Arsenic Entrapment in Reactive Columns of Residual Soils

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Abstract: The purpose of this research is to evaluate the aptitude of two residual soils for the remediation of arsenic (As) contaminated groundwater. Batch and soil column tests were performed to evaluate removal of As from water. Permeable soil columns were prepared with mixtures of sand (90%) and two lateritic soils (10%). Results showed that removal of As in batch tests ranged from 95–99% when using a solid-liquid ratio equal to 1:10. Experimental results obtained in the soil column tests and calibrated simulation models showed that the amount of water that can be decontaminated depends on the initial As concentration and the flow rate. Maximum adsorption capacities in bath test and removal efficiency in soil columns tests clearly relates with the amount of iron compounds in the solid phase. The quality of residual soil samples are related to a high iron content to favor As removal and low clay-size particle content to achieve acceptable flow rates for water purification in low-cost permeable filters and permeable reactive barriers. **DOI: 10.1061/(ASCE)EE.1943-7870.0000697.** © *2013 American Society of Civil Engineers.*

CE Database subject headings: Adsorption; Arsenic; Remediation; Groundwater pollution; Residual soils; Filters.

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Introduction

Aquifers containing arsenic (As) concentrations higher than that recommended for drinking water were identified in many places around the world. In general, the presence of arsenic was associated with either natural or anthropogenic sources. In any case, this situation was responsible for limitations in possible uses of groundwater as a source of drinking water or for agriculture purposes. The pH and redox potential affect the speciation of arsenic. In general, inorganic arsenic was found in surface water and groundwater either as arsenite (As III) under reducing conditions or arsenate (As V) under oxidizing conditions (Masscheleyn et al. 1991; Smedley et al. 2002).

The ingestion of water containing As has been related to serious health problems including cancer, skin problems, vascular disease, and neuropathy (Smith et al. 2002; Aballay et al. 2012). This situation has become of fundamental importance in many places around the world where groundwater is the main source of drinking water, such as in Bangladesh and India, and when groundwater is the only source of water for dispersed and rural population in Latin America (Francisca and Carro Perez 2009; Bundschuh et al. 2010). The maximum As concentration suggested by the World Health Organization (WHO) for drinking water is 0.01 mg/L (WHO 2006).

Removal of As is a challenging problem in many places around the world where aquifers contain concentrations of this substance that exceed drinking water standards. Different remediation techniques were developed in the past decades for the removal of arsenic from water. Alternatives available for arsenic removal include chemical oxidation, precipitation, coagulation, inverse osmosis, adsorption, biological degradation, enhanced bioremediation, electrokinetic, phytoremediation, biosorption, and photochemical oxidative technologies (Litter et al. 2010). Among them, adsorption is frequently preferred because of its low cost and abundance of reactive materials that can be used for the sequestration of arsenic.

The adsorption in a waste by-product, in zero valent iron, iron nanoparticles, and natural products attracted the attention of several researchers (Daus et al. 2004; Kanel et al. 2005; Chen et al. 2007; Jovanovĭcand Rajakovĭc2010; Mlilo 2010; Tuutijärvi et al. 2010). Indeed, previous research with activated carbon, bauxite, hematite, goethite, gibbsite, zeolites, and clay minerals showed that arsenic was successfully removed from water (Litter et al. 2010). Among the existing sorbent materials, residual soils present the advantage of their abundance and low cost, which is fundamental to find economical arsenic remediation techniques. Both As(III) and As(V) were successfully removed from water in batch tests with lateritic soils (Maiti et al. 2007).

Weathering of rocks generates different horizons within a soil profile. Residual and lateritic soils form in a wet and tropical climate and are rich in iron oxides and aluminum hydroxides. The accumulation of iron compounds in these soils gives the possibility of using these materials for the removal of As. Micro-scale particle-fluid interaction mechanisms are responsible for the attraction between the As and iron compounds, leading to the adsorption of dissolved As ions. Therefore, the As concentration in water reduces. This behavior was successfully confirmed by means of batch tests (Maji et al. 2008; Gibbons and Gagnon 2010). However, in the case of permeable reactive filters, the influence of flow conditions and initial As concentration on the sequestration of As in the residual soil still needs to be determined.

The purpose of this study was to evaluate the potential of two samples from the B-horizon within a soil profile for the decontamination of As contaminated water. The main interest was to

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determine the effect of adsorption mechanisms and flow rate conditions on the sequestration of arsenic ions dissolved in the liquid used as permeating fluid in reactive soil columns.

Underlying Physical Concepts

A brief review of the fundamental mass transport phenomenon is presented in this section, giving that advection and diffusion mechanisms are used to explain the displacement of As within the pores of a reactive soil column or permeable barrier.

