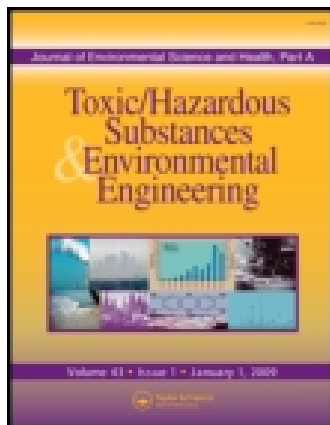


This article was downloaded by: [Cristina Zalazar]

On: 02 March 2015, At: 17:54

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lesa20>

Arsenic sorption onto titanium dioxide, granular ferric hydroxide and activated alumina: Batch and dynamic studies

Maia R. Lescano^a, Claudio Passalía^{bc}, Cristina S. Zalazar^{ab} & Rodolfo J. Brandi^{ab}

^a INTEC (UNL-CONICET), Santa Fe, Argentina

^b FICH (UNL), Environmental Department, University City, Santa Fe, Argentina

^c CONICET, Faculty of Engineering and Hydric Sciences, Santa Fe, Argentina

Published online: 27 Feb 2015.



[Click for updates](#)

To cite this article: Maia R. Lescano, Claudio Passalía, Cristina S. Zalazar & Rodolfo J. Brandi (2015) Arsenic sorption onto titanium dioxide, granular ferric hydroxide and activated alumina: Batch and dynamic studies, *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering*, 50:4, 424-431, DOI: [10.1080/10934529.2015.987552](https://doi.org/10.1080/10934529.2015.987552)

To link to this article: <http://dx.doi.org/10.1080/10934529.2015.987552>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Arsenic sorption onto titanium dioxide, granular ferric hydroxide and activated alumina: Batch and dynamic studies

MAIA R. LESCANO¹, CLAUDIO PASSALÍA^{2,3}, CRISTINA S. ZALAZAR^{1,2} and RODOLFO J. BRANDI^{1,2}

¹INTEC (UNL-CONICET), Santa Fe, Argentina

²FICH (UNL), Environmental Department, University City, Santa Fe, Argentina

³CONICET, Faculty of Engineering and Hydric Sciences, Santa Fe, Argentina

The aim of this work was to evaluate and compare the efficiencies of three different adsorbents for arsenic (As) removal from water: titanium dioxide (TiO₂), granular ferric hydroxide (GFH) and activated alumina (AA). Equilibrium experiments for dissolved arsenite and arsenate were carried out through batch tests. Freundlich and Langmuir isotherm models were adopted and their parameters were estimated by non-linear regressions. In addition, dynamic experiments were performed in mini fixed bed columns and breakthrough curves were obtained for each combination of sorbate/adsorbent. Experimental results obtained by column assays were compared with predictions of well-known breakthrough models (Bohart–Adams and Clark). Results indicate that As(V) is more easily adsorbed than As(III) for AA and GFH, while TiO₂ has a similar behavior for both species. The titanium-based material is the most efficient adsorbent to carry out the process, followed by the GFH.

Keywords: Adsorption columns, adsorption isotherms, arsenic removal, breakthrough curves.

Introduction

The occurrence of dissolved arsenic in groundwater is a major issue in many countries throughout the world.^[1–4] Long-term human exposure to arsenic is associated to a variety of health diseases.^[5,6] Accordingly, the World Health Organization^[7] has established a guideline for arsenic in drinking water of 0.01 mg L⁻¹.

The main aqueous species of arsenic in groundwater are the inorganic forms arsenite (As(III)) and arsenate (As(V)) and their relative abundance is essentially dependent upon pH and redox conditions. Arsenite is the dominant form in typical anaerobic groundwater and is more toxic than the oxidized species.

There are a large number of water treatment technologies for arsenic removal that have been developed and discussed in the literature. Among them, adsorption is the most employed technology because of its relative low cost, simple implementation and operation keeping high removal efficiencies.^[8–10] The selection of an appropriate adsorbent for arsenic removal and its efficiency depends on the existing range of concentrations, the presence of

other dissolved species and pH adjustment. There are publications that deal with arsenic species adsorption onto titanium dioxide based materials, some of which present high removal efficiencies.^[11–13] On the other hand, iron and aluminium oxides and hydroxides have also been assayed, being suitable for arsenic removal from water.^[14,15] Activated alumina, for instance, seems to be efficient only at pH values lower than the ones encountered in natural groundwater. The group of iron compounds (oxides and hydroxides, including amorphous hydrated ferric oxide (FeOOH) and goethite) shows high removal efficiency and keeps a relative low cost when they were compared with other adsorbents.

