

New functionalized magnetic materials for As⁵⁺ removal. Adsorbent regeneration and reuse

*Juan Saiz, Eugenio Bringas and Inmaculada Ortiz**

Dept. Ingenierías Química y Biomolecular, ETSIIyT, Universidad de Cantabria, Avda Los Castros s/n, 39005 Santander, Spain
Tel.: +34 942201585; Fax: +34942201591
E-mail: ortizi@unican.es

Viability results

Arsenate desorption may be affected by several operational variables like contact time, pH, desorption agent concentration or adsorbent/adsorbate characteristics.^{1,2} Table S1³⁻¹⁵ compiles information about different works reported in the literature dealing with the regeneration and reusability of several adsorbents employed in the removal of arsenic.

The desorption performance from arsenate-loaded M3 materials ($20.9 \text{ mg As}^{5+} \text{ g}^{-1}$) was studied at different contact times (1-15 hours) employing HCl 0.05 mol L^{-1} and NaOH 0.05 mol L^{-1} as regeneration agents. Water rinsing was also performed to quantify the influence of the solvent on arsenic elution.¹⁰ The reusability of the previously unloaded materials and the quantification of iron leaching during the desorption step, as evidence of the loss of F2 functionalization, were also assessed.

Figure S1 shows the mean values of the desorption percentages and the effect of the solvent on the arsenic elution.⁴

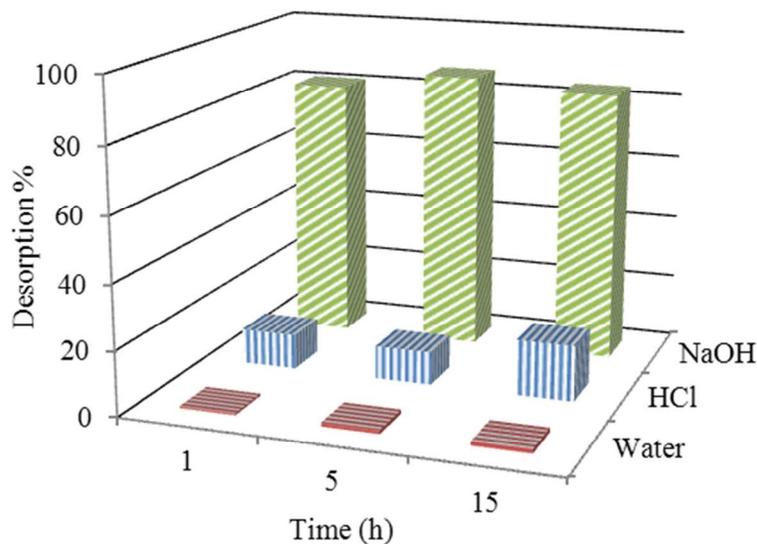


Figure S1. Efficacy of arsenate desorption employing water, $0.05 \text{ mol HCl L}^{-1}$ and $0.05 \text{ mol NaOH L}^{-1}$ ($q_e=20.9 \text{ mg g}^{-1}$; $V_d=15 \text{ mL}$; $m_d=15 \text{ mg}$).

Table S1. Literature information about arsenic desorption and re-adsorption employing nanoadsorbents.

Material	Metal	Desorption agent	Concentration (mol L⁻¹)	Time (h)	Desorption (%)	Re-adsorption (%)
Amine modified silica gel³	As ⁵⁺	HNO ₃	3	4	94.8	-
		HCl	3	4	95.2	-
Maghemite⁴	As ⁵⁺	NaOH	1	50	100	-
		Na ₂ CO ₃	0.1	50	80	-
Amino functionalized densified cellulose⁵⁻⁷	As ⁵⁺	NaCl	0.1	1	99.9	97
		NaOH	0.1	1	96	98
Chitosan⁸	As ⁵⁺	H ₂ SO ₄	0.05	6	36	-
		NaOH	0.05	6	99	-
Phosphonium silane coated magnetic nanoparticles⁹	As ⁵⁺	NaOH	0.01	4	89.4	-
		Na ₂ HPO ₄	0.01	4	38.5	-
		NaHCO ₃	0.01	4	39.9	-
		Na ₂ CO ₃	0.01	4	64	-
Activated carbon¹⁰	As ⁵⁺	NaOH	0.5	72	100	-
		NaCl	0.5	72	100	-
		NaNO ₃	0.5	72	100	-
Ferric-manganese oxide¹¹	As ⁵⁺	HCl	6	48	100	-
Funtionalized biopolymers¹²	As ⁵⁺	HCl	0.01	0.5	-	100
Iron oxide coated cement¹³	As ³⁺	NaOH	2.5	2	98.8	98.8
Amino-alkyl alkoxy silanes silica nanoparticles¹⁴	As ⁵⁺	HCl	1	10	99	87
Akaganeite cristals¹⁵	As ⁵⁺	NaOH	0.01	24	75	75
Amino-alkyl alkoxy silanes magnetic silica nanoparticles (this work)	As ⁵⁺	HCl	0.05-4	1-15	80-0	0-94
		NaOH	10 ⁻³ -0.05	0.25-15	90-99	0-100