Mass Transport in Granular Filters

Displacement of dissolved ions inside porous media is controlled by chemical diffusion, advection, and mechanical dispersion. The relationship between these phenomena mainly depends on soil properties and is frequently evaluated by analyzing the Peclet's number (Fetter 1993). Assuming homogeneous and isotropic media, saturated with a fluid that follows Darcy's law, and considering one-directional flow, the total mass transport per unit area and time F [kg/(m$^2 \cdot$ s)] is

$$F = n_e v_e C - n_e D_L^* \frac{\partial C}{\partial x} \tag{1}$$

$$\frac{\partial F}{\partial x} = -n_e \frac{\partial C}{\partial t} \tag{2}$$

where t (s) = time; n_e = effective porosity; v_e (m/s) = seepage velocity; C (kg/m^3) = contaminant concentration; and D_L^* (m^2/s) = longitudinal hydrodynamic dispersion coefficient. The presence of high ionic strength solutions or extreme pH conditions affects the particle surface charge and modifies the hydraulic conductivity and seepage velocity (Jo et al. 2001).

The partial differential equation that describes the solute transport in reactive porous media is obtained by incorporating diffusion and advection as mass transport mechanisms and the effect of source/sink for the chemical substance under consideration (Sharma and Reddy 2004)

$$D_L^* \frac{\partial^2 C}{\partial x^2} - v_e \frac{\partial C}{\partial x} \pm \frac{r}{n_e} = \frac{\partial C}{\partial t} \tag{3}$$

where $r = -(B_d/\theta).(\partial C^*/\partial t)$ (kg/m^3/s) = rate of mass production/consumption given by the kinetic model of reaction; B_d (kg/m^3) = porous media bulk density; θ = volumetric water content (or porosity for saturated media); and C^* = adsorbed mass on soil particles per unit weight of solids. The amount of As adsorbed on soil particles can be further related to the initial contaminant concentration (C_0) through any adsorption isotherm.

Adsorption delays contaminant percolation and transport. The time, or pore volume of flow, needed by the center of mass of a contaminant plume to pass through a soil column, with respect to the expected time or volume for nonreactive transport (diffusion + advection only) defines a retardation factor (R). The solution of Eq. (3) depends on the boundary and flow conditions. However, for advection-dominated systems and all possible boundary conditions, the solution to Eq. (3) becomes (Ogata and Banks 1961)

$$C_{(x,t)} = \frac{C_0}{2} erfc\left(\frac{R.x - v.t}{2\sqrt{D_L^*.t.R}}\right) \tag{4}$$

The retardation factor R can be either computed from calibrated isotherms or directly measured in soil column tests.

Materials and Methods

Soils

The tested materials included sand and two different residual soils that were identified as lateritic soils.

The sand was taken from the Anisacate River in Córdoba, Argentina. An optic diffraction test reveals that this coarse grain soil is mainly composed by pure minerals, including quartz (43%), feldspars (12%) and muscovite (1%), and rock fractions composed by granite (38%) and other clasts in a less percentage. The sand was classified as poorly graded sand according to the Unified Soil Classification System (ASTM 2007). The mean particle diameter determined from sieve analysis was 1 mm, and only 10% of grains (by weight) have a particle diameter lower than 0.41 mm. Montoro and Francisca (2010) determined that this sand was nonreactive and highly permeable and that it showed no significant physicochemical interactions with high ionic strength solutions.

The two residual samples were obtained from a B-horizon in a weathering profile from 1 m below the surface at two sampling points 10 m apart from each other, in Oberá, Misiones, Argentina (Table 1). The two samples had high content of particles smaller than 2 μm (ASTM 2007). The liquid limit, plastic index (ASTM 2007), and amount of particles smaller than 74 μm (ASTM 2007) showed that specimens A and B classified as CL and CH according to the Unified Soil Classification System, which corresponded to inorganic clays of medium and high plasticity, respectively (ASTM 2007). High amounts of aluminum and iron oxides were identified in the semiquantitative chemical composition determined from scanning electron microscopy (SEM) images and energy dispersive X-ray (EDX) analyses (Fig. 1). The EDX-spectra were obtained from a visual field of 5 μm $\times$ 5 μm. X-ray diffraction tests revealed that sample A was mainly composed of quartz, hematite, and kaolinite and in less proportion of plagioclase and lithiophorite. In sample B, the most abundant minerals were quartz, goethite, kaolinite, anatase, plagioclase, and titanite (Fig. 2). The minerals identified in the X-ray diffraction tests are in good agreement with the chemical composition determined from the EDX spectra.

