

Arsenic sorption onto natural hematite, magnetite, and goethite

Javier Giménez^{a,*}, María Martínez^a, Joan de Pablo^{a,b}, Miquel Rovira^b, Lara Duro^c

^a *Departament d'Enginyeria Química, Universitat Politècnica de Catalunya (UPC), Av. Diagonal 647, 08028 Barcelona, Spain*

^b *CTM Centre Tecnològic, Avda. Bases de Manresa 1, 08240 Manresa, Spain*

^c *ENVIROS-Spain S.L., Passeig de Rubí 29-31, 08197 Valldoreix, Spain*

Received 24 May 2006; received in revised form 10 July 2006; accepted 11 July 2006

Available online 15 July 2006

Abstract

In this work the sorption of As(III) and As(V) on different natural iron oxides (hematite, magnetite, and goethite) has been studied as a function of different parameters. The sorption kinetics for the three iron oxides shows that equilibrium is reached in less than 2 days and the kinetics of sorption seems to be faster for goethite and magnetite than for hematite. The variation of the arsenic sorbed on the three different sorbents as a function of the equilibrium arsenic concentration in solution has been fitted with a non-competitive Langmuir isotherm. The main trend observed in the variation of the arsenic sorbed with pH is the decrease of the sorption on the three sorbents at alkaline pH values, which agrees with results found in the literature. Highest As(III) sorption was observed on hematite surface in all the pH range compared to goethite and magnetite. Natural minerals studied in this work had similar sorption capacities for arsenic than synthetic sorbents.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Iron oxides; Langmuir isotherm; Metal sorption; Sorption kinetics

1. Introduction

Arsenic is a trace element toxic for the entire biota and it has been sometimes implicated in accidents with human mortality or disease [1–4]. Depending on the redox conditions, arsenic occurs in nature as As(III) and As(V), and due to the relatively slow arsenic redox transformations both oxidation states are often observed, being As(III) more toxic than As(V) [5–7].

The sorption of As(III) and As(V) onto iron oxides has been studied previously, actually, iron oxides seem to be responsible of the attenuation of arsenic in soils, and lacustrine and marine sediments [8–10 and references therein]. Different studies have been carried out on the As(III) and/or As(V) sorption on amorphous iron oxides [6,9,11,12] and on the arsenic sorption onto goethite, especially related to the As(V) sorption. In this sense, Grossl and Sparks [13] observed that the sorption of As(V) on goethite decreased with the increase of pH in the range 6–11, and Matis et al. [14] showed that both As(V) and

As(III) sorption on goethite decreased at neutral to alkaline pH and the variation of the sorption with the initial concentration of As(V) followed the Langmuir isotherm. Manning et al. [9] also observed a decrease of the As(V) sorption on goethite with pH while As(III) had a range of pH of maximum sorption between 5 and 9. A similar trend on the influence of pH on the sorption of arsenic(III) and (V) onto goethite was observed by Dixit and Hering [3] and Lenoble et al. [15]. The study of Bowell [16] showed that the sorption of arsenic (either As(III) and As(V)) is higher in a natural goethite than in a natural magnetite and higher for As(V) than for As(III). The variation of the sorption with pH showed a maximum at neutral pH. The sorption of As(V) on the natural goethite at pH 7 obtained by Bowell was calculated to be much lower than the one determined for freshly precipitated goethite [7]. In the case of the sorption of arsenic on hematite, Xu et al. [17] observed a decrease of the sorption of As(V) with the increase of pH. Singh et al. [18] also studied the sorption of As(V) on a natural hematite, they found that the sorption followed first-order kinetics and the data fitted a Langmuir isotherm. The variation of the sorption with pH showed a maximum at pH 4.2. Few studies can be found on the arsenic sorption on magnetite. Dixit and Hering [3] observed that As(III) sorption on magnetite increased with

* Corresponding author. Tel.: +34 934017388; fax: +34 934015814.
E-mail address: francisco.javier.gimenez@upc.edu (J. Giménez).

pH at pH values lower than 9 while at more alkaline pH the sorption decreased. A high sorption of both As(III) and As(V) on magnetite was observed by Parga et al. [19] when removing arsenic from a Mexican contaminated groundwater by using electrocoagulation.

In this work, we have tested the sorption of arsenic on natural magnetite, hematite, and goethite in order to compare the sorption capacity of these minerals with the one obtained by different authors when working with synthetic sorbents, because the minerals used in this work are naturally abundant and relatively low-cost materials. In this sense, the kinetics of sorption, the Langmuir isotherms as well as the influence of pH on the sorption of arsenic on the different natural iron oxides was studied.