Arsenite (As(III)) exists in groundwater mainly as the non-charged form of H₃AsO₃, while the dominant forms of arsenate (As(V)) are H₂AsO₄⁻ and HAsO₄²⁻. The negatively charged species of As(V) have higher affinity than non-charged As(III) species to the surface of different adsorbents.^[16,17] Due to this fact, an oxidation step prior to the adsorption process arises as an enhancement factor of the overall arsenic removal efficiency. The oxidation process of arsenic in water containing high levels of As(III) was addressed in some publications.^[18–20]

In the present work, three commercially available adsorbents were completely tested in laboratory experiments to assess their efficiency for As(III) and As(V) removal from water. Titanium, aluminium and iron based materials were employed to determine their adsorptive

Address correspondence to Maia R. Lescano, INTEC (UNL-CONICET), Güemes 3450, Santa Fe 3000, Argentina; E-mail: mlescano@intec.unl.edu.ar

Received August 13, 2014.

properties in stirred beakers (batch) and mini fixed bed columns experiments. Through the batch tests assays, equilibrium adsorption isotherms could be determined. In addition, employing mini fixed bed columns operated in continuous, breakthrough curves could be represented for each material providing key parameters concerning to the design and scaling up of the process.

Material and methods

Chemicals and materials

Throughout the whole set of experiments (batch and column tests), 1000 mg L⁻¹ stock solutions of As(III) and As(V) were prepared in ultrapure water (< 0.06 μS cm⁻¹) from sodium (meta) arsenite (AsNaO₂, ≥ 99%, Sigma-Aldrich, USA) and sodium arsenate dibasic heptahydrate (Na₂HAsO₄·7H₂O, 99 – 102%, Sigma-Aldrich, ACS reagent) respectively. The desired arsenic concentration for each run was obtained by fresh dilution of the stock solution on a daily basis.

Three commercial adsorbents were tested: granular titanium dioxide (TiO₂, Adsorbis As500, Dow Chemical Company, USA), granular ferric hydroxide (GFH, Pro H₂O, USA) and activated alumina (AA, AxSorb A, Axens, France). The main characteristics and physical properties of the three materials are summarized in Table 1.

Experimental set-ups and procedures

Batch experiments. Adsorption equilibrium tests were carried out in a batch system at room temperature using a Jar-Test (Velp Scientifica, Italy) with four beakers (1000 mL). Solutions with different arsenic concentration ranging from 100 to 5000 μg L⁻¹ were prepared by dilution of the stock solutions and 100 mg of adsorbent material were added to each beaker. The pH of the solutions was adjusted to 7 with dilute sodium hydroxide solution and it was measured during the experiments. The mixing speed was set at 200 rpm. The suspensions were stirred for 48–72 h until the arsenic concentration reached a constant value, the equilibrium concentration.

Fixed-bed column experiments. Arsenic dynamic adsorption was tested in laboratory scale fixed bed columns for the three materials. Pyrex glass columns (0.87 cm inner diameter) were loaded with the adsorbents. Quartz wool stoppers were placed at the bottom and top of the adsorbent bed (8.5 cm height) to keep the uniformity and packing of the column. A volumetric flow (10 mL min⁻¹) of arsenic solution (200 μg L⁻¹) was circulated using a peristaltic pump (Cole Parmer, USA). The pH of the solution was adjusted to 7 with dilute sodium hydroxide and it was measured during the experiments at the outlet of the columns. Samples were taken at even time intervals at the outlet of the column until the breakthrough point was reached, i.e., when the arsenic concentration began to rise. The occurrence of the breakthrough point was considered when the relative concentration C/C_0 reached the value of 0.05. In this case, such concentration (0.01 mg L⁻¹) represents the upper limit established by the World Health Organization^[7] as a guideline for drinking water.

Analytical methods

Arsenic concentrations were determined by atomic absorption spectrometry preceded by sample filtration with 0.45 μm Nylon filters (Microclar, Argentina), employing a Perkin Elmer Analyst 800 atomic absorption spectrometer (ASS) equipped with a Perkin Elmer Model TGHA graphite furnace.

Each analysis was repeated three times in order to obtain the average value and its relative standard deviation (%RSD). The RSD value of replicated samples of each analysis was below 2.5%. The ASS calibration for arsenic was carried out in the 2–200 μg L⁻¹ range using standard arsenic solutions. The analytical procedure for arsenic determination was conducted according to EPA Method 200.9.^[21] pH was controlled by HI 98127 Hanna pHmeter (accuracy: ± 0.1)

Results and discussion

Adsorption isotherms

Adsorption isotherms are functional forms that describe the solute concentration in equilibrium with a certain

Table 1. Characteristics and physical properties of the adsorbents.