The sand was mixed with either sample A or sample B to prepare permeable soil columns. Different mixtures were prepared to evaluate the behavior of the soil columns. Very low hydraulic conductivity was observed when the amount of residual soil was higher than 20%, and fine particle migration was observed when the residual soil content was lower than 2.5%. Then, soil mixtures were prepared with 90% of sand and 10% of either sample A or sample B (by weight). The amount of residual sample from the B-horizon in the mixture was selected to obtain hydraulic conductivities higher than 5×10^{-8} m/s to facilitate liquid displacement inside the pores and to avoid the effect of fine particle migration. The sand formed a rigid skeleton containing the silt and clay size particles of the residual soil which created a reactive matrix.

Table 1. Relevant Properties of the Soils

Property	Sample		
	A	B	T1:1
Liquid limit (%)	45.3	65.0	T1:3
Plastic index (%)	18.6	39.7	T1:4
Fine particles <74 μm (%)	100	100	T1:5
Clay size particles <2 μm (%)	75	66	T1:6
Specific gravity	2.79	2.80	T1:7
Specific surface (m^2/g)	3.7	3.7	T1:8
Fe content (% in w/w)	5.47	2.98	T1:9
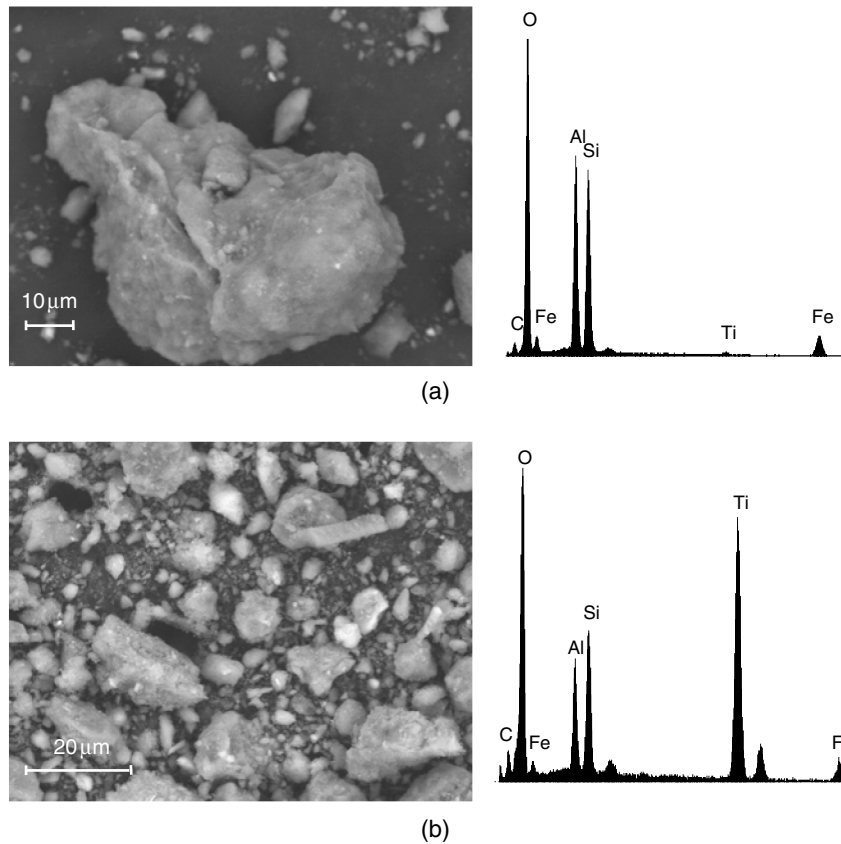
Fig. 1. SEM images and EDX microanalysis of samples: (a) A; (b) B
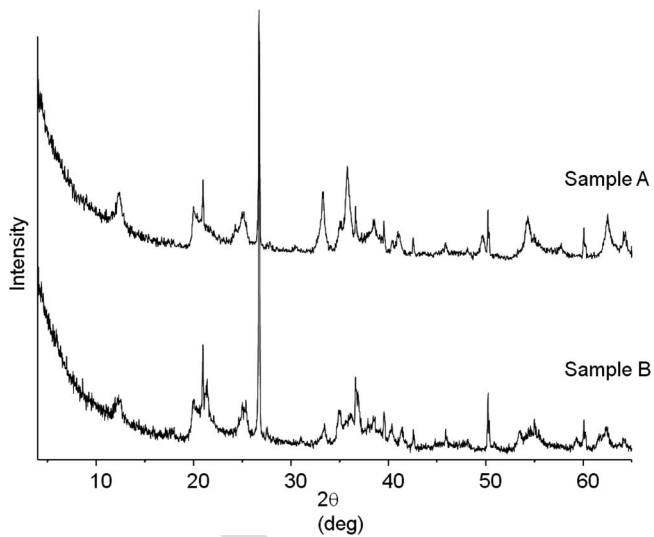
Fig. 2. XRD patterns of tested residual soils