2. Experimental

The solids used in this work were natural magnetite from Kiruna (Sweden), and hematite and goethite from Cerro del Hierro (Spain). The solids were crushed and sieved to the desired particle size (0.25 mm for hematite and goethite, and 0.1 mm for magnetite).

The surface area of the solids was determined by the BET methodology, the results obtained were: $0.381 \pm 0.002 \text{ m}^2 \text{ g}^{-1}$ for hematite; $2.009 \pm 0.004 \text{ m}^2 \text{ g}^{-1}$ for goethite, and $0.890 \pm 0.002 \text{ m}^2 \text{ g}^{-1}$ for magnetite.

The studies were carried out by sorption batch experiments at room temperature following the same experimental methodology than in [28]. The first series of tests (see below) indicated that the systems reached equilibrium in less than 2 days of contact. Once the equilibrium was reached, the tubes were centrifuged and samples of the supernatant solution were withdrawn and filtered through $0.22 \mu\text{m}$ pore size filters, and the arsenic content was determined by inductively coupled plasma atomic emission spectrometry (ICP).

The concentration of arsenic attached to the solids, $\{\text{As}\}_s$ in mol m^{-2} , was calculated by subtracting the final As concentration, $[\text{As}]$, to the initial As concentration added to the solution, $[\text{As}]_0$, and normalizing with the surface area (SA, in m^2) to volume (V , in dm^3) ratio:

$$\{\text{As}\}_s = ([\text{As}]_0 - [\text{As}]) \frac{V}{\text{SA}}$$

Three series of experiments were carried out for the sorption of As(V) and As(III) on each of the three solids (0.1 g of the solid were always used):

- (1) Variation of the sorption of arsenic (initial arsenic concentration: $2 \times 10^{-5} \text{ mol dm}^{-3}$) with time. The pH of the experiments was always between 6.5 and 7.5.
- (2) Variation of the initial metal concentration in solution (between 10^{-6} and $10^{-3} \text{ mol dm}^{-3}$) at a constant initial pH and solid/liquid ratio.
- (3) Variation of solution pH (between 3 and 12), at constant initial arsenic concentration ($2 \times 10^{-5} \text{ mol dm}^{-3}$).

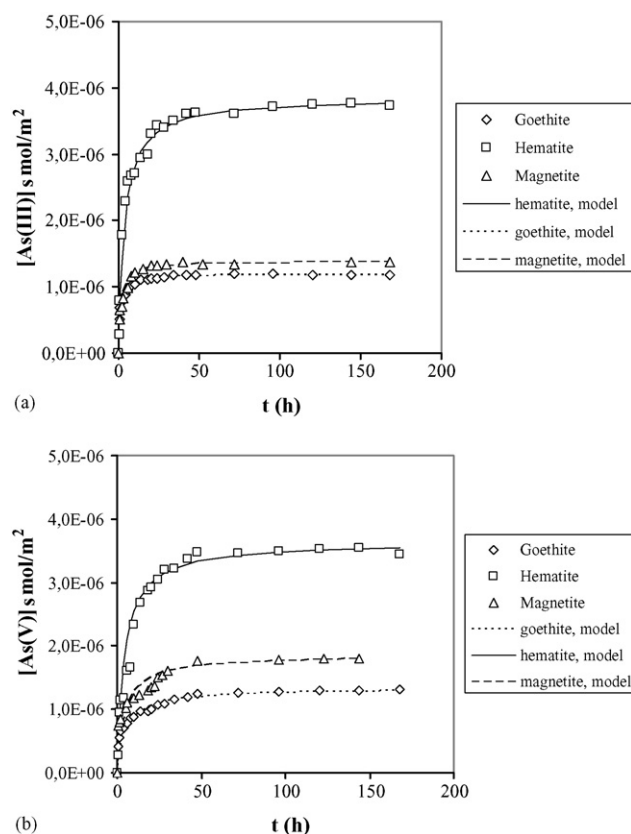


Fig. 1. Kinetics of sorption of (a) As(V), and (b) As(III) on the different solids used in this work. The experimental conditions were $[\text{As}]_0 = 2 \times 10^{-5} \text{ M}$ and 0.1 g of solid. The lines represent the fitting of the pseudo-second order rate equation.