	Adsorbent		
	Granular Titanium Dioxide	Granular Iron Hydroxide	Activated Alumina
Active substance	TiO ₂	Fe(OH) ₃ – β-FeOOH	Al ₂ O ₃
Particle size (mm)	0.25–1.19	0.32 – 2.0	0.42 – 1.0
Bulk density (g mL ⁻¹)	0.48	1.07	0.86
Specific area (m ² g ⁻¹)	200	280	320

amount of adsorbent material in an aqueous suspension. By the use of an isotherm, it is possible to evaluate if the adsorption process is favourable or not to remove a specific solute and provide an estimated value of the maximum adsorption capacity. The two equations more widely used to describe the relation between the adsorbed and bulk concentrations of a substance are the Langmuir and Freundlich isotherms.

The Langmuir isotherm can be expressed as:

$$q_{eq} = q_m \frac{bC_{eq}}{1 + bC_{eq}} \quad (1)$$

and can be linearized as follows:

$$\frac{1}{q_{eq}} = \frac{1}{q_m b C_{eq}} + \frac{1}{q_m} \quad (2)$$

where q_{eq} is the solid phase sorbate concentration in the adsorbent (g g^{-1}), C_{eq} is the sorbate equilibrium concentration in the bulk solution (g L^{-1}), b is the Langmuir adsorption constant (L g^{-1}) and q_m is the maximum sorption capacity per unit mass of adsorbent (g g^{-1}).

On the other hand, the Freundlich isotherm is an empirical formulation that can be expressed as:

$$q_{eq} = K C_{eq}^{1/n} \quad (3)$$

or in its linearized form:

$$\ln q_{eq} = \ln K + \frac{1}{n} \ln C_{eq} \quad (4)$$

where K is a constant representing the adsorption capacity and n is related to the intensity of adsorption. Larger K values denote a larger capacity, while a low n value is related with stronger adsorption of the solute.

The parameters of Langmuir and Freundlich isotherms were obtained through non-linear estimations. The values

of the two model coefficients are summarized in Table 2 for the three adsorbent tested and the two target species.

From the results shown in Table 2, it can be seen that the adsorption isotherm obtained for both species, As(V) and As(III), when TiO_2 is used, is better represented with Freundlich model. On the other hand, the model that best fits the adsorption isotherm of As(V) or As(III) on granular ferric hydroxide and activated alumina is the Langmuir model.

The results for batch tests are summarized in Figure 1, which shows a representation of the different isotherms with the obtained parameters for each tested adsorbent. In Figure 1a, the experimental points and adsorption isotherm models for TiO_2 are depicted. Batch tests results for GFH and AA isotherms (experimental data and models) are shown in Figure 1b and Figure 1c, respectively.

As can be observed in Figure 1, As(V) is more efficiently adsorbed onto granular ferric hydroxide and activated alumina than As(III) in a wide range of As concentrations in the liquid phase. On the other hand, the adsorption over titanium dioxide based material is different from the other adsorbents. At lower concentrations, As(III) is more easily adsorbed than As(V), but at higher concentrations both species show the same behavior even though As(V) shows little better adsorption capacity than As(III). The following discussion will be focused on the estimated adsorption parameters only for As(V).

The adsorption isotherm parameters presented in Table 2 are comparable with the ones found in other published arsenic adsorption studies. Even so, it is very complex to compare directly the estimated isotherm parameters because of the different conditions employed for the experiments (pH, initial As concentration) or different kind of adsorbents (particle size, superficial area) and type of water used (groundwater, drinking water, distilled water).

There are a number of publications that have evaluated the aqueous As(V) isotherm parameters for iron, aluminium and titanium dioxide based materials under different conditions.^[13,14,22] Dutta et al.,^[22] Gosh and Yuan,^[23] Singh et al.^[24] found Langmuir fitting values of q_m : 0.002, 0.011 and 0.009 g g^{-1} , respectively for AA under similar experimental conditions in comparison with the present work. In the case of GFH, Sperlich et al.^[14] obtained a Freundlich fitting value of $q_m = 0.032 \text{ g g}^{-1}$ and Driehaus et al.^[25] obtained a Langmuir fitting with a q_m value of 0.0085 g g^{-1} . It can be seen that the parameters related to maximum capacity obtained from the present work (see Table 2) are in the same order of the parameters found in other works employing similar conditions.

The values of the adsorption parameters found in literature for TiO_2 based materials with Freundlich fitting are different from our findings. The discrepancy is probably due to differences in the superficial area of the adsorbents and particle size. On the other hand, Nabi et al.^[11] and Dutta et al.^[22] found a q_m value of 0.022 and 0.021 g g^{-1} , respectively, with Langmuir fitting employing similar

Table 2. Estimated isotherm parameters.

		Adsorbent					
		TiO_2		GFH		AA	
Isotherm		As (V)	As (III)	As (V)	As (III)	As (V)	As (III)
	Freundlich	K	0.346	0.021	0.065	0.085	0.051
n		1.683	5.999	4.965	3.222	2.890	2.639
R^2		0.999	0.987	0.964	0.975	0.931	0.983
Langmuir	$q_m(\text{g g}^{-1})$	0.015	0.007	0.018	0.013	0.008	0.005
	b (L g^{-1})	805.36	26843	58565	15967	2315	1423
	R^2	0.993	0.704	0.992	0.997	0.993	0.997

Bolded values indicate best fittings.

