CHEMICAL ENGINEERING TRANSACTIONS
VOL. 47, 2016

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Angelo Chianese, Luca Di Palma, Elisabetta Petrucci, Marco Stoller

ISBN 978-88-95608-38-9; **ISSN** 2283-9216

DOI: 10.3303/CET1647041

Design of Novel Adsorption Processes for the Removal of Arsenic from Polluted Groundwater Employing Functionalized Magnetic Nanoparticles

Jenifer Gómez-Pastora, Eugenio Bringas*, Inmaculada Ortiz

Dept. Chemical and Biomolecular Engineering, University of Cantabria, Avda. los Castros s/n, 39005, Santander (Spain)
bringase@unican.es

For many developing countries, groundwater is the main source for water consumption in rural and urban areas. The occurrence of arsenic in groundwater is an environmental problem due to its high toxicity. Although the removal of arsenic by different technologies has been proven, adsorption is one of the best alternatives due to its simplicity and low cost. In particular, nanoadsorbents incorporating magnetic properties are promising separation agents because of their advantageous and efficient potential recovery in a magnetic field, characteristic that is very attractive and of utmost relevance in the development of low cost technologies to provide drinking water in developing countries. In this work, Fe_3O_4 and Fe_3O_4/SiO_2 magnetic nanoparticles functionalized by amino derivatives coordinated with Fe^{3+} were synthesized and characterized and further evaluated as adsorbents to remove arsenate from groundwater. The adsorption equilibrium of As^{5+} was satisfactorily described at 298 K by the Langmuir model with the following parameters: a) Fe_3O_4: q_m=20.4±0.3 mg g^{-1} and K_L=0.373±0.003 L mg^{-1} and b) Fe_3O_4/SiO_2: q_m=121±4.1 mg g^{-1} and K_L=0.383±0.066 L mg^{-1}. At low arsenate concentrations, 50-1000 μg L^{-1}, the adsorption equilibrium As^{5+}- Fe_3O_4/SiO_2 was described by linear isotherms with equilibrium parameters K_H=278.8 L g^{-1} in monocomponent systems and K_H=1.80 L g^{-1} in the presence of competing ions, being carbonate and especially phosphate the main species affecting the process with contributions to the loss of efficacy around 70%. Finally, the material reuse after regeneration with NaOH 10^{-3} mol L^{-1} was assessed under several composition scenarios reaching adsorption yields similar to those obtained with fresh materials.

1. Introduction

Groundwater, constituting 97% of global freshwater and being used for drinking by more than 50% of the world population, serves as the only economically viable option for many communities in developing countries. However, the presence of several naturally occurring and human induced elements may greatly degrade the water quality (Mara, 2003). One of the most harmful pollutants to the human health, recognized worldwide by the World Health Organization is arsenic. The level of arsenic in natural waters generally ranges from 1 and 2 μg L^{-1} (Hindmarsh and McCurdy, 1986; USNRC, 1999). However, its concentration may increase up to 500-1000 μg L^{-1} due to natural phenomena such as the leaching from volcanic rocks and sulfide mineral deposits (Hindmarsh and McCurdy, 1986). Therefore, the guideline value for arsenic is 10 μg L^{-1} adopted by the WHO in 1993, and lowered by EPA from the previous value of 50 μg L^{-1} in 2001 (Murcortt, 2012).

Several methods of arsenic removal are already available including precipitation, electrochemical reduction, solvent extraction, nanofiltration and reverse osmosis (Mayo et al., 2007). Among the available technologies to remediate groundwater containing arsenic, adsorption and ion exchange are efficient alternatives because of their simplicity, sludge-free operation, easy regeneration of the separation agent and cost effectiveness (Jadhav et al., 2015). In particular, nanomaterials exhibit an array of properties such as the ease of functionalization and large surface area, which make them suitable for designing novel selective separation processes (Hristovski et al., 2007). If magnetic properties are incorporated in the nanosized structure, the high gradient magnetic separation of the magnetic nanoparticles (MNPs) from the fluid phase can be performed (Gómez-Pastora et al., 2014).