Arsenic Solutions

Solutions containing different As concentrations were prepared from the dissolution of arsenic trioxide (As_2O_3) in an alkaline medium obtained with sodium hydroxide (NaOH) and distilled water. Arsenic concentrations were 0.1; 0.5; 1; 5; 10; 15; 20; and 25 mg/L, which includes the registered concentration in most aquifers in the center of Argentina. The pH and Eh of the obtained solutions were pH = 7.3–7.9 and Eh = 175–230. Thus, the main expected arsenic speciation was $HAsO_4^{2-}$ according to Masscheleyn et al. (1991).

Arsenic Measurements

The arsenic concentrations were determined by means of arsenic test strips (Arsen 10 and Arsen 50 from Quantofix). The color of a paper strip after reacting with arsine gas was compared with color charts to obtain the arsenic concentration. This colorimetric method was improved to enhance the accuracy of the measurements. An improved analysis of reactions was implemented with the purpose of eliminating the operator influence on results. The implemented method consisted of taking 10 high resolution pictures of the paper strip from a specific distance, camera setting, and illumination conditions in the first minute after the reaction. These color RGB pictures were converted to 8-bit gray scale images and then analyzed to obtain histograms of digital levels.

Two calibration curves were obtained by measuring solutions with known arsenic concentrations. Then, As concentrations of samples under test conditions were obtained from the digital level of the arsenic strips and the calibration curves developed in this work. Limit of detection (LOD) using this technique was 6.5 μg/L. A complete description of this method can be found in Carro Perez and Francisca (2013).

Selected samples were also tested by using gaseous hydride/atomic absorption spectrometry (GHAA), following the procedure suggested by the USEPA (1999). Obtained results correlate with each other with a coefficient of determination $R^2 = 0.99$ (Carro Perez and Francisca 2013).

Experimental Tests

Batch and soil column tests were performed to evaluate arsenic adsorption in samples A and B. In both cases, tests were carried out at room temperature (20°C).

Batch tests were performed by following the ASTM D4646 Standard (ASTM 2007) using a 250-mL flask, 200 mL of arsenic solutions with concentrations from 0.1–25 mg/L, 20 g of dry soil particles, and stirring times between 2 and 24 h. After that, the mixture was centrifuged at 4000 rpm for 60 minutes, and the recovered liquid was analyzed to determine the arsenic concentration.

The soil column tests were performed in transparent cells having 5 cm in diameter and 5 cm in length (Fig. 3). Laterite-sand mixtures were moistened with distilled water and placed in the cell in three layers of equal height by giving 25 blows per layer with a 10.95-mm diameter blunt tip bar. All columns were prepared with porosity and dry unit weight equals to 0.3 and 19 kN/m³, respectively. Two porous stones and Fisherbrand qualitative grade P5 filter papers were placed at the top and bottom of the specimens. The sand forms a rigid skeleton containing the finer particles of samples A and B, which create a reactive matrix. These samples were permeated with distilled water by following the constant head technique (ASTM 2007) until obtaining constant hydraulic conductivity. Then, the specimens were permeated with a solution of 1 mg/L of As without modifying the hydraulic gradient (Fig. 3). The liquid permeated through the samples was collected in the outlet port and the presence of arsenic was determined at different times (or pore volumes of flow) during 150 days. The pore volume of flow (U) is a dimensionless ratio and is computed as the total volume of liquid permeated through the specimen divided by the volume of voids. The monitoring of the relationship between the effluent's concentrations measured at different pore volume of flow allowed computing the retardation factor as previously indicated.

Adsorption of As on lateritic soil particles was verified by measuring the zeta potential of soil particles at different pH conditions. The arsenic concentrations ranged from 1–20 mg/L. The zeta potential measurements were performed after the sorption/reaction of particles with the arsenic solutions in the batch tests. These measurements were performed by using the Zeta-Meter 3.0+ equipment, which includes a microscope, a voltage generator, a zeta potential meter, and an electrophoretic cell with platinum electrodes. The number of particles, zeta potential, standard deviation of the measurements, voltage change, and velocity factor were recorded during the tests.