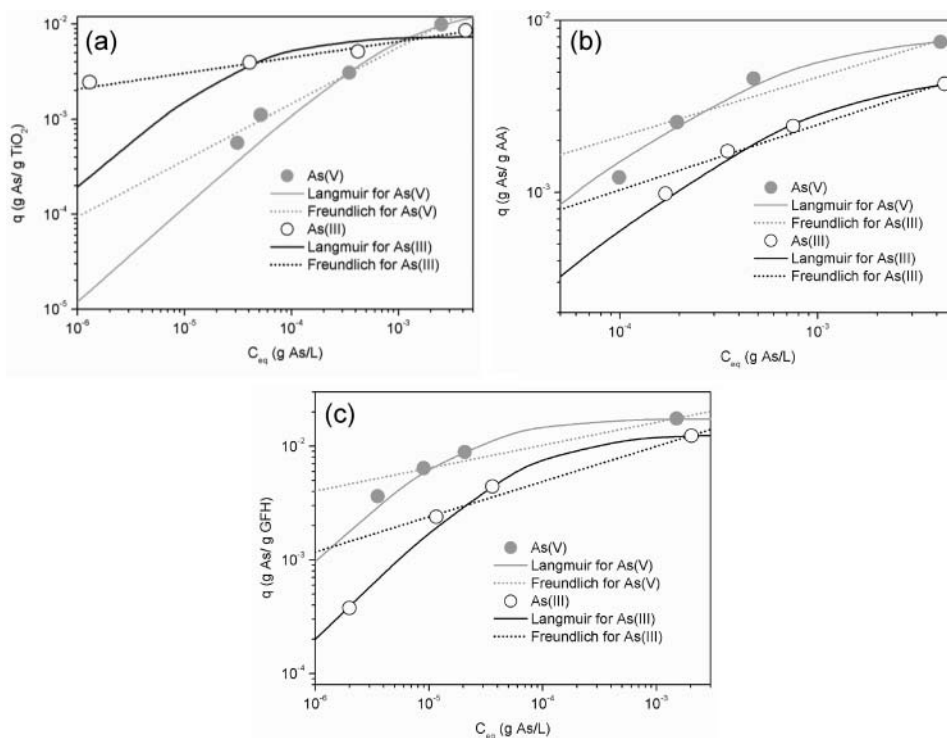


Fig. 1. Adsorption isotherms employing (a) TiO_2 , (b) GFH, (c) AA. Experimental data for As(V) (●) and As(III) (○). Models: Langmuir (—) and Freundlich (⋯).

conditions to our experimental setup. These values are in the same order of the one obtained in this work employing Langmuir fitting (0.015 g g^{-1}). Because pH affects the adsorption of arsenic, it was measured during all the experiments and remained nearly constant at the adjusted neutral pH.

Breakthrough curves and simulations

Adsorption experiments in mini fixed bed columns are dynamic tests which, unlike batch assays, operate under non-equilibrium conditions. A continuous flow feeds the top of the column filled with the adsorbent, where the solute is transferred from the mobile liquid phase to the solid phase (adsorbent bed). The progressive movement of the adsorption zone within the bed of adsorbent can be represented by the so called breakthrough curve, a plot of the relative inlet concentration (measured at the column outlet) as a function of time. The key parameter emerging from a breakthrough curve is the breakthrough point, i.e., the time at which the relative concentration rapidly increases until bed saturation. Fixed bed columns can be mathematically modelled from the first principles of momentum and mass transport through a porous media. Solutions to these balances under different assumptions provide different models for breakthrough curves. Among them, the model developed by Thomas is usually employed. The expression found for Thomas

model considers a highly favourable isotherm ($bC > > 1$) to give:

$$\frac{C}{C_0} = \frac{1}{1 + \exp\left(\frac{k_{Th}q_0X}{Q} - k_{Th}C_0t\right)} \quad (5)$$

The model can be linearized as follows:

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{k_{Th}q_0X}{Q} - k_{Th}C_0t \quad (6)$$

where C_0 is the initial arsenic concentration (mg L^{-1}), k_{Th} is the kinetic constant ($\text{L mg}^{-1} \text{ min}^{-1}$), q_0 is the maximum solute concentration in the solid phase (g g^{-1}), Q is the volumetric flow rate (mL min^{-1}), X is the mass of adsorbent in the column (g).