From the results depicted in Figure S1 it is concluded that arsenate desorption is pH dependent (see Figure S1) as was expected from the strong influence of this variable on the As^{5+} adsorption equilibria since the pH affects both the arsenic speciation and the specific charge on the material surface; similar trends have been already reported for a wide range of functionalized nanoscale adsorbents.^{6,8,9} On the other hand, the process is not time dependant reaching equilibrium conditions after the first contact analyzed ($t=1$ hour).

The low release of arsenic ($<1.5\%$) confirms the negligible effect of water on the arsenic elution fact that is explained by the extremely favored adsorption equilibrium at neutral pH conditions observed in previous works.^{4,16} The average As^{5+} desorption percentages obtained with 0.05 mol L^{-1} solutions of HCl and NaOH were 17.2% and 84% , respectively. Therefore, at the same concentration level desorption in basic media is approximately 5 times more effective than in acidic conditions. The promising results obtained with NaOH are attributed to the fast deprotonation of the amino groups therefore recovering their initial basic form.¹⁷ Figure S2 depicts the adsorption percentages obtained by contacting during one hour an arsenate solution (20 mg L^{-1}) with either the functionalized material as synthesized (M3) or with the materials that have been subjected to one desorption cycle. These experiments were performed immediately after the desorption tests employing the material without neither F1 nor F2 regeneration stages.

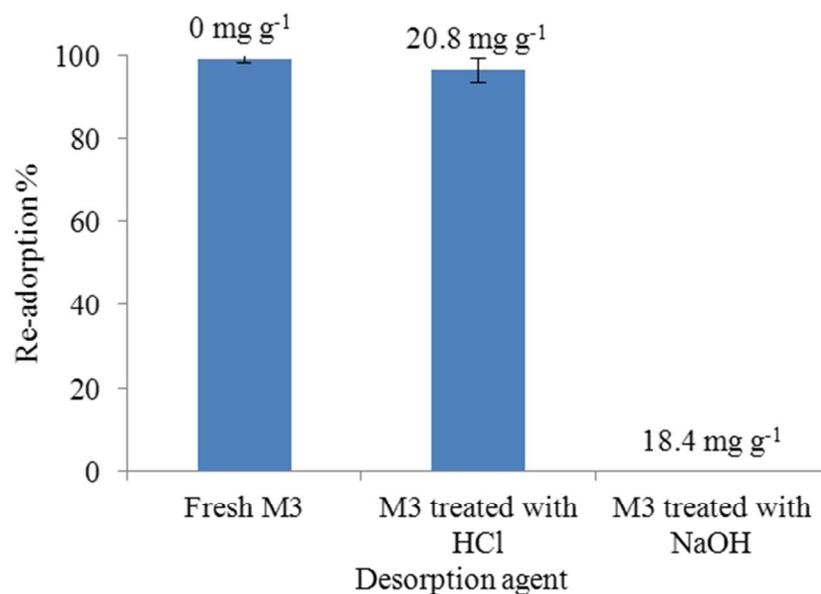


Figure S2. Comparisson of arsenate adsorption efficacy with fresh (material M3) and unloaded materials ($C_i=20 \text{ mg L}^{-1}$; $V_a=15 \text{ mL}$; $m_a=15 \text{ mg}$). The values above the bars refer to the arsenic concentration on the solid before the adsorption step (q_0).