Results and Analysis

Batch Tests

Removal of arsenic in batch tests was from 95–99% for sample A and 92–99% for sample B. The amount of As adsorbed on soil particles (C^*) showed a nonlinear behavior with the equilibrium concentration (C) for all tested initial As concentrations. Theoretically, the nonlinear Freundlich and Langmuir isotherms models were fitted to the experimental data by using a least square fitting technique (Fig. 4). Table 2 shows the obtained equations. The higher coefficient of determinations were $R^2 = 0.985$ and $R^2 = 0.922$ for the Freundlich and Langmuir isotherm when fitting experimental results of sample A and B, respectively (Table 2). However, the Langmuir isotherm fitted the experimental results of sample A almost with the same coefficient of determination as the Freundlich model. Then, the use of the Langmuir model is preferred for the two tested residual soils, and therefore, estimated maximum adsorption capacities were 0.295 and 0.262 mg/g for the samples A and B, respectively. These values resulted slightly higher than that determined by Maji et al. (2008) for laterite soil and suggested that tested residual soils can be used for the remediation of As contaminated water. Even tested soils have a low efficiency in removing As in comparison with synthetic materials (Table 3); however, residuals soils have the advantage that they are natural, abundant, and low-cost materials.

The zeta potential at pH higher than the point of zero charge (PZC ~ 3.5) was negative. The obtained values were attributed to the simultaneous contribution of the negative electrical charges of clay particles and the positive electrical charges of the iron oxides in the tested samples. The effect of adsorption on the surface charge was obtained by testing solutions with different initial
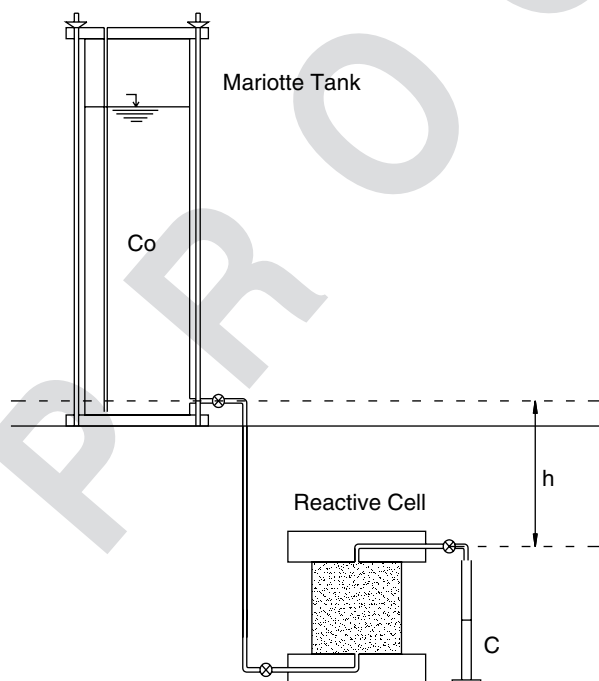
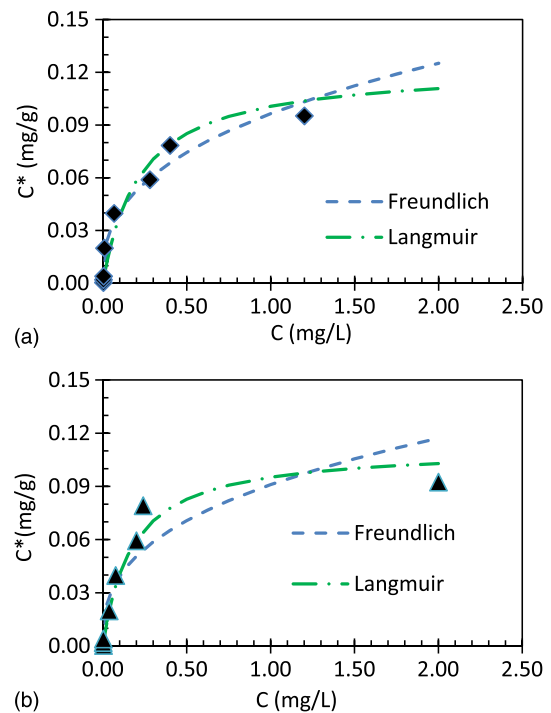**Fig. 3.** Schematic representation of the soil column tests

Fig. 4. Adsorbed (C^*) and equilibrium (C) arsenic concentrations from batch sorption tests performed with: (a) sample A; (b) sample B

Table 2. Modeling Equations for the Fitted Isotherms

		Sample A			Sample B	
T2:1	Model	Equation	R^2		Equation	R^2
T2:3	Freundlich	$C^* = 0.225C^{0.215}$	0.985		$C^* = 0.22C^{0.2}$	0.913
T2:4	Langmuir	$C/C^* = (1/0.887) + (C/0.295)$	0.962		$C/C^* = (1/0.987) + (C/0.262)$	0.922

Table 3. Comparison of Maximum Sorption Capacities (C^*_{max}) of Natural and Synthetic Adsorbents used for the Removal of As from Water