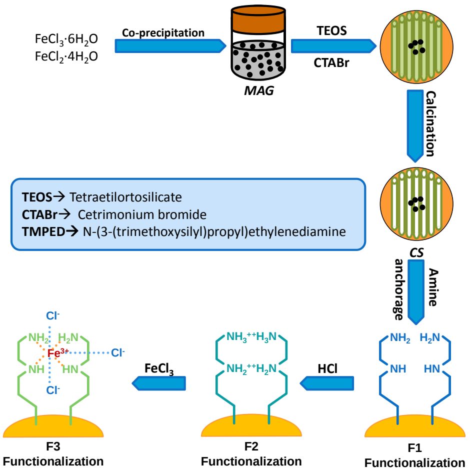
Please cite this article as: Gomez-Pastora J., Bringas E., Ortiz I., 2016, Design of novel adsorption processes for the removal of arsenic from polluted groundwater employing functionalized magnetic nanoparticles, Chemical Engineering Transactions, 47, 241-246
DOI: 10.3303/CET1647041

However, arsenic adsorption on mineral surfaces could be affected or even suppressed, by the presence of competing ions typically found in groundwater, i.e. phosphate, silicate, nitrate, chloride, carbonate, and sulphate, due to their competition with the target compound to reach active adsorption sites and thus limiting the feasibility of the separation processes (Badruddoza et al., 2013). In addition, the regeneration process of loaded MNPs that needs of a first step for the recovery of the MNPs and the final management of both the spent regeneration solution and the exhausted adsorbent are crucial stages that should be evaluated in order to bring the MNPs-based adsorption technology a step forward (Gómez-Pastora et al., 2014).

The work deals with the analysis of the adsorption and regeneration stages when functionalized Fe_3O_4 and Fe_3O_4/SiO_2 magnetic nanoparticles are employed as selective adsorbents to remove arsenate from aqueous solutions. In particular, batch adsorption experiments were performed using single-component solutions containing As^{5+} at two concentration levels: i) 5-750 mg L^{-1} to describe the complete adsorption isotherms and ii) 50 μg L^{-1} and 1000 μg L^{-1} in order to analyse the adsorption equilibrium at concentrations typically found in groundwater; then, a multicomponent analysis was performed in order to evaluate the influence of potential competitive ions usually found in natural water on the arsenate adsorption. Finally, the viability of the adsorbent regeneration and reuse under different scenarios of groundwater composition was assessed.

2. Material and methods

Figure 1 summarizes the different steps followed in the synthesis and functionalization of the materials analysed in this work: i) *MAG*: superparamagnetic Fe_3O_4 nanoparticles, ii) *CS*: magnetite cores coated by a mesoporous silica layer in order to reduce the damage on the structure of Fe_3O_4 during adsorption and desorption stages, iii) *F1*: amine base-functionalized materials, iv) *F2*: amine acid-functionalized material and v) F3: Fe^{3+}-coordinated to amine acid-functionalized material to provide higher affinity towards arsenic species due to the acid-base interactions between Fe^{3+} (hard Lewis acid) and arsenate (hard Lewis base). Moreover, the non-magnetic mesoporous silica material MCM-41 with different degree of functionalization was employed as reference material. Table 1 compiles the main properties of materials CS-F3 and MAG-F3 (Saiz et al., 2014a).



TEOS→ Tetraetilortosilicate
CTABr→ Cetrimonium bromide
TMPED→ N-(3-(trimethoxysilyl)propyl)ethylenediamine

Figure 1: Synthesis of solids MAG and CS with functionalizations F1, F2 and F3.

Table 1: Properties of magnetic materials CS-F3 and MAG-F3.

Property	CS-F3	MAG-F3
Specific surface area (m^2 g^{-1})	293.6	54.7
Average particle size (nm)	160.9	46.8
Zeta potential (mV)	47	41.7
% Surface functionalization	≈20%	≈12%
Magnetic saturation (emu g^{-1})	11.6	52.9

Initially, the viability of the adsorption step was evaluated through batch adsorption experiments in which 15 mL of arsenate ($NaAsO_2$, Aldrich) solutions with concentrations of 20 mg L^{-1} were contacted at constant temperature under stirring conditions with 50 mg of the synthesized materials (MAG and CS) and the functionalized reference material (MCM-41). Once equilibrium was reached, the solution and the adsorbent were separated being the supernatant liquid characterized in terms of arsenic concentration by inductively coupled plasma mass spectrometry (model ICP-MS 7500ce by Agilent). The material stability was evaluated through the determination of both the particle size and the surface zeta potential measurements by Dynamic Light Scattering (DLS) (model ZetaSizer Nano by Malvern Instruments). Then, the complete adsorption equilibrium isotherms of As^{5+} were determined at 298 K working with the functionalized magnetic materials following the aforementioned procedure and employing arsenate solutions with concentrations in the range 5-750 mg L^{-1} and solid amounts between 5-50 mg. After analysis of the residual arsenic concentration the amount of arsenic adsorbed per unit mass, (q_e, mg g^{-1}) was calculated and the comparison of experimental adsorption equilibrium data with theoretical Langmuir isotherms was performed with the following equations:

