

# Arsenic Removal Technology From Water Based on Nanomaterials and Sunlight

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## Abstract

A new technology for arsenic (As) removal have been addressed by mean of the design and construction of a treatment prototype equipment. *This prototype is mainly composed of a solar collector as a photo-reactor and the use of a bi-functional material based on a specific semiconductor (TiO<sub>2</sub>) and an activated carbon (AC).* Preliminary results about the influence of the radiation wavelength (UV and/or Visible) and the radiation flux (W/m<sup>2</sup>) on the photo-oxidation of As (III) was obtained in a laboratory scale. For this, it was considered a small-scale photo-reactor with different configurations of UV-Vis lamps, 200ml of As (III) solution and a selected load of material suspended in the contaminant solution. It was observed that the incorporation of visible lamps increases the radiation flux in about 40W/m<sup>2</sup>, however, the photo-oxidation time increases up 90 minutes, demonstrating that the photo-efficiency of the system is more influenced by the wavelength of the light instead of the radiation power. Then, the prototype was built as a photo-reactor type coupled to a composite parabolic collector (CPC), and a simulated solar illumination system. The efficiency to remove As was evaluated for a synthetic solution of As (III) (1000 and 5000 ppb, pH 4). In presence of TiO<sub>2</sub>-AC a higher adsorption capacity of As (V) and lower time for disappearance of As (III) were observed, with respect to using TiO<sub>2</sub> alone, demonstrating a synergistic effect between both solids. In summary, it was determined that the system TiO<sub>2</sub>-AC presented a high removal efficiency (> 90%), which involves the photo-oxidation of As (III) between 30-60 min and the progressive adsorption of As (V), reaching irrigation water quality standards.

*Keywords: Arsenic, Nanomaterials, Composite Parabolic Cylinder, Photocatalysis*

## 1. Introduction

Water contaminated by arsenic (As) represents a serious environmental and public health issue, considering the toxicity of this element, affecting more than 150 million people in the world (USA, India, China, Chile, Bangladesh, Taiwan, Argentina, Mexico) [1]. For removing the As, there are technologies such as oxidation, coagulation/precipitation, sedimentation, filtration, adsorption, ion exchange, reverse osmosis, biological treatments, which have advantages and disadvantages according to the species of As to deal with (usually As (III) and As (V)). Advanced oxidation methods such as heterogeneous photocatalysis, have been proposed due to their low cost and the possibility of using solar radiation as an energy source. Such methods commonly consider using solar collectors as photo-reactors aiming to capture and focus sunlight through compound parabolic collectors (CPC) [2]. Heterogeneous photocatalytic processes require using photoactive semiconductors, being the titanium dioxide (TiO<sub>2</sub>) the most used due to its high photoactivity under UV radiation, chemical stability, and low toxicity. However, its efficiency for removing As is rather low, since it presents a low adsorption capacity of As (III) and radiation absorptivity in the range of the UV spectrum. Some researchers have proposed at a laboratory scale measures to improve the performance of TiO<sub>2</sub> reactors, such as the production of material in the nanometric range, by doping it with metals and non-metals, or by combining it with co-adsorbent materials in the form of nanocomposites [3-4]. In spite of the aforementioned approaches, to date, there is not available in the market a standardized technology for arsenic removal, based on TiO<sub>2</sub> combined to an adsorbent material, such as activated carbon and sunlight, which attends the levels recommended by international standards (WHO, <10 µg / L or ppb).

This opportunity has been addressed by developing new technology, based on the design of a bi-functional material (photo-oxidant-adsorbent) based on nano TiO<sub>2</sub> and activated carbon with specific morphological properties, surface chemistry and mass ratio, placed in suspension and recirculation within the photo-reactor system. That by functional material is tested by designing and constructing a prototype equipment for the arsenic removal, which uses the photo-reactor as a solar collector. This compact technology (TiO<sub>2</sub>-Activated Carbon and the solar photocatalytic system) represents a technological alternative to the complex and expensive treatment systems for arsenic removal that are currently in operation. In addition to that, this approach could constitute a potential solution for remote locations presenting this type of pollutant (e.g. Northern Chile), and potentially extrapolated to an industrial scale and meet the higher water demands.

The present work describes the results of the prototype efficiency using simulated solar light for arsenic removal (III and V) in high concentrations.