It is observed that in spite of the low desorption efficacies obtained by washing the materials with water (<1.5%) and HCl 0.05 mol L^{-1} (<20%) the adsorption percentages of As^{5+} were almost 100% and close to the values obtained with the fresh solid M3. This behavior is related to the lower values of the effective arsenic concentration on the surface of the washed solid (depicted above the bars in Figure S2) as compared to the maximum adsorption capacity reported for material M3, $121 \pm 4.1 \text{ mg As}^{5+} \text{ g}^{-1}$.¹⁶ Therefore, the theoretical values of the removal percentages calculated by Eq. (1) and the Langmuir equation with the parameters obtained by Saiz et al.,¹⁶ ($q_m=121 \pm 4.1 \text{ mg g}^{-1}$ and $K_L=0.383 \pm 0.066 \text{ L mg}^{-1}$) are approximately 94% thus falling in the range of the experimental values. When the material treated with NaOH 0.05 mol L^{-1} , was reused for adsorption purposes the removal of arsenic was negligible as shown in Figure S2; these results can be explained by the fact that at pH values lower than $\text{pK}_a \approx 9-10$ typically found for primary, secondary and tertiary amines and corresponding to

the adsorption solutions, the amino groups were associated with hydrogen ions forming RNH_3^+ , RNH_2^+ and RNH^+ whereas at higher pH values (not used in the experiments), the number of hydrogen ions available decreased and hence the density of basic amino groups increases affecting the ability of the material to uptake arsenate oxyanions.^{8,16} In addition Figure S3 shows the measurement of the surface zeta potential of water suspensions containing the functionalized materials as synthesized and after their regeneration with hydrochloric acid (0.05 mol L^{-1}) and sodium hydroxide (0.05 mol L^{-1}).

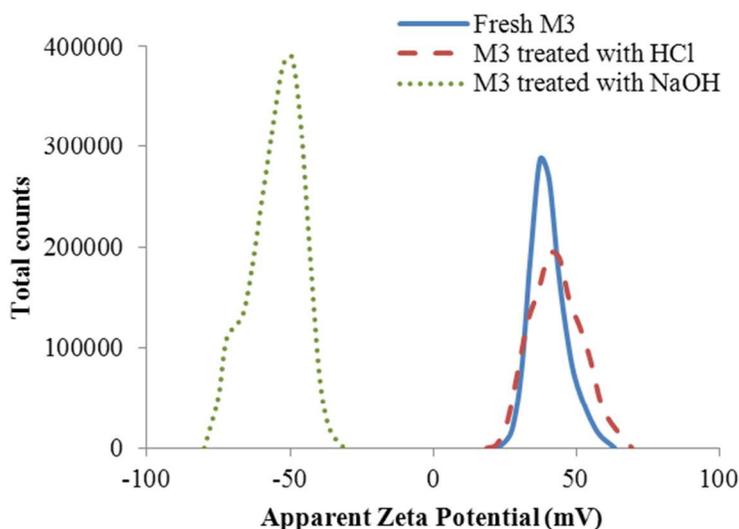


Figure S3. Comparison of the surface zeta potential corresponding to fresh solids and materials after desorption.

The zeta potential is a function of the surface charge of the particle and any layer adsorbed at the interface and the nature and composition of the medium in which the particle is suspended. The results obtained confirm the material stability since values of zeta potential over 30 mV (negative or positive) are usually related to particles electrically stable while lower values promoted agglomeration phenomena.¹⁸⁻²¹ It is also concluded that the fresh material and the solid treated with HCl have positive values of zeta potential near 36.5 mV thus confirming the positive charge of the surface that allows the uptake of arsenate

oxyanions as observed in the data reported in Figure S2. On the other hand, the material washed with NaOH reported negative zeta potential values around -52.6 mV that explain the negligible re-adsorption capacity depicted in Figure S3 due to repulsion effects. The discussion of the results in Figures S2 and S3 leads to the conclusion that after the desorption process with NaOH the functionalization F1 of the sorbent material is affected and therefore a re-functionalization stage with HCl is required to turn the amino groups into the acidic form. On the other hand, this stage is not needed for acid regeneration. Yokoi and collaborators¹⁴ described the release of iron into the solution as the desorption of the target species takes place for a material similar to M3. Therefore the leaching of iron from material M3 under acid and basic conditions was analysed and results are reported in Figure S4.

