+1) and concentrations of TiO_2-N between 0.05 (–1) and 0.1 (+1) g L^{-1}. The design considered an experimental matrix Full Fac (3 levels) with 12 reactions.

2.3. Kinetics

Once the optimized values of the experimental variables were obtained, the kinetic reactions were carried out in order to verify whether the response over time provided by the model was correct.

2.4. Determination of arsenic.

The arsenic concentrations before and after the photo catalytic treatment were determined with the Merckquant test (As Mquant TM-Merck, quick method for arsenic test) in two measurement ranges, from 0.005 to 0.5 mg L^{-1} and from 0.02 to 3.0 mg L^{-1}. The concentrations were subsequently verified with atomic emission spectroscopy method (ICP-Plasma icap 6000, limit of detection 0.02 mg) with inductive coupling plasma. A reading range was established between 189 and 280 nm, as arsenic absorbs at 193.7 nm.

2.5. Arsenic determination by x-ray fluorescence spectrometry

The X-ray fluorescence spectrometry is a method for analyzing the characteristic radiation generated by a sample when it is irradiated with X-rays. This technique allows a quick and non-destructive chemical analysis and can be applied to a large number of chemical elements simultaneously. In order to verify that arsenic disappears from the treated solution, the method EFR-X was used. A drop from a mix of a 5 µL of sample and 5 µL of gallium solution (5 mg L^{-1}) were placed on a quartz plate, dried, and read in the s2 Picofox Bruker equipment.

2.6. Daphnia magna toxicity test

In the bioassay with *Daphnia magna*, infants were exposed to different concentrations of arsenic (0.5, 1.0, 2.0, 2.5, 3.0 ppm) for a period of 24 h. A negative control with reconstituted water (water for analysis class 4) from solutions of inorganic salts, with a final pH between 7.8–8.0 and a hardness of 250 mg L^{-1} of $CaCO_3$, was used A toxic standard of potassium dichromate ($K_2Cr_2O_7$) was used as a positive control. Each essay was performed in triplicate, each with 5 infants of *Daphnia magna* in 5 mL volumes.

The bioassays were conducted at 20 ± 2°C for 24 h with no replacement of water or food. The responses were evaluated as mortality at 24 h of exposure and expressed as percentages of survival. The LC-$_{50}$ was determined with the statistical program Tostat [20].

3. Results and discussion

The TiO_2 doped with nitrogen from urea was analyzed by FTIR (Fig. 1). The pristine TiO_2 has two well-pronounced absorption bands. The band around 3350 cm^{-1} is attributed to OH stretching vibration. When nitrogen is incorporated, the intensity of absorption band decreased due to the formation of Ti-O-N bonds. The same is observed in the band around 1600 cm^{-1} [21–23].

3.1. Multivariate analysis

In order to determine the values of the experimental variables that allow the largest amount of arsenic removal, an experimental design with variable pH and semiconductor concentration was used. The model considered an experimental matrix of 12 experiments which were conducted randomly, as shown in table 1. The responses were entered into the model that provided a contour map (Fig. 2), which shows that TiO_2-N under visible light achieved two maximal responses, shown in the red zones, one with 0.06 g L^{-1} of TiO_2-N at pH 2.0 and the other with 0.1 g L^{-1} of TiO_2-N at pH 7.0.

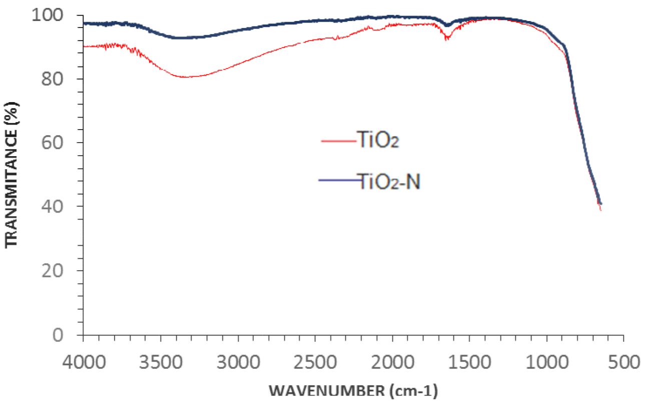

Fig. 1. FTIR spectra of pristine TiO_2 and TiO_2–N.

Table 1
Experimental matrix As (III) removal from water

Exp. name	Run order	TiO_2-N	pH	As (III) removed (%)
N1	6	0.05 (–1)	2.0(–1)	83.3
N2	1	0.075 (0)	2.0 (–1)	66.7
N3	2	0.10 (+1)	2.0(–1)	43.3
N4	5	0.05 (–1)	4.5 (0)	43.3
N5	10	0.075 (0)	4.5 (0)	66.7
N6	12	0.10 (+1)	4.5 (0)	66.7
N7	7	0.05 (–1)	7.0 (+1)	21.3
N8	9	0.075 (0)	7.0 (+1)	43.3
N9	3	0.10 (+1)	7.0 (+1)	83.3
N10	4	0.075 (0)	4.5 (0)	66.7
N11	8	0.075 (0)	4.5 (0)	66.7
N12	11	0.075 (0)	4.5 (0)	66.7