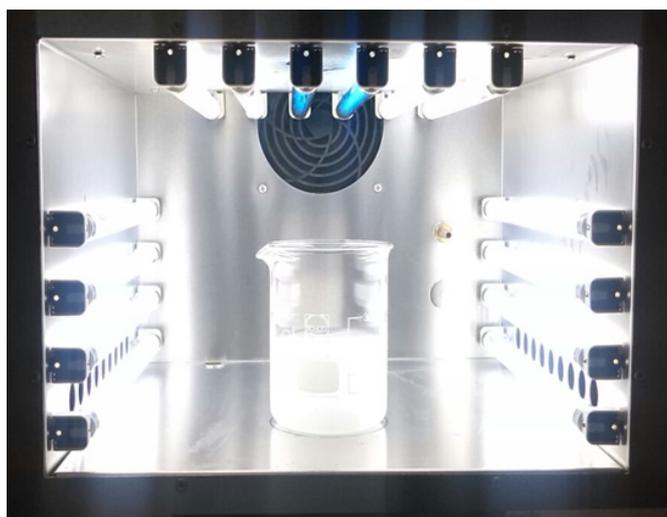
## 2. Methodology

### 2.1. Synthesis of materials.

A semiconductor TiO<sub>2</sub> was synthesized by Sol-gel methodology and later characterized as suggested in [5]. Subsequently, an adsorbent activated carbon was synthesized by physical activation from agro-industrial waste and chemically modified with iron (AC) based on previous experiences [5].

### 2.2 Laboratory photocatalytic set-up

Studies in laboratory scale by using laboratory photo-reactor (solar simulator, Figure 1) and 200 ml of As (III) solution (5000 ppb, pH 4) were developed. The pH condition was selected as a model case similar to national river Azufre and acid springs from other places of the world [6,7]. The optimal material mix (TiO<sub>2</sub>: AC) and the best material load were previously selected [5].



**Figure 1.** Photoreactor on a laboratory scale

Preliminary studies about the influence of the proportion of UV-Visible light on photo-oxidation rate was evaluated. For this, changes in the photo-reactor lamps to vary the proportion of UV-Visible light and the radiation flux were carried out on photo-oxidation experiments (Table 1) allowing to assess the photo-oxidation times for

each case. Radiation was measured with an SP-Lite pyranometer.

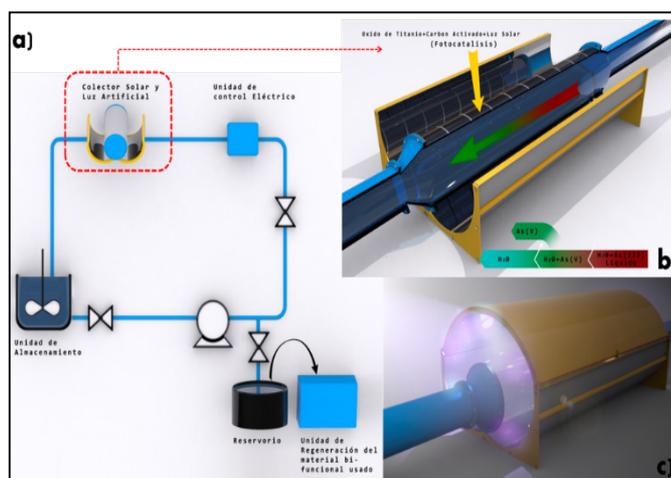
**Table 1. Configuration conditions of the laboratory photoreactor: Type of light and radiation power for each studied case.**

Lamp configuration (number of lamps employed)	% Visible light/ % UV light	Radiation Power (W/m <sup>2</sup> )
12 Vis – 2 UV C	86/ 14	45
12 Vis – 2 UV A	86/ 14	42
12 Vis	100/ 0	46
2 UV C	0/ 100	2
2 UV A	0/ 100	1

In general, arsenic removal test (photo-oxidation-adsorption) consisted of two stages: the first stage of adsorption in the dark in which the suspended materials were placed in the agitation tank. Once the adsorption equilibrium was reached by the material, the lamps of the photo-reactor started. Kinetics of adsorption and photo-oxidation were analyzed by assessing the aliquots for different times and their concentration of arsenic species (As III and As V) by applying the colorimetric method [5].

### 2.3 Prototype photocatalytic test.

Once the conditions of the bi-functional material were selected, prototype scale tests were carried out. Figure 2 shows the components of the prototype which consists of 1) a dark cylinder with mechanical agitation (20 L), 2) a photo-reactor type composite parabolic cylinder (CPC), consisting of a truncated parabola of material reflector, a borosilicate tube and a simulated solar light illumination system (lamps with a percentage of visible light versus UV of approximately 90% and 10%, respectively), 3) a peristaltic pump, 4) a double-jacket cooling system, 5) a reservoir. The efficiency for arsenic removal on the prototype was evaluated by using 7L of synthetic solution with 1000 and 5000 ppb of As (III) as initial concentrations and pH 4. The stages of arsenic removal test on the prototype were the same to laboratory-scale described above.