$$q_e = \frac{(C_i - C_e) \cdot V}{m} \tag{1}$$

$$q_e = \frac{q_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \tag{2}$$

where C_i and C_e are the initial and equilibrium arsenic concentrations in the solution (mg L^{-1}), m is the dry mass of contacted solid (g), V is the volume of solution (L), q_m is the maximum adsorption capacity of the solid (mg g^{-1}) and K_L is the Langmuir adsorption constant (L mg^{-1}).

Additionally, the adsorption equilibrium for the system CS-F3/As^{5+} was evaluated at 298 working with single-component solutions containing arsenate at concentrations in the range 50-1000 μg L^{-1} and other aqueous systems that simulate the typical characteristics of groundwater: a) multicomponent solutions containing arsenate and several potential competitive species namely carbonate (12-20900 mg L^{-1}), chloride (2-10700 mg L^{-1}), sulphate (2-7800 mg L^{-1}), silicate (3-1700 mg L^{-1}), nitrate (1-1200 mg L^{-1}), phosphate (0.5-55 mg L^{-1}), iron(III) (0.5-120 mg L^{-1}) and fluoride (0.4-115 mg L^{-1}) and b) multicomponent solutions with a similar formulation than (a) but free of phosphate (Kar et al., 2010). The experimental adsorption equilibrium data were fitted to linear isotherms given by Eq. (3):

$$q_e = K_H \cdot C_e \tag{3}$$

where K_H is the adsorption equilibrium parameter (L g^{-1}).

Finally, several adsorption/desorption cycles were performed to analyse the reusability of the material CS-F3 following the methodology reported in previous works (Saiz et al., 2014b). Desorption with sodium hydroxide solutions and two material re-functionalization stages with HCl (F2) and $FeCl_3$ (F3) were carried out working with feed solutions with the aforementioned characteristics

3. Results and discussion

Figure 2 shows the final values of As^{5+} concentration after contacting the synthesized materials with solutions containing 20 mg L^{-1} of arsenate at mass/volume ratio of 10:3 mg mL^{-1}.

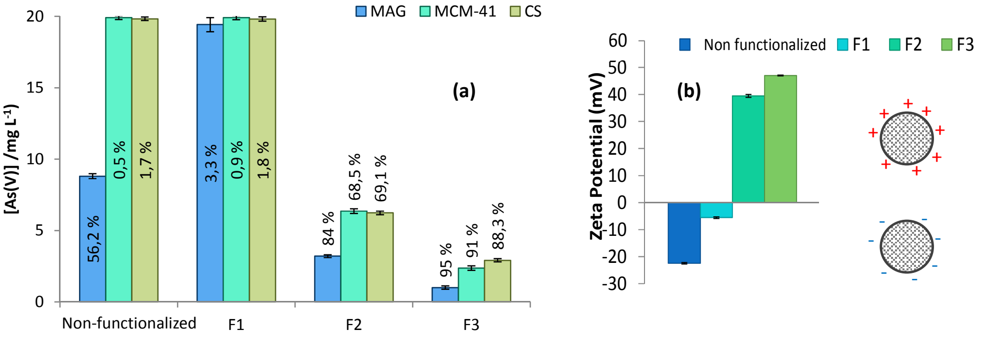


Figure 2: a) Removal of As^{5+} for materials MAG, CS and MCM-41 with F1, F2 and F3 functionalization; b) values of zeta potential for material CS as synthesized and with different levels of functionalization.