Another model was developed by Bohart–Adams assuming a rectangular equilibrium isotherm. A simplified version of this model is usually found as:

$$\frac{C}{C_0} = \frac{1}{1 + \exp\left(k_{BA}N_0\frac{Z}{U_0} - k_{BA}C_0t\right)} \quad (7)$$

or in its linearized form:

$$\ln\left(\frac{C_0}{C} - 1\right) = k_{AB}C_0t - k_{AB}N_0\frac{Z}{U_0} \quad (8)$$

where C_0 is the initial arsenic concentration (mg L^{-1}), k_{BA} is the kinetic constant ($\text{L mg}^{-1} \text{min}^{-1}$), N_0 is the concentration of saturation (mg L^{-1}), U_0 is the superficial velocity (cm min^{-1}) and Z is the column height (cm).

The Bohart–Adams model can be thought as a limiting case of Thomas model when the adsorption isotherm is highly favourable.^[26] On the other hand, Clark model defines a different simulation approach of breakthrough curves. It combines a Freundlich isotherm and the concept of a mass transfer coefficient to give:

$$\frac{C}{C_0} = \left(\frac{1}{1 + Ae^{-rt}}\right)^{\frac{1}{n-1}} \quad (9)$$

or in its linearized form:

$$\ln\left[\left(\frac{C_0}{C}\right)^{1-n} - 1\right] = \ln(A) - rt \quad (10)$$

where C_0 is the initial arsenic concentration (mg L^{-1}), n is the Freundlich isotherm parameter; A and r are parameters of the model.

It can be noticed that the simplified models of Thomas, Bohart–Adams and Clark model for $n=2$ can be written in the same mathematical equation:

$$\frac{C}{C_0} = \frac{1}{1 + \exp(\alpha - \beta t)} \quad (11)$$

which is a form of the logistic function with a sigmoid shape, typical of the breakthrough curves.

Breakthrough models provide information to perform the scaling-up of the adsorption columns. By using the mathematical expressions of these models, a comparative performance analysis of the different adsorbent materials can be made, together with a few additional parameters.

For instance, the degree of saturation^[27] is defined by:

$$DS = 1 - f \frac{Z_{ads}}{Z} \quad (12)$$

and gives an idea of the saturation of the column. In the above equation, Z_{ads} is the length of the adsorption zone and f is the fractional capacity of the adsorption zone:

$$Z_{ads} = Z \frac{(t_E - t_B)}{\int_0^{t_E} \left(1 - \frac{C}{C_0}\right) dt} = Z \frac{(t_E - t_B)}{\int_0^{t_B} \left(1 - \frac{C}{C_0}\right) dt + f(t_E - t_B)} \quad (13)$$

$$f = \frac{1}{(t_E - t_B)} \int_{t_B}^{t_E} \left(1 - \frac{C}{C_0}\right) dt \quad (14)$$

In Eqs. 13 and 14, the relative concentration C/C_0 can be put in the analytical form given by the explicit models. The breakthrough time (t_B) and the exhaustion time (t_E) of the columns are arbitrarily defined at 5% and 95% of the inlet concentration, respectively.

Another simple but useful parameter is the total pollutant removal:

$$R_T = \frac{1}{t_E} \int_0^{t_E} \left(1 - \frac{C}{C_0}\right) dt \quad (15)$$

which constitutes a relative measure of the pollutant mass removed.

The experimental datasets of As(III) and As(V) concentrations for mini fixed bed columns employing AA and GFH were used in this work to simulate the breakthrough curves employing Bohart–Adams model. Thomas model has not been used due to the fact that it reduces to the Bohart–Adams model for highly favourable isotherms (this is the present case according to isotherm parameters in Table 2). On the other hand, Clark model was used in breakthrough curves simulations for TiO_2 because it is more frequently used and more appropriate when a Freundlich type isotherm gives a better equilibrium description. The estimated parameters of Clark model for the adsorption of both arsenic species onto the TiO_2 bed

Table 3. Estimated parameters of Bohart–Adams and Clark models.

		GFH		AA		TiO ₂		
Bohart-Adams		As(V)	As(III)	As(V)	As(III)	Clark Model	As(V)	As(III)
Linearized	K_{B-A} ($\text{L mg}^{-1} \text{min}^{-1}$)	0.0435	0.0375	0.0245	0.031	ln A	8.745	40.48
	N_0 (mg L^{-1})	87.81	74.89	194.0	72.51	r (h^{-1})	0.672	2.964
	R^2	0.933	0.967	0.910	0.983	R^2	0.944	0.923
Non-linear	K_{B-A} ($\text{L mg}^{-1} \text{min}^{-1}$)	0.0329	0.0302	0.0305	0.031	ln A	6.625	68.93
	N_0 (mg L^{-1})	91.67	78.77	175.3	65.39	r (h^{-1})	0.493	6.086
	R^2	0.952	0.971	0.932	0.989	R^2	0.965	0.982

Bolded values indicate best fittings.

are presented in Table 3. Also, it summarizes as well the obtained estimated parameters of Bohart–Adams model for the adsorption of both arsenic species onto GFH and AA. According to the regression coefficients, the non-linear expression seems to give better fittings than linear equations for both adsorbent and species.