**Figure 2.** Schematic view of the prototype system for arsenic removal.

## 3. Results

### 3.1 Influence of type of light and radiation power on the photo-oxidation of As (III).

The influence of the proportion of UV-Visible light on the photo-oxidation rate of arsenic was studied. To do so, several tests were carried out on the photo-reactor, considering different proportions of UV-Visible lamps, measuring the radiation power for each case. First of all, the number of lamps was configured in order to simulate a portion of the solar spectrum, considering 86% of visible lamps and 14% of UV lamps. In addition to that, 100%Vis and 100% UV-A and UV-C were also considered for comparing the results.

Figure 3 shows the radiation power ( $\text{W/m}^2$ ) for each lamps' configuration. It is observed that this remains constant over time. Moreover, the incorporation of visible lamps in the system increases significantly the radiation over  $40\text{W/m}^2$  with respect to UV light, which has an insignificant intensity of the radiation (about  $2\text{W/m}^2$ ).

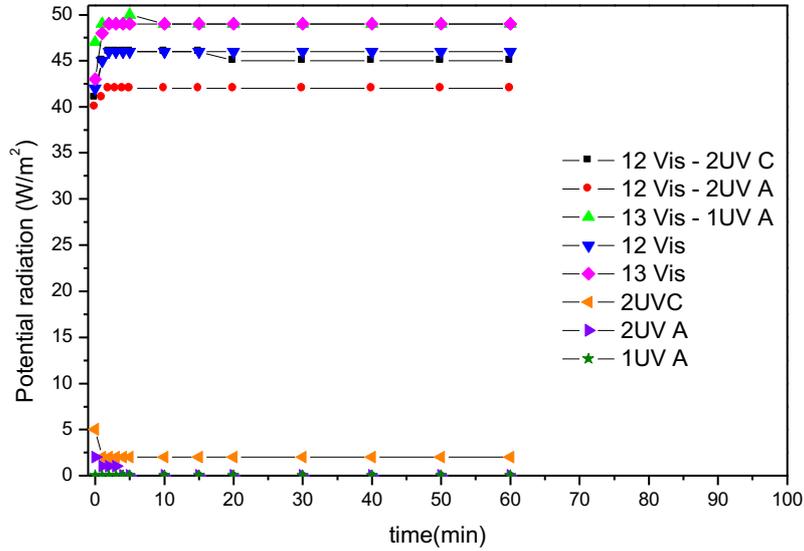


Figure 3. Intensity of radiation power for each type of light configuration.

Thus, the influence of the wavelength of the light and the radiation power of the photoreactor on the photo-oxidation of As (III) in the presence of  $\text{TiO}_2$  was evaluated. In a first instance, the behavior of the  $\text{TiO}_2$  for removing the arsenic under laboratory conditions for a specific configuration lamp (86% + 14%) is shown in Figure 4. It can be noticed that the system achieves the photo-oxidation of As (III) to As (V) and partial adsorption capacity of As (V) at the same time. This tendency was observed for all studied configuration lamps.

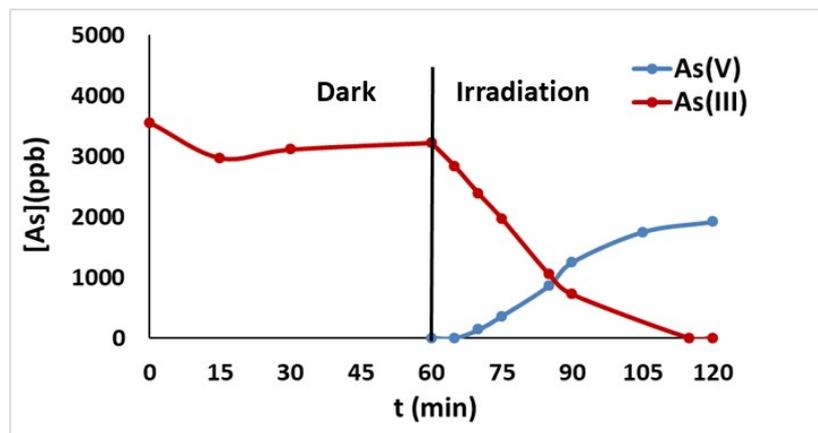


Figure 4. Kinetics of arsenic removal in presence of  $\text{TiO}_2$  under simulated solar light of laboratory photoreactor