As depicted in Figure 2a, the minimum differences observed in the results obtained with the magnetic (CS) and non-magnetic (MCM-41) materials led to the conclusion that the incorporation of MAG cores into the mesoporous silica structure does not affect the adsorption performance. It is also noticed that the adsorption percentages of arsenate by solids CS and CS-F1 and the analogous reference materials are almost negligible

(<1%). The surface of the non-functionalized (NF) materials CS and MCM-41 contains silanol groups (SiH_3OH) that are expected to be found as neutral or negative species on the silica surface at the pH operation conditions (pH~8). The amino groups (–NH and –NH_2) on the surface of F1-functionalized materials behave in a similar way as was demonstrated by the negative values of the surface zeta potential reported in Figure 2b. From these results, it is possible to conclude that the adsorption of negatively charged arsenate species ($HAsO_4^{2-}$ and $H_2AsO_4^{-}$) with non-functionalized and F1-functionalized CS materials is limited by the weak electrostatic interactions between the solid surface and the adsorbate. Once amino groups grafted on the surface of material CS are protonated (F2) and then coordinated with Fe^{3+} (F3), the removal percentages of arsenate increased to 69.1 % and 88.3 %, respectively. These results are directly related to the positive values of the surface zeta potential reported by F2 and F3 functionalized materials (see Figure 2b). In addition, the better adsorption performance of F3 functionalization when compared with F2 is related to the increase on the active adsorption sites when Fe^{3+} is coordinated to the protonated (H^+) amino groups.

The functionalized MAG nanoparticles exhibit a similar or even better performance than the observed for CS and MCM-41 with F1, F2 and F3 functionalization. However, the non-functionalized magnetite material reported percentages of arsenate adsorption higher than 50%. This behavior is explained by the positive values of zeta potential of non-functionalized MAG nanoparticles (not shown), fact attributed to the operation below the material isoelectric point.

If kinetic phenomena are neglected, adsorption equilibrium, which depends on both the adsorbate/adsorbent characteristics and temperature, quantifies the maximum amount of the target species potentially collected by the solid and the thermodynamic behavior of the adsorption process. Figure 3 shows the adsorption isotherms of arsenate at 298 K with materials MAG-F3 and CS-F3 that reported the best adsorption performance in the viability analysis.

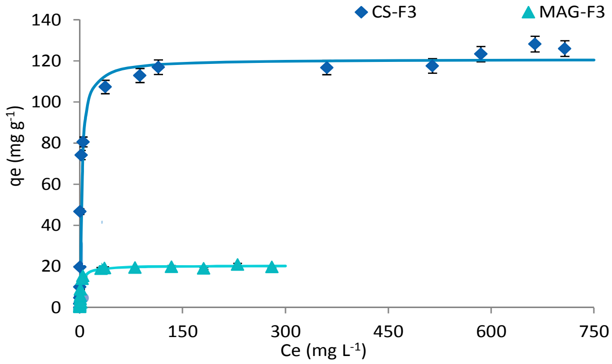


Figure 3: Adsorption isotherms of As^{5+} for materials CS-F3 and MAG-F3. Dots are experimental data and continuous lines represent the predicted isotherms using the Langmuir model (Eq.(2)).

First of all the shape of the equilibrium isotherms, vertical and closed to the ordinate axis, confirms from a qualitative point of view the favorable adsorption equilibrium specially at low arsenic concentration levels. A further analysis of the equilibrium results leads to the following conclusions, which are in good agreement with the viability analysis previously discussed: (i) the experimental equilibrium data were satisfactorily fitted to the Langmuir model (Eq.(2)) with the following parameters: MAG-F3, qm=20.4±0.3 mg g-1 and KL=0.373±0.003 L mg-1 and CS-F3, qm=121±4.1 mg g-1 and KL=0.383±0.066 L mg-1; (ii) at low equilibrium concentrations, (Ce<20 mg L-1 and qe<40 mg g-1), the solids CS-F3 and MAG-F3 exhibit similar efficacy on the arsenate removal; iii) at high equilibrium concentrations, (Ce>20 mg L-1 and qe>40 mg g-1), the solid CS-F3 reported a better performance than the material MAG-F3 as concluded from their maximum adsorption capacities, 121 and 20.4 mg g-1, respectively. This fact is explained by the increase in the specific surface area when magnetite nanoparticles (~60 m2 g-1) are encapsulated into the mesoporous silica matrix (912 m2 g-1).