	Adsorbent	C^*_{max} (mg/g)	Arsenic type	Reference
T3:1				
T3:2	Naturals			
T3:3	Sample A	0.295	As(V)	This study
T3:4	Sample B	0.262		
T3:5	Siderite	0.516	As(V)	Guo et al. (2007)
T3:6		1.040	As(III)	
T3:7	Algae *Lessonia nigrescens*	28.2–45.2	As(III)	Hansen et al. (2006)
T3:8	Oxisol			
T3:9	Goethite	12.4	As(V)	Ladeira et al.
T3:10		7.5	As(III)	(2004)
T3:11	Gibbsite	4.6	As(V)	
T3:12		3.3	As(III)	
T3:13	Kaolinite	0.23	Total	
T3:14	Laterite soil	0.18	Total	Maji et al. (2008)
T3:15	Natural iron ores	0.4	As(V)	Zhang et al. (2004)
T3:16	Kaolinite	0.86	As(V)	Mohapatra et al.
T3:17	Montmorillonite	0.64		(2007)
T3:18	Illite	0.52		
T3:19	Zeolite (clinoptilolite)	0.0015	As(V)	Bilici Baskan and Pala (2011)
T3:20	Synthetics			
T3:21	Fe_3O_4 nanoparticle-coated boron nitride nanotubes	0.96	As(V)	Chen et al. (2011)
T3:22	Synthetic zeolites	34.8–35.8	As(V)	Chutia et al. (2009)
T3:23	Chitosan zero valent iron	94 ± 1.5	As(III)	Gupta et al. (2012)
T3:24	Nanoparticles	119 ± 2.6	As(V)	
T3:25	Bone char	4.00	As(III)	Mlilo et al. (2010)
T3:26		4.58	As(V)	
T3:27	Iron oxide-coated sand	0.02857	As(III)	Gupta et al. (2005)
T3:28	Iron oxide Fe_2O_3	0.66	As(V)	Jeong et al. (2007)
T3:29	Aluminum oxide Al_2O_3	0.17		
T3:30	Nanoscale	1.8	As(III)	Kanel et al. (2005)
T3:31	Zero-valent iron			
T3:32	Granular activated carbon	2.5	As(V)	Di Natale et al. (2008)
T3:33	Iron-treated clinoptilolite	0.008–0.009	As(V)	Bilici Baskan and Pala (2011)
T3:34	Activated carbon oat hulls	3.09	As(V)	Chuang et al. (2005)
T3:35	Amorphous iron(III) phosphate $FePO_4$	10	As(V)	Lenoble et al. (2005)
T3:36	Crystalline iron(III) phosphate $FePO_4$	9		
T3:37	Hydrolyzed acid treated	21.6	As(V)	Maiti et al. (2012)
T3:38	laterite	9.4	As(III)	

(a)

(b)
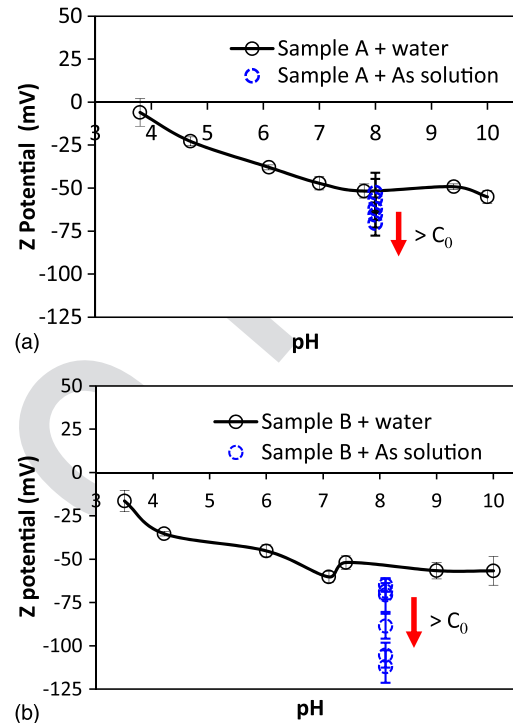
Fig. 5. Z-potential for samples: (a) A; (b) B before and after in contact with arsenic solutions; arrows indicate increasing adsorbed arsenic (C^*) from 0.004–0.08 mg/g, and error bars corresponds to a confidence interval of 95%

concentrations of As. In all cases, the obtained z-potential became more negative with the As adsorption given that positive surface charges of the iron oxides were partially balanced by the negative charge of the arsenate $HAsO_4^{2-}$ (Fig. 5). Then, the higher the C^*, the more negative the electrical surface charge.