A model validation is graphically performed for each combination of adsorbent and arsenic species studied. The non-linear fitting of Clark model (Eq. 9) and the experimental data of adsorption onto TiO_2 , are shown in Figure 2a. The experimental breakthrough curve and the Bohart-Adams model for GFH adsorbent are presented in Figure 2b. Finally, Figure 2c depicts the fitting of Bohart-Adams model when AA is used. As can be seen from Figure 2, experimental breakthrough points for As(V) (for all the adsorbents tested) are placed at higher times than the experimental points for As(III). Considering the experimental results, it can be inferred that arsenate can be removed from water and concentrations below the acceptable guideline limit of $10 \mu\text{g L}^{-1}$ can be reached. In all dynamic experiments, the pH of the solutions at the outlet of the columns did not vary significantly from the initial conditions. It is worth noting the different timescales and relative concentration ranges in Figure 2b and Figure 2c, an evidence of the higher adsorptive capacity of the GFH bed compared to the AA. This result is consistent with larger N_0 values found for GFH, as it was presented in Table 3. As can be seen in the figures, simulations of breakthrough curves by Clark model for TiO_2 and the

Bohart–Adams model for GFH and AA provide satisfactory results and predict fairly well the experimental data. These findings are important for practical purposes, because the first part of the curves determines the useful capacity of fixed bed columns.^[28]

A comparative performance analysis of different adsorbents was made, using predicted breakthrough curves by the adjusted models. The parameters t_B , DS and R_T were calculated for both species and are presented in Table 4.

It can be seen that AA is the least efficient material in comparison with the other two adsorbents: for As(V) it has the shortest breakpoint time and a low degree of saturation; for As(III) it is practically useless. On the other hand, TiO_2 shows the longest breakthrough time and degree of saturation, for both arsenic species. From the results obtained in our batch tests, As(III) is slightly more easily adsorbed on TiO_2 than As(V), as it can be seen in Figure 1. On the other hand, Figure 2 (dynamic experiment), shows larger breakthrough times for As(V) suggesting a better adsorption when it is compared to As(III). Nevertheless, other performance parameters calculated indicate that the column is better used for As(III).

The total As(III) removal is 91.5%, while the total As(V) is 71.8%; besides, the degree of saturation is also larger for As(III). Finally, the breakthrough times only differ by less than 8%. It can be concluded from these results that the performance of TiO_2 for both As species is very similar. In

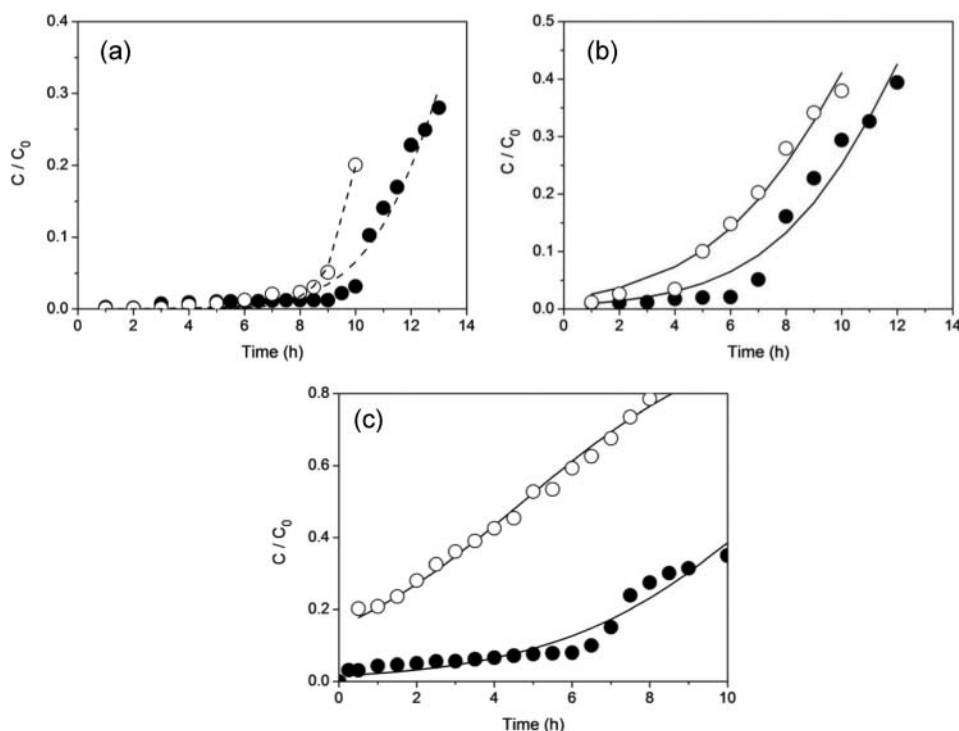


Fig. 2. Experimental and simulated breakthrough curves for (a) TiO_2 , (b) GFH, (c) AA. Experimental data for As(V) (●) and As(III) (○). Model: Clark (—); Bohart-Adams (---).