3. Results

3.1. Sorption kinetics

The variation of the As(V) and As(III) sorption with the time of contact on the three solids is shown in Fig. 1 as $\{\text{As}\}_s$ versus time. As it can be seen, the equilibrium is always reached in less than 2 days.

The model of the kinetic data has been carried out using a pseudo-second order rate equation [20], which has been widely used to describe metal sorption (and also organic compounds sorption) on different sorbents [20,21]. The pseudo-second order kinetic rate equation is:

$$\frac{t}{\{\text{As}\}_s} = \frac{1}{k\{\text{As}\}_{s,\text{eq}}^2} + \frac{1}{\{\text{As}\}_{s,\text{eq}}}t$$

where $\{\text{As}\}_{s,\text{eq}}$ is the amount of metal sorbed at equilibrium (in mol m^{-2}), k the rate constant of sorption (in $\text{m}^2 \text{ mol}^{-1} \text{ h}^{-1}$) and $\{\text{As}\}_s$ is the amount of metal sorbed on the surface of the solid (in mol m^{-2}) at any contact time, t (in h).

When the experimental data from Fig. 1 were introduced into the equation, straight lines were obtained by plotting $t/\{\text{As}\}_s$ against t , indicating that the process follows the pseudo-second order rate equation. The results of the fitting of the model to the data are shown in Table 1. The good fitting of the model to

Table 1
Kinetic data of the sorption of As(III) and As(V) onto the natural solids

	Rate constant, k ($\text{m}^2 \text{mol}^{-1} \text{h}^{-1}$)	$\{\text{As}\}_{\text{s,eq}}$ ($\times 10^{-6} \text{mol m}^{-2}$)	R^2
As(III)–hematite	0.52 ± 0.01	3.84 ± 0.02	0.9996
As(III)–goethite	1.00 ± 0.01	1.19 ± 0.01	0.9998
As(III)–magnetite	0.82 ± 0.01	1.39 ± 0.01	0.9998
As(V)–hematite	0.48 ± 0.02	3.64 ± 0.03	0.998
As(V)–goethite	0.44 ± 0.02	1.33 ± 0.02	0.9990
As(V)–magnetite	0.47 ± 0.02	1.85 ± 0.02	0.998

the experimental data indicates that in all the cases the process follows a pseudo-second order rate. The fitting of the model to the experimental data is also shown in Fig. 1.

As it can be seen in Table 1, the rate constants for As(V) sorption on the three solids are very similar, while in the case of the As(III), the rate constant for the arsenic sorption onto hematite is lower than the ones for goethite and magnetite. The rate constants for As(III) are always higher than for As(V).

The fit of the experimental data to this equation could indicate that the process controlling the rate may be a chemical sorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate [22,23].

3.2. Effect of initial arsenic concentration

The variation of the arsenic sorbed on the three different solids as a function of the equilibrium As concentration in solution, $[\text{As}]$, is shown in Fig. 2 for both As(V) and As(III).

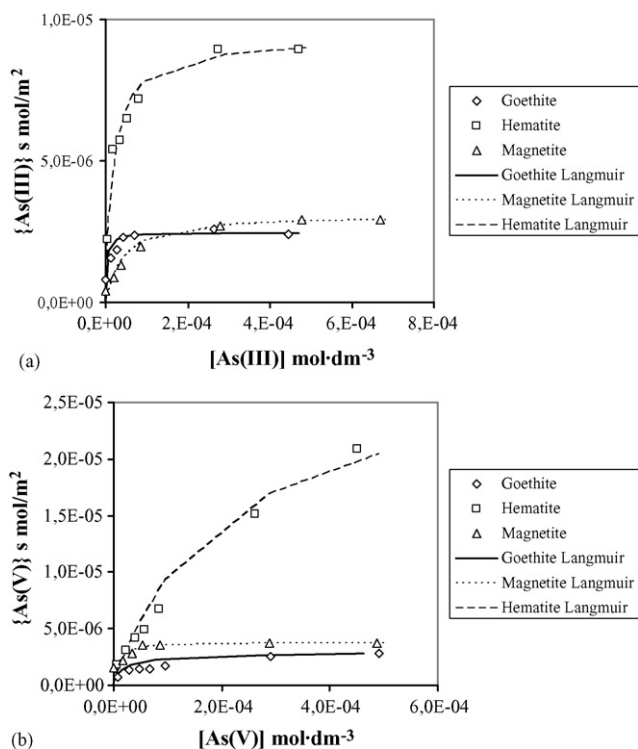
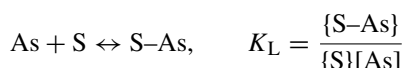


Fig. 2. Langmuir isotherms for (a) As(III), and (b) As(III) in hematite, goethite, and magnetite. 0.1 g of solid at pH 7.3, 6.5, and 7.5 for hematite, magnetite, and goethite, respectively.