The calibrated adsorption isotherms allowed computing the retardation factor theoretically (Fetter 1993), which can be used for the estimation of the expected behavior of soil columns with different bulk densities. The direct measurement of retardation factor was also preformed to obtain reliable values for long-term tests in permeating soil columns (Sharma and Reddy 2004).

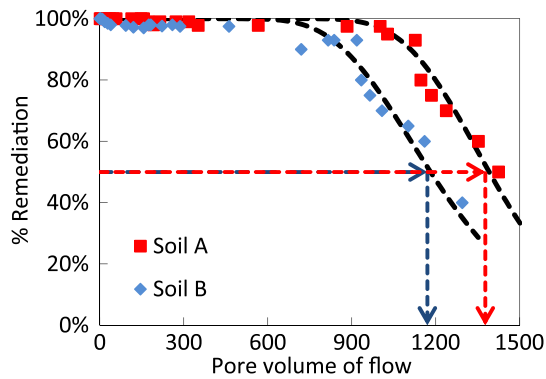### Soil Column Tests

The removal of arsenic (%) was determined by measuring the arsenic concentration of the liquid collected in the outlet port (Fig. 6). Flow rate was equal to 6.48×10^{-6} m/s for the sample A and 5.28×10^{-6} m/s for the sample B. Soil columns were very effective in reducing the arsenic concentrations when the pore volume of flow was lower than 900 and 600 for sample A and B, respectively. Given that porosities were 0.3, the amount of water that can be purified was 270 and 180 times the total volume of the columns, respectively. The As concentration in the effluent showed a removal higher than 98% before the threshold pore volumes of flow; thereafter, remediation efficiency decreased dramatically.

The high remedial efficiency observed during the first days of permeation was produced as a result of arsenic adsorption. Arsenic was retained inside the soil column given that close-to-zero concentrations were measured in the effluent even when the volume of water permeated through the specimens was several times higher than the pore volume. This produced a retardation effect delaying the presence of arsenic in the outlet port. Thus, adsorption clearly prevailed over the advection and diffusion of arsenic ions inside the soil pores.

Fig. 6. Influence of the pore volume of flow on the remediation
efficiency

Discussion and Practical Application

Concentration of arsenic in the outlet port increased with the number of pore volume of flow. The influence of pore volume of flow (U) on the final concentration (C) experimentally measured was successfully modeled by Eq. (4) by using a least-squares fitting technique (dashed lines in Fig. 6). The soil hydraulic conductivity, porosity, and cell dimensions were included as experimentally determined in the soil column tests. The model parameters that better fitted the experimental results obtained for the sample A were hydrodynamic dispersion coefficient $D_L^* = 3.7 \times 10^{-12}$ (m²/s) and retardation coefficient $R = 1,377$, while for sample B they were $D_L^* = 6.5 \times 10^{-12}$ (m²/s) and $R = 1,170$.

Obtained results confirms that the sample with higher iron content (sample A) identified in the EDX analysis has a higher maximum adsorption capacity (Tables 1 and 2). This trend is in agreement with the higher retardation factor obtained for sample A in comparison with sample B (Fig. 6). In addition, the internal redistribution of As caused by spatial distribution of redox gradients may also be responsible for this observation (Masue-Slowey et al. 2011).

The flow rate, which is controlled by the hydraulic conductivity and gradient, and the initial arsenic concentration determined the time of As percolation through soil columns or permeable reactive barriers. The lifetime of the permeable reactive filters is defined as time of permeation required to observe concentrations higher than 0.01 mg/L in the outflow, if the water is been used for drinking (WHO 2006). Lifetime can be obtained from the pore volume of flow, hydraulic gradient, barrier thickness, and Eq. (4). Fig. 7 shows that the lower the initial concentration and gradient, the larger the number of pore volumes of flow needed to reach arsenic concentrations higher than 0.01 mg/L in the outflow when assuming null changes in porosity and hydrodynamic dispersion.

Initial concentration and hydraulic gradient were the two fundamental parameters for the design of permeable reactive filters given that they control the lifetime and the volumetric flow rate. At high As concentration (e.g., $C_0 > 0.1$ mg/L, one order of magnitude higher than the allowed concentration for drinking water), the main factor controlling the lifetime of reactive soil columns was the hydraulic gradient or seepage velocity. The modeling of soil barriers 0.1 m in length, initial concentration $C_0 = 1$ mg/L, and hydraulic gradient $i = 0.01$ showed that As concentrations in the effluent were lower than 0.01 mg/L during more than 2,800 and 1,600 days for samples A and B, respectively. Then, these materials can be used for the remediation of aquifers by means of permeable reactive barriers. However, lifetime reduces significantly

(a)