Table 4. Calculated column adsorption performances from breakthrough models.

	<i>GFH</i>		<i>AA</i>		<i>TiO₂</i>	
	<i>As(V)</i>	<i>As(III)</i>	<i>As(V)</i>	<i>As(III)</i>	<i>As(V)</i>	<i>As(III)</i>
Breakthrough time t_B (h)	5.3	3.2	2.8	—	9.6	8.9
Degree of saturation, DS (%)	41.6	25.8	28.4	—	61.5	91.1
Total As removal, R_T (%)	62.6	56.9	57.8	37.3	71.8	91.5

between the performance of TiO_2 and AA there is the GFH, with lower breakpoint times and saturation degrees than TiO_2 . Besides, GFH is more efficient for As(V) removal. Also, the results concerning to the total As removal (%), calculated by Eq. 15, are consistent with the experimental and model data with higher values for TiO_2 adsorbent.

Conclusions

A complete adsorption study for As(III) and As(V) removal from aqueous medium was performed. Three commercial adsorbents were tested: titanium dioxide, granular ferric hydroxide and activated alumina.

Adsorption isotherm assays and dynamic experiments were conducted for the two arsenic species and the three adsorbents tested. Langmuir and Freundlich models were applied and their parameters were satisfactory estimated. Freundlich model showed a better correlation for As(III) and As(V) adsorption on TiO_2 surface, while Langmuir isotherm better represents the experimental data for GFH and AA for both arsenic species.

Experimental breakthrough curves were obtained and two mathematical fixed bed sorption models were applied. The Bohart-Adams model represented accurately the experimental data for GFH and AA, while the Clark model better represents the experimental data for TiO_2 . Both models rendered satisfactory predictions of the breakthrough curves.

According to all the experiments carried out in these work, it can be concluded that the employed titanium-based material seems to be the most suitable adsorbent to perform the process, followed by the granular ferric hydroxide. It is important to mention that it would be necessary in a future work, to study the effect of different ions that are usually present in natural waters that may compete with arsenic species in the adsorption process.

Funding

The authors gratefully acknowledge the financial support of Universidad Nacional del Litoral (UNL), Consejo Nacional de Investigaciones Científicas y Técnicas

(CONICET), and Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT) of Argentina.

References

- [1] von Brömssen, M.; Markussen, L.; Bhattacharya, P.; Ahmed, K.; Hossain, M.; Jacks, G.; Sracek, O.; Thunvik, R.; Hasan, M.; Islam, M.; Rahman, M. Hydrogeological investigation for assessment of the sustainability of low-arsenic aquifers as a safe drinking water source in regions with high-arsenic groundwater in Matlab, south-eastern Bangladesh. *J. Hydrol.* **2014**, *518*, 373–392.
- [2] Sharma, A.; Tjell, J.; Sloth, J.; Holm, P. Review of arsenic contamination, exposure through water and food and low cost mitigation options for rural areas. *Appl. Geochem.* **2014**, *4*, 11–33.
- [3] Bundschuh, J.; Litter, M.; Parvez, F.; Román-Ross, G.; Nicolli, B.; Jean, J.; Liu, C.; López, D.; Armienta, M.; Guilherme, L.; Gomez Cuevas, A.; Cornejo, L.; Cumbal, L.; Toujaguez, R. One century of arsenic exposure in Latin America: A review of history and occurrence from 14 countries. *Sci. Total Environ.* **2012**, *429*, 2–35.
- [4] Bundschuh, J.; Bhattacharya, P.; Sracek, O.; Mellano, M.; Ramírez, A.; Storniolo, A.; Martín, R.; Cortes, J.; Litter, M.; Jean, J.-S. Arsenic removal from groundwater of the Chaco-Pampean Plain (Argentina) using natural geological materials as adsorbents. *J. Environ. Sci. Health Pt. A* **2011**, *46*, 1297–1310.
- [5] Sun, H.-J.; Rathinasabapathi, B.; Wu, B.; Luo, J.; Pu, L.-P.; Ma, L. Arsenic and selenium toxicity and their interactive effects in humans. *Environ. Int.* **2014**, *69*, 148–158.
- [6] Bhattacharjee, P.; Chatterjee, D.; Singh, K.; Giri, A. Systems biology approaches to evaluate arsenic toxicity and carcinogenicity: An overview. *Int. J. Hyg. Envir. Heal.* **2013**, *216*, 574–586.
- [7] WHO (World Health Organization). *Guidelines for Drinking-Water Quality*; 4th edition, WHO Press: Switzerland, 2011.
- [8] Mohan, D.; Pittman, C. Arsenic removal from water/wastewater using adsorbents - A critical review. *J. Hazard. Mater.* **2007**, *142*, 1–53.
- [9] Qu, J. Research progress of novel adsorption processes in water purification: A review. *J. Environ. Sci.* **2008**, *20*, 1–13.
- [10] Fu, F.; Wang, Q. Removal of heavy metal ions from wastewaters: A review. *J. Environ. Manage.* **2011**, *92*, 407–418.
- [11] Nabi, D.; Aslam, I.; Qazi, I. Evaluation of the adsorption potential of titanium dioxide nanoparticles for arsenic removal. *J. Environ. Sci.* **2009**, *21*, 402–408.
- [12] Jegadeesan, G.; Al-Abed, S.; Sundaram, V.; Choi, H.; Scheckel, K.; Dionysiou, D. Arsenic sorption on TiO_2 nanoparticles: Size and crystallinity effects. *Water Res.* **2010**, *44*, 965–973.
- [13] Pirilä, M.; Martikainen, M.; Ainassaari, K.; Kuokkanen, T.; Keiski, R. Removal of aqueous As(III) and As(V) by hydrous titanium dioxide. *J. Coll. Interf. Sci.* **2011**, *353*, 257–262.
- [14] Sperlich, A.; Schimmelpfennig, S.; Baumgarten, B.; Genz, A.; Amy, G.; Worch, E.; Jekel, M. Predicting anion breakthrough in granular ferric hydroxide (GFH) adsorption filters. *Water Res.* **2008**, *42*, 2073–2082.