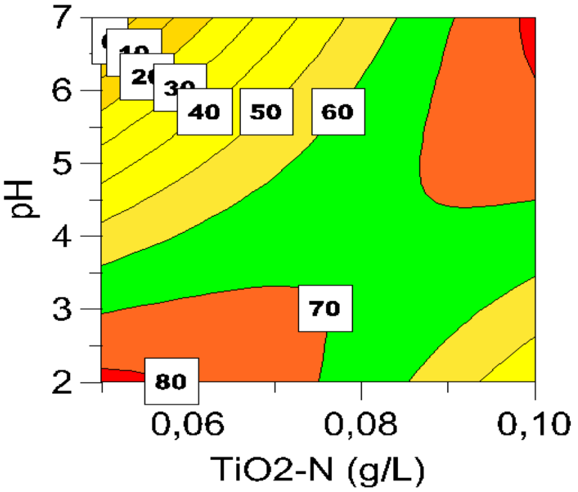

Fig. 2. Contour map of As (III) removal.

A modeling equation [Eq. (1)] was obtained with the statistical program MODDE 7.0, which shows the average percentage of As (III) removed and the influence of each variable on the removal. The equation shows that As (III) removal increases with increasing concentration of TiO_2 and decreasing pH. However, there is a maximum, which is observed in the negative values in the second order coefficients. Fig. 2 shows a high dependency of pH and semiconductor concentration.

$$Y(\%) = 65.6(\pm 1.3) + 12.8(\pm 1.5)[TiO_2] - 12.8(\pm 1.5)[pH] - 8.4(\pm 1.8)[TiO_2]^2 - 8.4(\pm 1.8)[pH]^2 + 33.36(\pm 2.0)[TiO_2][pH], p \le 0.0001 \tag{1}$$

3.2. Kinetics of the reaction.

Fig. 3 shows the Arsenic (III) reduction over time using the optimized values of the experimental variables; pH 2.0 with 0.06 g L^{-1} of TiO_2-N and pH 7.0 with 0.1 g L^{-1} of TiO_2-N. In order to compare the methods, the residual arsenic concentrations were determined with the Mquant method and ICP-plasma. Fig. 3 shows that at pH 2.0 the arsenic removal reaches 96.7% at 120 min of photo catalytic treatment and a 99.3 % removal at 150 min. At pH 7.0 the removal process is slower, with a removal of only 80% at 90 min of reaction, with no further removal. The adsorption process of arsenic on the semiconductor is faster at low pH in the first thirty minutes of treatment due to TiO_2 surface charge. After this, the adsorption process remains constant and the arsenic removal is due only to the photo catalytic process [24].

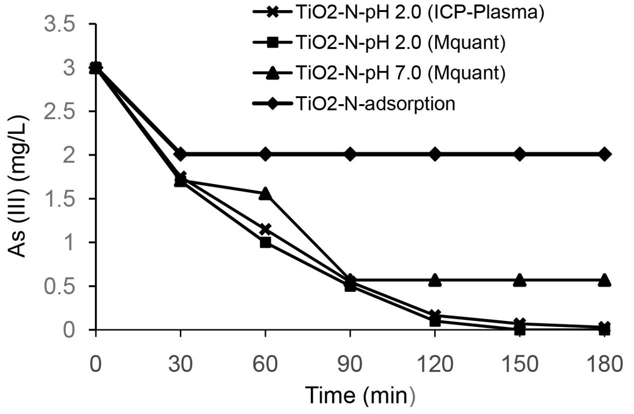

Fig. 3. Kinetics of As (III) removal with TiO_2-N under visible light.

3.3. X-ray fluorescence spectrophotometry

Fig. 4 shows the peak of arsenic from the initial solution of 3 mg L^{-1} and Fig. 5 shows the complete disappearance of the peak after the photo catalytic treatment. This suggests that at acidic pH, arsenic (III) is transformed to arsenic (IV) or (V) and these species are adsorbed on the surface of the catalyst. This was also observed by the authors of the equations 2–4 [25,26]. The process of As (III) oxidation, catalyzed by TiO_2 occurs as follows: first, the adsorption of As (III) on the surface of TiO_2, then the oxidation of As (III) to As (IV) or to As (V), and finally, if As (III) is transformed to As (V), the desorption of As (V) from the surface of TiO_2 may occur. However, under acidic pH, desorption does not occur. Indeed, As (V) is strongly retained in the semiconductor surface; the same happens with As (IV) [27,28,29]. The equilibrium constants [Eqs. (2)–(4)] suggest that As (IV) would be retained in the structure of the semiconductor, which would explain the disappearance of arsenic signs in x-ray fluorescence spectrophotometry.

$$As(III) + h_{VB}^{+} \rightarrow As(IV) - adsorbed\left(k = 9\times 10^{9} M^{-1}s^{-1}\right) \tag{2}$$

$$As(III) + O_2^{\bullet -} + H^{+} \rightarrow As(IV) + HO_2^{-}\left(k = 3.6\times 10^{9} M^{-1}s^{-1}\right) \tag{3}$$

$$As(IV) + O_2 \rightarrow As(V) + O_2^{\bullet -}\left(k = 1.1\times 10^{9} M^{-1}s^{-1}\right) \tag{4}$$