Table 2 shows the radiation flux for the different lamps combinations as well as the efficiency of As (III) photo-oxidation, and the maximum time of photo-oxidation for each case. It is possible to notice that the maximum arsenic photo-oxidation was reached under all the lamp configurations, disappearing nearby 100% of the contaminant. However, significant differences in maximum disappearance times of As III were observed between these configurations. For example, in the case of 100% UV-C lamps, the minimum radiation was observed with

only 2 W/m<sup>2</sup>, however, the photo-oxidation time was faster about 20 minutes. On the other hand, it is observed that the incorporation of visible lamps increases the radiation power about 40W/m<sup>2</sup>, yet, the photo-oxidation time increases up to 90 minutes. TiO<sub>2</sub> is a photoactive material in UV range [8-11], thus, these results demonstrated that the biggest influence on the photo-efficiency of the system is the wavelength of the light applied, rather than of the intensity of radiation.

Table 2. Arsenic removal efficiency tests on photoreactor with TiO<sub>2</sub> material under different light configuration.

Light configuration	86% Vis/14% UV-A	100% UV-A	86% Vis/14% UV-C	100% UV-C	100% Vis.
Radiation Power (W/m <sup>2</sup> )	42.0	1.0	45.0	2.0	46.0
Photo-oxidation efficiency (%)	98.2	99.4	99.4	99.3	99.3
Photo-oxidation time (min)	60.0	45.0	60.0	20.0	90.0

3.2 Photo-oxidation of As (III) in presence of TiO<sub>2</sub> and TiO<sub>2</sub>-AC under solar simulator.

The arsenic removal capacity under a laboratory photoreactor with the aforementioned proportion of UV-Visible light, and in the presence of TiO<sub>2</sub> coupled to AC was studied. In the figure can be noticed that the system TiO<sub>2</sub>-AC achieves the photo-oxidation of As (III) (a more toxic and harder to adsorb species) to As (V) (less toxic and easier to adsorb species) and its progressive adsorption in a single reaction system (Figure 5).

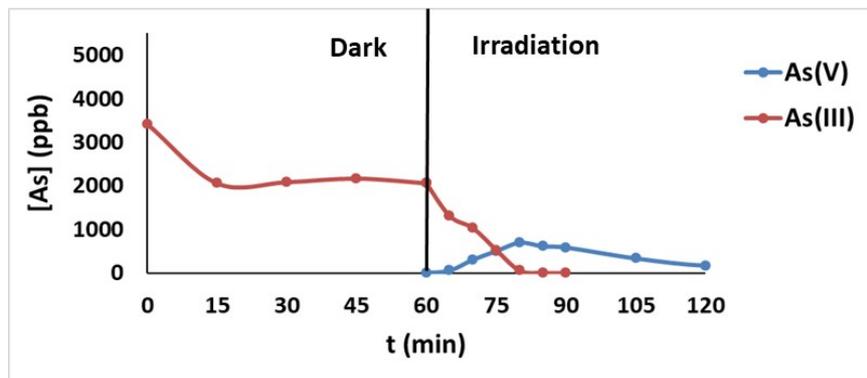


Figure 5. Kinetics of arsenic removal in presence of TiO<sub>2</sub>-AC under simulated solar light of laboratory photoreactor

In presence of TiO<sub>2</sub>-AC a higher adsorption capacity of As (V) and lower time for disappearing the As (III) were observed with respect to the use of TiO<sub>2</sub> alone, as is shown in table 3. That result demonstrates the synergistic effect between TiO<sub>2</sub> and AC for removal arsenic which is in concordance other reports using a similar system of TiO<sub>2</sub>-AC to photodegrade organic compounds [8-11].

Table 3. Arsenic removal efficiency tests on laboratory photoreactor with simulated sunlight and in the presence of TiO<sub>2</sub> and TiO<sub>2</sub>-AC (Co: 5000ppb, Volume 200 mL)

Material	TiO <sub>2</sub>	TiO <sub>2</sub> -AC
Adsorption of As (V) (%)	59	95
Photo-oxidation time (min)	60	25

The photo-oxidation of As (III) in the presence of TiO<sub>2</sub> and TiO<sub>2</sub>-AC under prototype system was also developed. The arsenic removal efficiency was evaluated for arsenic solution with 1000 ppb and 5000 ppb of As (III) and the results are shown in tables 4 and 5, respectively. It was determined that for solutions with an initial concentration of As (III) of about 1000 ppb, the system presented higher removal efficiencies (> 90%, see table 1), reaching water quality standards appropriate for irrigation purposes (NCh 1333, < 100 ppb). This threshold was achieved in one-step, which involves the photo-oxidation of As (III) in 45 mins and the progressive adsorption of As (V). On the other hand, for solutions with higher concentrations (5000 ppb) of As (III), it is necessary to carry out a two-step process. The first step considering the photo-oxidation of As (III) and the

progressive adsorption of a part of the As (V) and the second step for the adsorption of the remaining As (V). This operation mode allows achieving a removal efficiency larger than 90%, reaching drinking water quality standards (WHO).