Figure 4 shows the adsorption isotherms for the system CS-F3/As5+ at 298 working with monocomponent solutions containing arsenate at the typical concentrations observed in polluted groundwaters and with multicomponent systems containing potential competitive species. The results reported for single-component arsenate solutions confirm the favourable adsorption equilibrium at low arsenic concentration levels being these results in good agreement with the analysis at higher concentration levels. It is also concluded that more than 90% of equilibrium data are below the concentration value of 10 μg L^{-1} recommended by the WHO. From the comparison of the equilibrium parameters, K_H, it is concluded that the value obtained for multicomponent systems, 1.80 L g^{-1}, is 150 times lower than the value resulted when single-component solutions are employed, 278.8 L g^{-1}, thus being the efficacy of the process limited by the competitive adsorption. From the fitting of the equilibrium data obtained with multicomponent solutions free of phosphate to Eq. (3), a value of K_H=20.3 L g^{-1} was obtained. The average arsenic adsorption percentage in the absence of phosphate is close to 82%, which is within the average values of removal efficacies observed in monocomponent systems, 98%, and multicomponent solution containing phosphate, 30%. These results are explained by the similar chemical structure and basic character of arsenate and phosphate anions that promotes the competition between both species to reach acid Fe^{3+} adsorption sites.

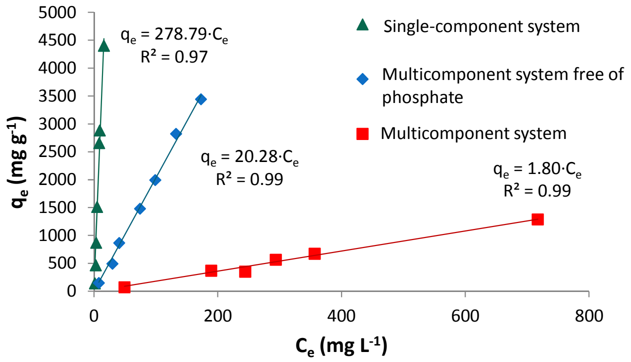


Figure 4: Adsorption isotherms of As^{5+} for material CS-F3 working with monocomponent and multicomponent solutions. Dots are experimental data and continuous lines represent the predicted isotherms using Eq.(3).

Finally, the material reuse after regeneration with NaOH 10^{-3} mol L^{-1} was assessed under several composition scenarios reaching adsorption yields similar to those obtained with fresh materials. Figure 5 shows the adsorption and desorption percentages of arsenate when the solid CS-F3 is subjected to five adsorption consecutive cycles followed by desorption and re-functionalization stages and final material re-use.

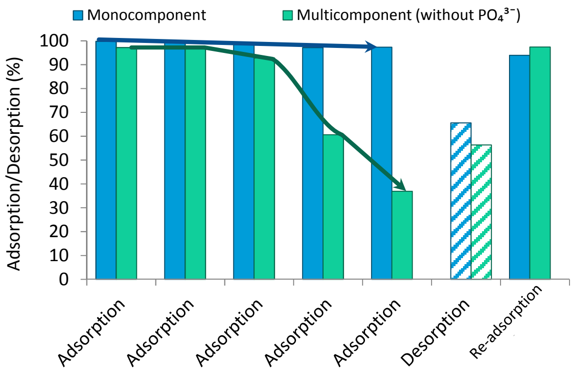


Figure 5: Influence of groundwater composition on the regeneration and reusability of the functionalized adsorbent CS-F3.

Arsenic removal percentages are close to 100% for the all the adsorption cycles performed under ideal conditions (single-component solutions). When multicomponent solutions free of phosphate are employed, the adsorption efficacy decreases from ≈100% in the first adsorption contact to values close to ≈40% after five adsorption stages due to the expected equilibrium limitations. On the other hand, desorption percentages varying from ≈70% in monocomponent systems to ≈60% in multicomponent solutions are obtained. Finally, the regenerated material subjected to a re-adsorption step exhibited adsorption efficacies similar to those obtained with the fresh material in the first adsorption contact.

4. Conclusions

This work aimed at the development of the methodology for analysing the performance of an adsorption process based on the use of functionalized magnetic nanomaterials as adsorbents, to carry out the selective separation of the target compound, arsenic, from a multicomponent mixture, which simulates the typical composition of polluted groundwater. Different nanomaterials with different composition and structure were synthesized: non-magnetic mesoporous silica (MCM-41), non-porous magnetite (MAG) and magnetic and porous Fe_3O_4/SiO_2 composites (CS). The material functionalization was performed in three in series steps: i) grafting of amino-alcoxysilanes by covalent bonding with the silanol or hydroxyl groups on the materials surface (F1), ii) protonation of the amino groups by contacting the material with an acid solution (F2) and iii) coordination of Fe^{3+} to the functional groups grafted on the surface.