The experimental data have been fitted with a non-competitive Langmuir isotherm, based on the following sorption equilibrium:



where K_L is the Langmuir constant, in $\text{dm}^3 \text{mol}^{-1}$, $\{\text{S-As}\}$ stands for the concentration of occupied surface sites, and $\{\text{S}\}$ for the free surface sites.

The Γ parameter, mol m^{-2} , is defined as the quantity of arsenic sorbed on the solid:

$$\Gamma = \frac{\{\text{S-As}\}}{\text{SA}}$$

and therefore:

$$\Gamma_{\text{max}} = \frac{\{\text{S}\}_{\text{tot}}}{\text{SA}}$$

where Γ_{max} is the maximum metal sorption, in mol m^{-2} , and $\{\text{S}\}_{\text{tot}}$ stands for the total number of surface sites:

$$\{\text{S}\}_{\text{tot}} = \{\text{S}\} + \{\text{S-As}\}$$

From these equations we can deduce:

$$\Gamma = \Gamma_{\text{max}} \frac{K_L[\text{As}]}{1 + K_L[\text{As}]}$$

The linearized form of this equation was used to obtain the values of the parameters Γ_{max} , and K_L :

$$\frac{[\text{As}]}{\Gamma} = \frac{[\text{As}]}{\Gamma_{\text{max}}} + \frac{1}{\Gamma_{\text{max}}K_L}$$

The linear plot of $[\text{As}]/\Gamma$ against $[\text{As}]$ resulted in the values shown in Table 2. The fitting of the Langmuir isotherm is shown in Fig. 2 together with the experimental values. A good applicability to the results obtained with arsenic(III), and with arsenic(V) sorbed on goethite and magnetite is observed, indicating a monolayer coverage on the iron mineral surface. However, a worse fitting is obtained for the sorption of As(V) onto hematite, actually, a constant $\{\text{As}\}_{\text{s}}$ is not reached even at the highest values of the $[\text{As}]$.

As we can see in Table 2, both As(III), and As(V) are more efficiently sorbed on hematite than in goethite or magnetite. The Γ_{max} varies between 2.5×10^{-6} and $9.0 \times 10^{-6} \text{mol m}^{-2}$ (except for the As(V) sorption on hematite), values that are in the range given by Davis and Kent [24] for most oxides and silicates: 1.7×10^{-6} to $1.7 \times 10^{-5} \text{mol m}^{-2}$.

Table 2
Parameters of the Langmuir isotherms obtained for As(V) and As(III) sorption on hematite (at $\text{pH}_{\text{eq}} 7.3$), magnetite (at $\text{pH}_{\text{eq}} 6.5$), and goethite (at $\text{pH}_{\text{eq}} 7.5$)

	K_L ($\text{dm}^3 \text{mol}^{-1}$)	Γ_{max} (mol m^{-2})	R^2
Hematite			
As(III)	$(5.5 \pm 0.1) \times 10^4$	$(9.3 \pm 0.2) \times 10^{-6}$	0.9990
As(V)	$(5 \pm 1) \times 10^3$	$(2.9 \pm 0.5) \times 10^{-5}$	0.85
Magnetite			
As(III)	$(2.50 \pm 0.01) \times 10^4$	$(3.1 \pm 0.1) \times 10^{-6}$	0.996
As(V)	$(1.4 \pm 0.5) \times 10^5$	$(3.8 \pm 0.2) \times 10^{-6}$	0.9994
Goethite			
As(III)	$(3.2 \pm 0.1) \times 10^5$	$(2.5 \pm 0.1) \times 10^{-6}$	0.998
As(V)	$(3.18 \pm 0.04) \times 10^4$	$(3.0 \pm 0.2) \times 10^{-6}$	0.986

The K_L parameter is related to the energy of sorption of the metal on the solid surface. From our results it can be deduced that As(III) is more strongly sorbed onto goethite, while As(V) onto magnetite, at the experimental pH and metal concentration range studied.