**Table 4. Arsenic removal efficiency tests on prototype (Co: 1000ppb, pH 4, Volume 7 L).**

Photo-oxidation time (min)	Adsorption (%) As total	[As] (ppb) final
45	91	92

**Table 5. Arsenic removal efficiency tests on prototype for different pH (Co: 5000ppb, Volume 7 L).**

Photo-oxidation time first-step (min)	Adsorption (%) second-step As total	[As] (ppb) final
30	96	8

## 4. Conclusions

A new technology for arsenic (As) removal have been developed, which is mainly composed of a solar collector as a photo-reactor and the use of a bi-functional material based on a specific semiconductor (TiO<sub>2</sub>) and an activated carbon (AC). For this system, the photo-efficiency was more influenced by the wavelength of the irradiated light instead of the radiation power. On the other hand, a synergistic effect between TiO<sub>2</sub> and AC on the photo-oxidation of As (III) and adsorption of As (V) was observed. Thus, the treatment system presented a high removal efficiency (> 90%), which involves the photo-oxidation of As (III) in a short time of irradiation and the progressive adsorption of As (V), reaching irrigation water quality standards in one-step.

## Acknowledgments

The authors gratefully acknowledge the financial support provided by the Fund for the Promotion of Scientific and Technological Development (FONDEF) of the Government of Chile (Project No. ID15I10086) and the AMTC for basal project.

## 5. References

1. Singh, R., Singh, S., Parihar, P., Pratap Singh, V., Prasad, M., 2015. Arsenic contamination, consequences and remediation techniques: A review. *Ecotoxicology and Environmental Safety*. 112, 247-270.
2. Ibhaddon, A., Fitzpatrick, P., 2013. Heterogeneous Photocatalysis: Recent Advances and Applications. *Catalysts* 3, 189-218.
3. Matos, J., Quintana, K., García, A., 2012. Influence of H-Type and L-Type Activated Carbon in the Photodegradation of Methylene Blue and Phenol under UV and Visible Light Irradiated TiO<sub>2</sub>. *Modern Research in Catalysis*, 1, 1-9.
4. Rosales, M., Zoltan, T., Yaradola, C., Gracia, F., García, A., 2019. The influence of the morphology of 1D TiO<sub>2</sub> nanostructures on photogeneration of reactive oxygen species and enhanced photocatalytic activity. *Journal of Molecular Liquids* 281:59-69.
5. García, A., Rodríguez, B., Quintero, Y., 2018. Patent Application INAPI No. 19872018, Material, method and system for removal of arsenic in waters.
6. Leiva, E., Rámila, C., Vargas, I., Escauriaza, C., Bonilla, C., Pizarro, G., Regan, J., Pasten, P. 2014. Natural attenuation process via microbial oxidation of arsenic in a high Andean watershed. *Science of The Total Environment* 467:490-502.
7. Lenoble, V., Omanović, D., Garnier, C., Mounier, S., Đonlagić, N., Le Poupon, C., Pižeta, I. 2015. Distribution and chemical speciation of arsenic and heavy metals in highly contaminated waters used for health care purposes (Srebrenica, Bosnia and Herzegovina). *Science of the Total Environment* 443:420–428.
8. Matos J, Quintana K, García A, 2012, Influence of Activated Carbon in the Photodegradation of Methylene Blue. *Eurasian Chemico-Technological Journal*. 14: 1, 1-4.

9. Matos J, Quintana K, García A, 2012, Influence of H-Type and L-Type Activated Carbon in the Photodegradation of Methylene Blue and Phenol under UV and Visible Light Irradiated TiO<sub>2</sub>. *J Modern Research in Catalysis*. 1, 1-9.
10. Hybrid photoactive materials from municipal sewage sludge for the photocatalytic degradation of methylene blue. Juan Matos, Maibelin Rosales, Andreina Garcia, Cesar Nieto, Jose Rangel. *Green Chemistry*. 2011, 13, 3431-3439.
11. Matos J, Garcia A, Zhao L, Titirici MM. 2010. Solvothermal carbon-doped TiO<sub>2</sub> photocatalyst for the enhanced methylene blue degradation under visible light. *Applied Catalysis A, General*. 390: 175-182.