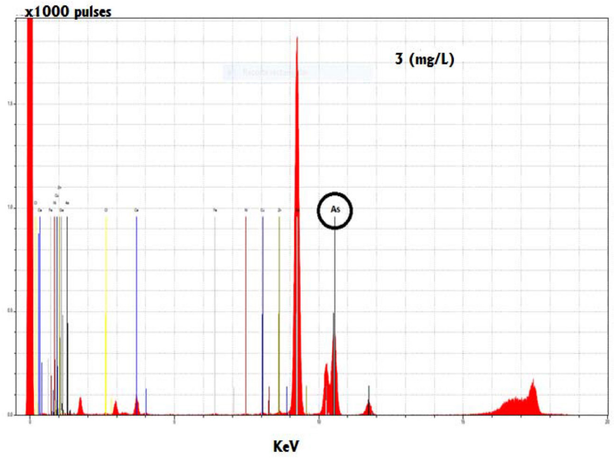

Fig. 4. Initial concentration of arsenic determined by x-ray fluorescence spectrometry.

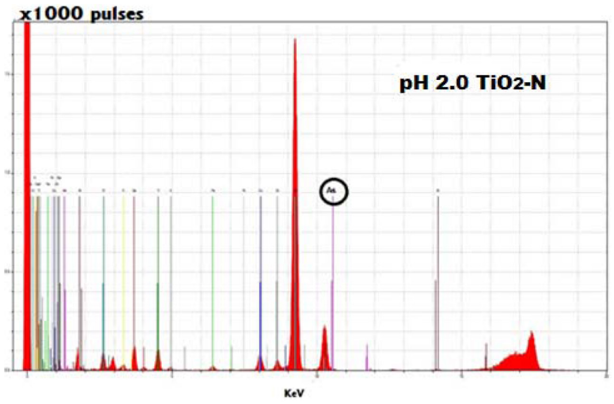

Fig. 5. Arsenic concentrations determined by x-ray fluorescence spectrometry after photo catalytic treatment.

3.4. *Daphnia magna bioassay*

To determine the effectiveness of arsenic removal by the photo catalytic treatment, toxicity tests with neonates of *Daphnia magna* were performed, to look for any reduction in toxicity. As expected, Fig. 5 shows that mortality of *Daphnia magna* increases with arsenic concentration. This is also consistent with the results reported by other authors, who found that the growth and reproduction of *Daphnia magna* are adversely affected when they are placed in arsenic concentrations between 0.633 and 1.32 (mg L^{-1}) [30–32]. Fig. 6 shows the mortality of *Daphnia magna* before and after the photo catalytic treatment. The mortality rate reached 89% at the initial arsenic concentration of 3 mg L^{-1}. In the positive control, with potassium dichromate, mortality was 48%. With the treated samples, the mortality rate was reduced to 30% in TiO_2-N at pH 2.0 and to 50% at pH 7.0. This is consistent with the effect of the larger arsenic removal at pH 2.0.

4. Conclusions

It was demonstrated that the TiO_2 doped with nitrogen from urea is efficient in the removal As (III) using visible spectrum radiation, and that As (III) removal increased with increasing semiconductor concentration and with decreasing pH. From the polynomial equation of the experimental design it was also shown that TiO_2-N and pH have a direct effect on the efficiency of the arsenic removal and that both have a maximum value according to the quadratic coefficients of the polynomial. The As (III) removal mechanism would be due to the adsorption in the hole of the valence band and reduction to As (V), which is strongly adsorbed on the surface of semiconductor at a low pH. This makes the system more efficient at a more acidic pH, which is also reflected in the significant reduction of toxicity after the treatment.

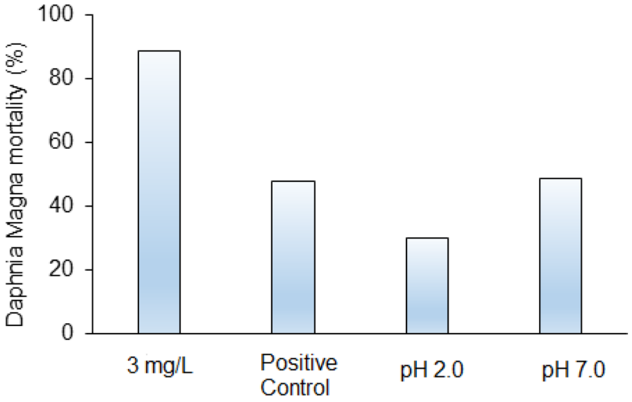

Fig. 6. *Daphnia magna* mortality before and after the photo catalytic treatment.

Besides, the experimental design is an effective tool that allows to obtain optimal responses of treatment systems in a short period of time. With this tool, optimal values for the experimental variables were determined which allowed to achieve a greater removal of As (III).

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