3.3. Variation of arsenic sorption with pH

The variation of As sorption with pH has been carried out at an initial arsenic concentration of $2 \times 10^{-5} \text{ mol dm}^{-3}$ and with 0.1 g of each solid. The results obtained for As(V) and As(III) are shown in Fig. 3. The main trend observed in this figure is the decrease of the sorption of either As(III) and As(V) on the three solids with equilibrium pH at alkaline pH values, which agrees with results obtained in previous works [3,9,14,18].

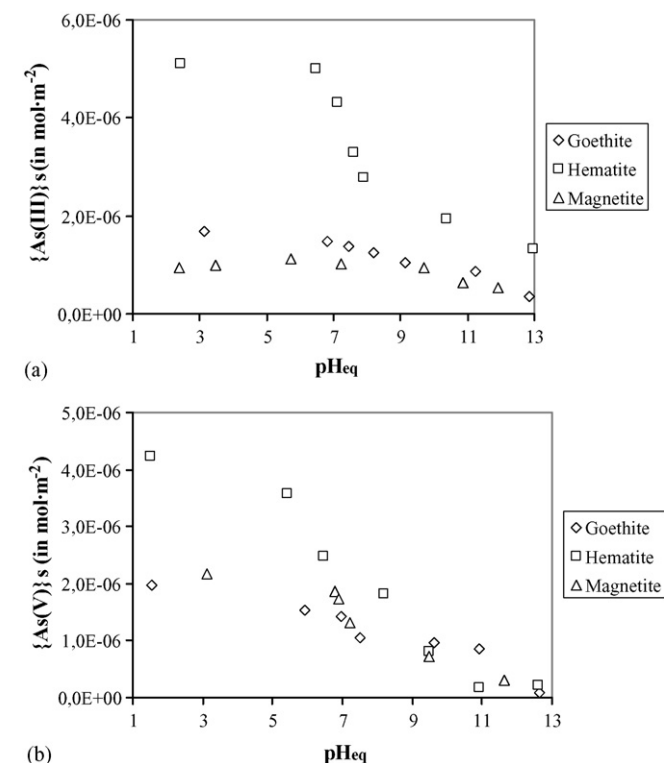


Fig. 3. Variation of the (a) As(V), and (b) As(III) sorption with pH. 0.1 g of solid and $[\text{As}]_0 = 2 \times 10^{-5} \text{ M}$.

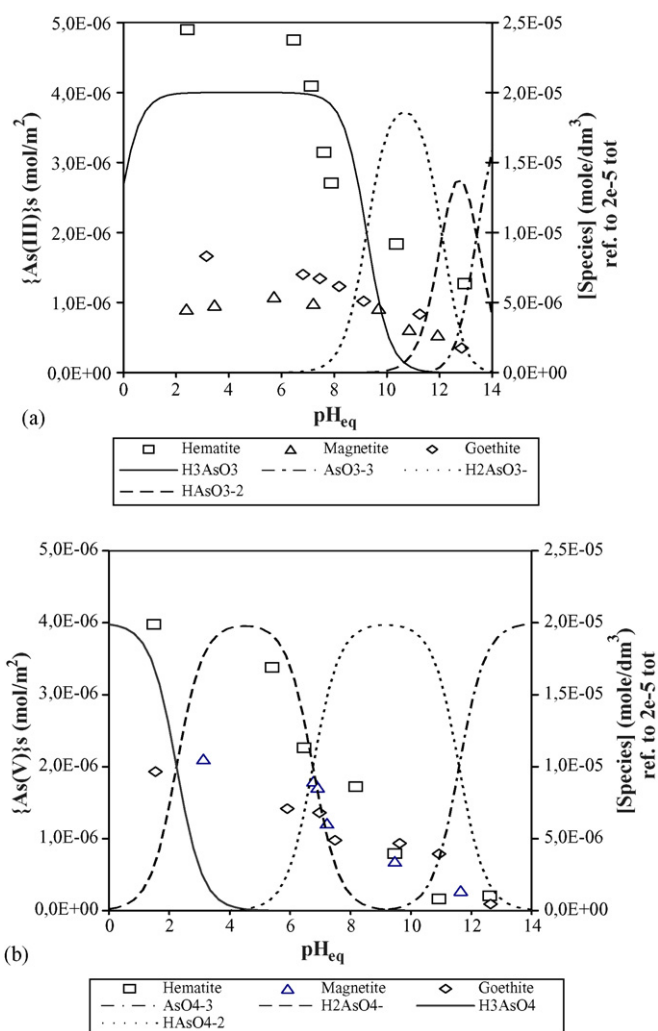


Fig. 4. Variation of the sorption of (a) As(III), and (b) As(V) with pH (points) together with the predominance of the different arsenic species in solution according to the MEDUSA code [25] with a total arsenic concentration of $2 \times 10^{-5} \text{ mol dm}^{-3}$ (lines).