F2 and F3 functionalized materials were able to efficiently remove arsenate anions (adsorption percentages from 70% to 95%) under neutral pH conditions due to their positive surface charge derived from the positive values of the zeta potential. From the analysis of the adsorption equilibrium, it is concluded that in the range of high concentrations, from 5 mg L^{-1} to 50 mg L^{-1}, the isotherms were accurately described by the Langmuir model. In addition, the material CS-F3 reported the best adsorption performance of As^{5+} being the maximum adsorption capacity 121 mg g^{-1}. In the range of low concentrations, from 50 μg L^{-1} to 1000 μg L^{-1}, the adsorption equilibrium for the system As^{5+}/CS-F3 were satisfactorily described by means of a linear isotherm being its characteristic parameter KH=278.8 L g-1. The similar chemical structure of arsenate and phosphate anions promotes the competition between both species leading to values of the adsorption percentage varying from 99% to 40% when the molar ratio PO43-/As5+ varied from 0.5 to 50.

Finally, the performance of the material after five adsorption cycles was assessed under several water composition scenarios. The adsorption efficacy decreased with the number of cycles being the decline more severe as the complexity of the chemical system increases. This adverse situation was overcome by regenerating the material after contact with NaOH solutions; in this case, the adsorption percentages were recovered and similar values to those obtained with the fresh material were reached.

Acknowledgments

Financial support from the Spanish Ministry of Economy and Competitiveness under the project CTQ2012-31639 (FEDER 2007-2013) is gratefully acknowledged.

Reference

Badruddoza, A.Z., Shawon, Z.B.Z., Rahman, T., Hao, K. W., Hidajat, K., Uddin, M.S, 2013, Ionically modified magnetic nanomaterials for arsenic and chromium removal from water. Chemical Engineering Journal, 225, 607-615.

Gómez-Pastora, J., Bringas, E., Ortiz, I., 2014, Recent progress and future challenges on the use of high performance magnetic nano-adsorbents in environmental applications, Chemical Engineering Journal, 256, 187-204.

Hindmarsh, J.T., McCurdy, R.F., 1986, Clinical and environmental aspects of arsenic toxicity, CRC Critical Reviews in Clinical Laboratory Sciences, 23:4, 315–347.

Hristovski, K., Baumgardner, A. and Westerhoff, P., 2007, Selecting metal oxide nanomaterials for arsenic removal in fixed bed columns: from nanopowders to aggregated nanoparticle media, Journal of Hazardous Materials,147:1, 265-274.

Jadhav, S.V., Bringas, E., Yadav, G.D., Rathod, V.K., Ortiz, I., Marathe, K.V., 2015, Arsenic and fluoride contaminated groundwaters: a review of current technologies for contaminants removal. Journal of Environmental Management, 162, 306-325.

Kar, S., Maity, J.P., Jean, J.S., Liu, C.C., Nath, B., Yang, H.J., Bundschuh, J., 2010, Arsenic-enriched aquifers: occurrences and mobilization of arsenic in groundwater of Ganges Delta Plain, Barasat, West Bengal, India, Applied Geochemistry, 25(12), 1805-1814.

Mara, D.D., 2003, Water, sanitation and hygiene for the health of developing nations, Public Health, 117:6, 452–456.

Mayo, J.T., Yavuz, C., Yean, S., Cong, L., Yu, W., Colvin, V. L., 2007, The effect of nanocrystalline magnetite size on arsenic removal, Science and Technology of Advanced Materials, 8:1, 71-75.

Murcott, S., 2012, Arsenic Contamination in the World. IWA Publishing, London, UK.

Saiz, J., Bringas, E., Ortiz, I., 2014a, Functionalized magnetic nanoparticles as new adsorption materials for arsenic removal from polluted waters, Journal of Chemical Technology and Biotechnology, 89, 909-918.

Saiz, J., Bringas, E., Ortiz, I., 2014b, New functionalized magnetic materials for As^{5+} removal: adsorbent regeneration and reuse. Industrial and Engineering Chemistry Research, 53, 18928−18934.

USNRC, 1999, Arsenic in drinking water, United States National Research Council, National Academy Press, Washington, DC, United States.