- [15] Bang, S.; Pena, M.; Patel, M.; Lippincott, L.; Meng, X.; Kim, K.-W. Removal of arsenate from water by adsorbents: a comparative case study. *Environ. Geochem. Hlth.* **2012**, *33*, 133–141.
- [16] Bowell, R. Sorption of arsenic by iron oxides and oxyhydroxides in soils. *Appl. Geochem.* **1994**, *9*, 279–286.
- [17] Zhang, F.; Itoh, H. Photocatalytic oxidation and removal of arsenite from water using slag-iron oxide- TiO_2 adsorbent. *Chemosphere* **2006**, *65*, 125–131.
- [18] Yoon, S.; Oh, S.; Yang, J.; Lee, J.; Lee, M.; Yu, S.; Pak, D. TiO_2 photocatalytic oxidation mechanism of As(III). *Environ. Sci. Technol.* **2009**, *43*, 864–869.
- [19] Lescano, M.; Zalazar, C.; Cassano, A.; Brandi, R. Arsenic (III) oxidation of water applying a combination of hydrogen peroxide and UVC radiation. *Photochem. Photobiol. Sci.* **2011**, *10*, 1797–1803.
- [20] Lescano, M.; Zalazar, C.; Cassano, A.; Brandi, R. Kinetic modeling of arsenic (III) oxidation in water employing the UV/ H_2O_2 process. *Chem. Eng. J.* **2012**, *211–212*, 360–368.
- [21] US EPA (Environmental Protection Agency). Supplement I-EPA/600/R-94-111. Method 200.9, revision 2.2: Determination of trace metals by stabilized temperature Graphite Furnace Atomic Absorption. In *Methods for the Determination of Metals in Environmental Samples*, Cincinnati, Ohio, USA, 1994.
- [22] Dutta, P.; Ray, A.; Sharma, V.; Millero, F. Adsorption of arsenate and arsenite on titanium dioxide suspensions. *J. Colloid Interf. Sci.* **2004**, *27*, 270–275.
- [23] Ghosh, M.; Yuan, J. Adsorption of arsenic and organoarsenicals on hydrous oxides. *Environ. Prog.* **1978**, *6*, 150–151.
- [24] Singh, T.; Pant, K. Equilibrium, kinetics and thermodynamic studies for adsorption of As(III) on activated alumina. *Sep. Purif. Technol.* **2004**, *36*, 139–147.
- [25] Driehaus, W.; Jekel, M.; Hildebrandt, U. Granular ferric hydroxide—a new adsorbent for the removal of arsenic from natural water. *J. Wat. Supply Res. T.* **1998**, *47*, 30–35.
- [26] Chu, K. Fixed bed sorption: setting the record straight on the Bohart-Adams and Thomas models. *J. Hazard. Mater.* **2010**, *177*, 1006–1012.
- [27] Treybal, R. *Mass-Transfer Operations*; Chemical Engineering Series, 3rd Edition, McGraw-Hill International Editions, New York; 1980.
- [28] Hashin, M.; Chu, K. Prediction of protein breakthrough behaviour using simplified analytical solutions. *Sep. Purif. Technol.* **2007**, *53*, 189–197.