The experimental data together with the fraction diagram of arsenic species, which has been obtained using the MEDUSA code [25] are shown in Fig. 4 for both oxidation states. In the case of As(V), the sorption decreases as the percentage of the aqueous species H_2AsO_4^- decreases, because at these pH values, the surface of the solids is positively charged, the pH_{ZPC} are: magnetite, 6.5; goethite, 6.8; hematite, 6.7 [26,27]. For As(III), the sorption edge coincides with the predominance of $\text{H}_3\text{AsO}_3(\text{aq})$. At more alkaline pH, anionic arsenic(III) species predominate and the surface of the solid is also negatively charged, thus making more difficult the interaction between arsenic and the minerals. It is also shown how the maximum sorption is observed in the case of hematite, indicating the larger affinity of this solid for the sorption of As, both in V and III oxidation states. The different behavior at acidic pH can be attributed to the relative dissolution of the minerals used in the studies, which would influence the total number of sorption sites [18].

Table 3
Surface area of the solids

Solid	Surface area ($\text{m}^2 \text{g}^{-1}$)	Reference
Goethite	134–139	[14]
Goethite	45	[9]
Goethite	54	[3]
Goethite	50	[13]
Natural hematite	14.4	[18]
Magnetite	90	[3]

3.4. Comparison of arsenic sorption on natural hematite, magnetite, and goethite with its synthetic forms

The sorption capacities obtained in this work (in terms of variation of arsenite sorption in mol m^{-2} with pH) with natural sorbents have been compared with previous results obtained using its synthetic forms. For the comparison of the sorption of As(III), different works have been considered: Matis et al. [14] who studied the arsenic sorption on a synthetic goethite; Manning et al. [9] who also worked with a synthetic goethite; and Dixit and Hering [3] who made arsenic sorption experiments on goethite and magnetite (both synthetic). As far as we know, the variation with pH has not been determined for the As(III) sorption on hematite. The comparison has been made normalizing the results given by these authors with respect to the surface area, which is shown for the different solids in Table 3. The arsenic(III) sorption variation with pH is shown in Fig. 5. As it can be seen, the results obtained with natural and with synthetic sorbents are similar. An approximately constant sorption of As(III) is obtained at acidic to neutral pH while it decreases at alkaline pH.

In the case of the As(V), no previous works on the influence of pH on the As(V) sorption onto synthetic hematite or synthetic magnetite were found. For this reason, the comparison was made

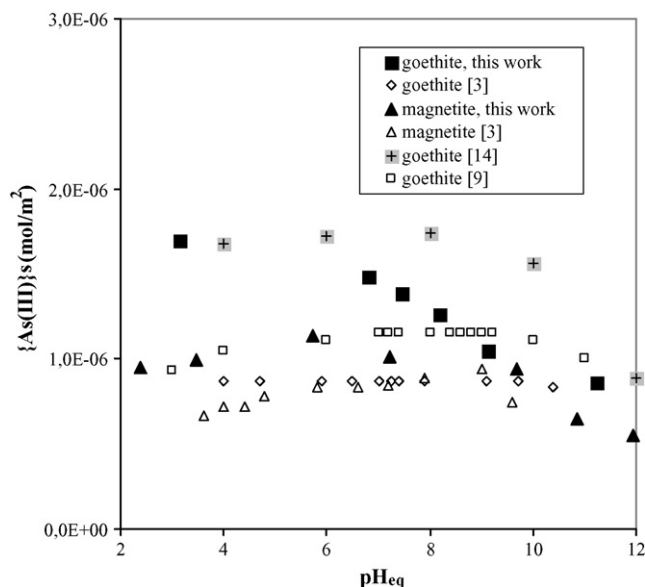


Fig. 5. Sorption variation with pH obtained in this work for As(III) compared to the results found by different authors.