(b)
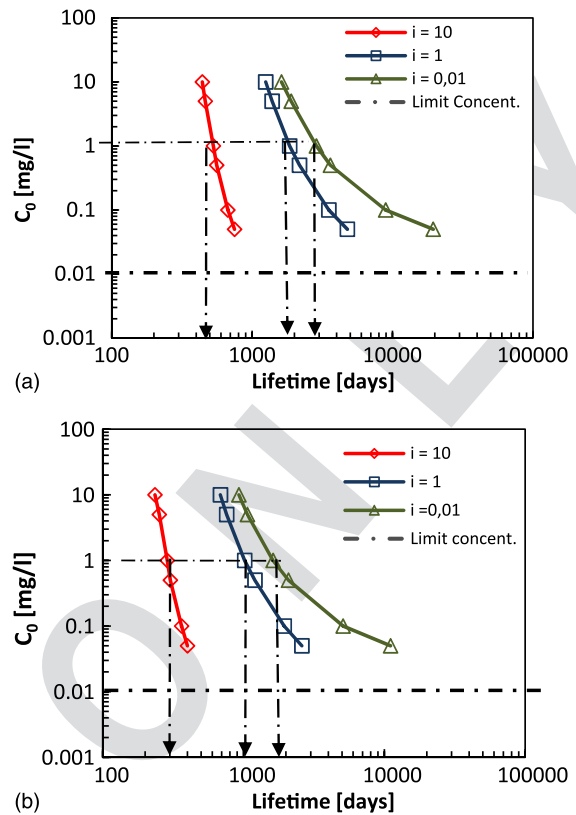
Fig. 7. Influence of the arsenic initial concentration (C_0) and hydraulic gradient (i) on the lifetime of permeable reactive soil columns: (a) sand-sample A mixture; (b) sand-sample B mixture — F7:1 F7:2 F7:3

when the hydraulic gradient increases, as in the case of filters in water purification systems (Fig. 7).

At very low As concentration ($C_0 < 0.1$ mg/L), the initial concentration has higher influence on lifetime than seepage velocity. In addition, regardless the hydraulic gradient, the lower the As concentration in the permeating liquid, the higher the lifetime of the reactive columns. At the limit, when $C_0 < 0.01$ mg/L, the expected lifetime was extremely long.

The higher maximum adsorption capacity of the lateritic sample A with respect to the lateritic sample B was associated with the higher amount of Fe (%) forming oxides and higher amount of particles less than 2 μm (clay size). The lateritic sample A contains Fe: 5.47% (w/w) and particles < 2 μm = 75%, while sample B contains only Fe: 2.98% (w/w) and particles < 2 μm = 66% (Table 1). Considering the minerals encountered in these samples of soils, the presence of hematite and goethite in samples A and B, respectively, is responsible for the adsorption and removal of As from the permeating liquid. Therefore, the higher the amount of Fe (%), the higher the lifetime of permeable reactive filters as observed from the comparison of Figs. 7(a and b).

Summary and Conclusions

Lateritic soils from the north of Argentina were very effective in removing arsenic in batch and soil column tests. Obtained results showed that this geomaterial can be used for the developing of alternative techniques for the remediation of arsenic contaminated groundwater.

More than 90% of arsenic removal was obtained in all batch tests. Inorganic As moved from aqueous solutions to the solid

phase by means of adsorption mechanisms that were successfully predicted by means of isotherm adsorption models. This observation was verified by measuring changes in the z-potential of the soil particles associated to the arsenic adsorption.

The Langmuir isotherm model well represented the experimental results obtained in this research with coefficient of determinations higher than $R^2 = 0.92$. The maximum adsorption capacity according to Langmuir equation resulted in the range of 0.262–0.295 mg/g.

Removal of As in reactive soil columns of laterite-sand mixtures reached values as high as 95–98% of the initial concentration. From the calibration of the mass transport equation, the longitudinal hydrodynamic dispersion coefficient and retardation factor resulted $D_L^* = 3.7 \times 10^{-12}$ (m^2/s) and $R = 1,377$ for the sample A and $D_L^* = 6.5 \times 10^{-12}$ (m^2/s) and $R = 1,170$ for the sample B.

The initial concentration and hydraulic gradient had a significant effect on the lifetime of soil columns and permeable reactive filters (until the As percolates). The effect of seepage velocity prevailed over the initial concentration when water contains high As levels. However, if initial concentration was lower than 0.03 mg/L, the influence of seepage velocity became of less importance, and the time required for the percolation of As became extremely long. These results confirm natural residual soils from the north of Argentina can be successfully used for the removal of As from water by means of low-cost reactive filters when the influence of competing ions can be neglected.

Acknowledgments

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