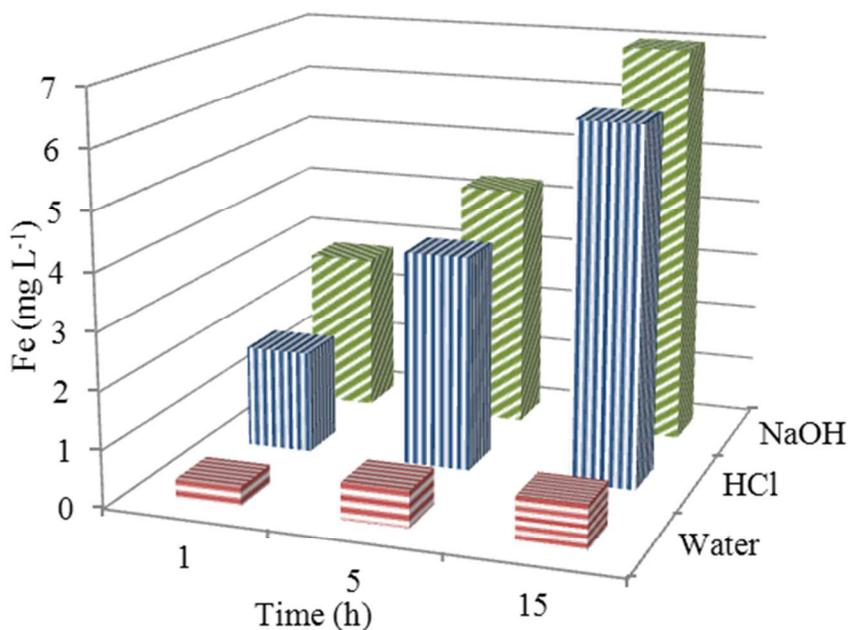


Figure S4. Influence of the contact time and the desorption agent on the leaching of iron (functionalization F2) from the material M3.

It is observed that the concentration of iron in water, contacted during 15 hours with the solid M3 is around 0.5 mg L^{-1} thus confirming the stability of the functionalized material at neutral pH conditions as was demonstrated in previous works.¹⁶ On the other hand, higher concentrations of iron (between 2 and 7 mg L^{-1}) are observed after contacting the solid with 0.05 mol L^{-1} solutions of HCl and NaOH being these values higher as the contact time increases.

In the case of desorption with NaOH, Figure S1 reports that yields up to 80% were reached in 1 hour remaining this value constant as the contact time increases; however, the leaching of iron continued increasing with time therefore suggesting that the desorption time should be controlled to avoid the surface functionalization F2 to be affected. Otherwise, iron should be coordinated again by a subsequent re-functionalization step.

Similar leaching results were found for HCl desorption. Although the analysis of the reusability results given in Figure S2 leads to the conclusion that functionalization F1 of the solid treated with HCl was not highly affected, the loss of Fe^{3+} alters the surface functionalization F2 in a similar way than the observed for alkaline conditions.¹⁴ The partial loss of functionalization F2 may not affect the process efficacy at low number of adsorption/desorption cycles since material M2 also possess the ability to absorb arsenate. On the other hand, the lower values of the maximum adsorption capacity of M2, ($45.5 \pm 2.0 \text{ mg As}^{5+} \text{ g}^{-1}$) and the lower iron content of material M2 as compared to material M3 might affect the long-term performance and selectivity of the process.¹⁶ It is therefore concluded that loaded material treated under acid and alkaline conditions should be subjected to regeneration by F2 re-functionalization.

The leaching of iron initially coordinated to alkoxysilane might be explained by the instability of those organo-metallic complexes under strong acidic conditions which promote the

protonation of amines. Vasiliev et al.,²¹ evaluated the leaching of different metallic compounds (Cu, Zn, Ni, Pb and Cd) previously adsorbed by coordination with aminoalkyl alkoxy silanes grafted onto porous materials. In spite of the percentages of metal leached depended on the metal, on the surface functionalization and on the pH conditions, in all the situations their values varied in the range between 45% and 100% when acetic acid 1.7 mol L⁻¹ was employed as leaching agent.

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