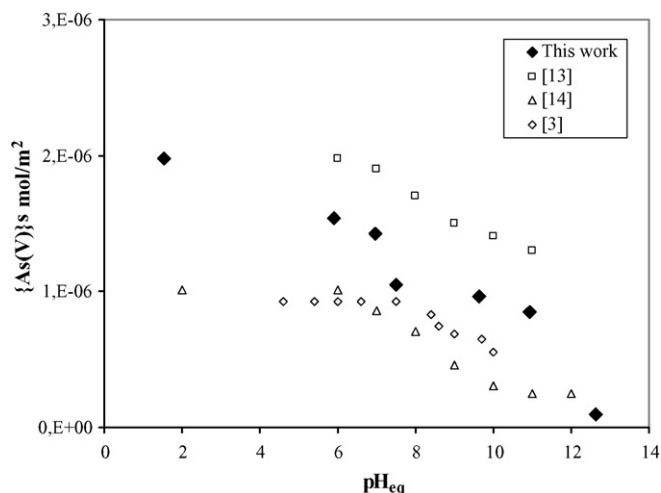


Fig. 6. Sorption variation with pH obtained in this work for the As(V) sorption onto goethite compared to the results found in the literature.

only with the results obtained by Singh et al. [18], who used a natural hematite from Noamundi. The $\{\text{As}\}_s$ values obtained in our work are more than one order of magnitude higher than the determined by Singh et al. [18] in almost all the pH range studied (only at pH values higher than 10, both $\{\text{As}\}_s$ are similar, data not shown). More works were found related to the sorption of arsenic(V) onto goethite: Grossl and Sparks [13], Matis et al. [14], and Dixit and Hering [3] used synthetic goethite (with surface area values shown in Table 3). As it can be seen in Fig. 6, the sorption capacity of the natural goethite is very similar to the sorption capacity of the synthesized material, as we observed for As(III).

The main point obtained from these comparisons is that the sorption capacities of the different solids (either natural or synthetic) are similar when are normalized with respect to the surface area, which is much lower in the natural minerals than in the synthetic materials. This could indicate that the arsenic sorption mechanism on the natural minerals used in this work would be similar to the one developed for synthetic materials [3,9,13–18].

4. Conclusions

Natural hematite, goethite, and magnetite are suitable agents to remove both As(III) and As(V) from solutions, being natural hematite the solid that presents the highest sorption capacity, especially at acidic pH.

The behavior of the natural solids is similar to the synthesized solids in the cases where we were able to make a comparison: As(III) with goethite and magnetite and As(V) with goethite. This indicates that the experimental methodologies applied are free of artifact effects which are relatively common in trace element sorption investigations. The similar sorption capacities of the natural solids used in this work and the synthesized materials used by different authors could indicate that the sorption mechanism is similar in both kinds of solids.

The natural iron oxide minerals used in this work are suitable candidates as sorbents in As(III) and As(V) removal technolo-

gies, considering that these sorbents are naturally abundant and relatively low-cost materials.

Acknowledgments

This work has been financially supported by the Spanish ‘Ministerio de Educación y Ciencia’ by means of the CGL2005-08019-C04-03 project and the ‘Ramón y Cajal’ programme.

References

- [1] R.T. Nickson, J. McArthur, W. Burgess, K.M. Ahmed, P. Ravenscroft, M. Rahman, Arsenic poisoning of Bangladesh groundwater, *Nature* 395 (1998) 338.
- [2] M. Berg, H.C. Tran, T.C. Nguyen, H.V. Pham, R. Schertenleib, W. Giger, Arsenic contamination of groundwater and drinking water in Vietnam: a human health treat, *Environ. Sci. Technol.* 35 (2001) 2621–2626.
- [3] S. Dixit, J.G. Hering, Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: implications for arsenic mobility, *Environ. Sci. Technol.* 37 (2003) 4182–4189.
- [4] V.K. Gupta, V.K. Saini, J. Neeraj, Adsorption of As(III) from aqueous solutions by iron oxide-coated sand, *J. Colloid Interf. Sci.* 288 (2005) 55–60.
- [5] W.R. Cullen, K.J. Reimer, Arsenic speciation in the environment, *Chem. Rev.* 89 (1989) 713–764.
- [6] S. Goldberg, C.T. Johnston, Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modeling, *J. Colloid Interf. Sci.* 234 (2001) 204–216.
- [7] P.L. Smedley, D.G. Kinniburgh, A review of the source, behaviour and distribution of arsenic in natural waters, *Appl. Geochem.* 17 (2002) 517–568.
- [8] B.A. Manning, S. Goldberg, Modeling competitive adsorption of arsenate with phosphate and molybdate on oxide minerals, *Soil Sci. Soc. Am. J.* 60 (1996) 121–131.
- [9] B.A. Manning, S.E. Fendorf, S. Goldberg, Surface structures and stability of arsenic(III) on goethite: spectroscopic evidence for inner-sphere complexes, *Environ. Sci. Technol.* 32 (1998) 2383–2388.
- [10] K.A. Sullivan, R.C. Aller, Diagenetic cycling of arsenic in Amazon shelf sediments, *Geochim. Cosmochim. Acta* 60 (1996) 1465–1477.
- [11] J.A. Wilkie, J.G. Hering, Adsorption of arsenic onto hydrous ferric oxide: effects of adsorbate/adsorbent ratios and co-occurring solutes, *Colloid Surf. A* 107 (1996) 97–110.
- [12] P.J. Swedlund, J.G. Webster, Adsorption and polymerization of silicic acid on ferrihydrate, and its effect on arsenic adsorption, *Water Res.* 33 (1999) 3413–3422.
- [13] P.R. Grossl, D.L. Sparks, Evaluation of contaminant ion adsorption/desorption on goethite using pressure-jump relaxation kinetics, *Geoderma* 67 (1995) 87–101.
- [14] K.A. Matis, A.I. Zouboulis, F.B. Malamas, M.D.R. Afonso, M.J. Hudson, Flotation removal of As(V) onto goethite, *Environ. Pollut.* 97 (1997) 239–245.
- [15] V. Lenoble, O. Bouras, V. Deluchat, B. Serpaud, J.-C. Bollinger, Arsenic adsorption onto pillared clays and iron oxides, *J. Colloid Interf. Sci.* 255 (2002) 52–58.
- [16] R.J. Howell, Sorption of arsenic by iron-oxides and oxyhydroxides in soils, *Appl. Geochem.* 9 (1994) 279–286.
- [17] H. Xu, B. Allard, A. Grimvall, Influence of pH and organic substance on the adsorption of As(V) on geologic materials, *Water Air Soil Pollut.* 40 (1988) 293–305.
- [18] D.B. Singh, G. Prasad, D.C. Rupainwar, Adsorption technique for the treatment of As(V)-rich effluents, *Colloid Surf. A* 111 (1996) 49–56.
- [19] J.R. Parga, D.L. Cocco, J.L. Valenzuela, J.A. Gomes, M. Kesmez, G. Irwin, H. Moreno, M. Weir, Arsenic removal via electrocoagulation from heavy metal contaminated groundwater in La Comarca Lagunera México, *J. Hazard. Mater.* 124 (2005) 247–254.
- [20] Y.S. Ho, G. McKay, Pseudo second-order model for sorption processes, *Process Biochem.* 34 (1999) 451–465.
- [21] M. Martínez, N. Miralles, S. Hidalgo, N. Fiol, I. Villaescusa, J. Poch, Removal of lead(II) and cadmium(II) from aqueous solutions using grape stalk waste, *J. Hazard. Mater. B* 133 (2006) 203–211.
- [22] V.C. Taty-Costades, H. Faudest, C. Porte, A. Delacroix, Removal of Cd(II) and Pb(II) ions, from aqueous solutions, by adsorption onto sawdust of *Pinus sylvestris*, *J. Hazard. Mater. B* 105 (2003) 121–142.
- [23] Y.S. Ho, W.T. Chiu, C.S. Hsu, C.T. Huang, Sorption of lead ions from aqueous solution using tree fern as a sorbent, *Hydrometallurgy* 73 (2004) 55–61.
- [24] J.A. Davis, D.B. Kent, Surface complexation modelling in aqueous geochemistry, *Rev. Mineral. Geochem.* 23 (1990) 177–260.
- [25] I. Puigdomènech, MEDUSA, 2004. <http://www.w1.156.telia.com/~u15651596>.
- [26] D.A. Sverjensky, Zero-point-of-charge prediction from crystal chemistry and salvation theory, *Geochim. Cosmochim. Acta* 58 (1994) 3123–3129.
- [27] D.A. Sverjensky, N. Sahai, Theoretical prediction of single-site surface-protonation equilibrium constants for oxides and silicates in water, *Geochim. Cosmochim. Acta* 60 (1996) 3773–3797.
- [28] M. Martínez, J. Giménez, J. de Pablo, M. Rovira, L. Duro, Sorption of selenium(IV) and selenium(VI) onto magnetite., *Appl. Surf. Sci.* 252 (2006) 3767–3773.