

Retention potential of contaminants by (nano)magnetite in batch and microfluidic systems

Papaslioti, E.M.^{1,2*}, Tabuteau H.³, Vantelon D.⁴, Le Bouteiller P.⁵, Greneche J.M.⁶, Fernández-Martínez A.¹, Charlet, L.¹

¹ Univ. Grenoble-Alpes, Univ. Savoie Mont Blanc, CNRS, IRD, Univ. Gustave Eiffel, ISTERre, 38000, Grenoble, France

² Department of Earth Sciences & Research Center on Natural Resources, Health and the Environment, University of Huelva, Campus "El Carmen", E-21071 Huelva, Spain

³ Univ Rennes, CNRS, IPR (Institut de Physique de Rennes)-UMR 6251, F-35000 Rennes, France

⁴ Synchrotron SOLEIL, L'Orme des Merisiers, Départementale 128, 91190 Saint-Aubin, France

⁵ HYMAG'IN, Grenoble, France

⁶ Institut des Molécules et Matériaux du Mans, CNRS UMR-6283, Le Mans Université, F-72085 Le Mans, France

*corresponding author: Papaslioti, E.M.

e-mail: evgenia-maria.papaslioti@univ-grenoble-alpes.fr

Abstract (Nano)magnetite (Fe_3O_4) has been suggested to be a significant reductant for contaminants due to its great adsorption capacity and ability to retain metals on its high specific surface. Its use has become an emerging technology for the treatment of contaminated land and water with a great potential to become an effective and low-cost alternative to conventional remediation techniques. We have taken advantage of a concept of the circular economy, exploiting an existing waste from the steel industry that HYMAG'IN company has transformed into magnetite, to study the immobilisation of As, Sb, and U in batch sorption systems and provide new insights into a new 'green' route for the decontamination of water. Moreover, given that polymeric coatings can maximize the adsorption capacity, we additionally, mimic those systems in a micro-scale format via the use of bionanocomposite and microfluidics to study time-dependent Sb reduction by nanomagnetite aggregates. Synchrotron X-ray Absorption Spectroscopy (XAS) is applied for the first time to such experimental systems to shed light into the role of nanomagnetite aggregates into the immobilization of Sb, as a novel remediation strategy.

Keywords: (Nano)magnetite; Redox sensitive contaminants; Microfluidics; Polymer aggregates; Remediation technique

1. Introduction

The problematic of drinking and waste water contamination by various inorganic toxic pollutants has gained a worldwide attention and the scientific community has greatly focused on the search for innovative decontamination techniques. Magnetite (Fe_3O_4) is an iron oxide containing both Fe^{2+} and Fe^{3+} ions, and it has been suggested to be a significant reductant for contaminants due to its ubiquity in the environment and its high specific surface area (Gorski et al., 2009). As such,

(nano)magnetite has been reported to be efficient in immobilising various inorganic contaminants, such as As (e.g. Zhang et al., 2010), U (e.g. Pan et al. 2020), and Sb (e.g. Kirsch et al., 2008). Controlled experimental systems mimicking in-situ conditions are necessary to study the geochemical processes controlling Fe transformation and subsequent retention or release of contaminants. The use of (nano)magnetite is becoming an emerging technology for the treatment of contaminated land and water with a great potential to become an effective and low-cost alternative to conventional remediation techniques.

The aim of this study is to fulfil some of the existing knowledge gaps on contaminants sorption by magnetite and to suggest management techniques for the remediation of drinking and waste water focusing on toxic, acidic, and phosphate rich waste leachates. Our purpose is to set the basis for an industrial process to decontaminate such effluent waters by (i) first, using ZVI to increase the pH of the water while producing Fe^{2+} , (ii) the precipitating of phosphate ions as vivianite, and (iii) finally, using magnetite to immobilize toxic pollutants under different pH conditions and high phosphate concentrations.

Polymeric coatings can additionally stabilize the iron oxide/hydroxide with respect to aggregation, maximizing the adsorption capacity (He et al., 2016). In porous media, such as bionanocomposite aggregates, the sorption processes and the surface reactions at the mineral water-interface depend on the water flow and the diffusive and advective transport of reactants in the pore space (Wielinski et al., 2022). Therefore, spatial resolved information on the distribution and speciation of the elements of interest is crucial to be studied at a microscale format in order to understand such processes. Microfluidics technology is suitable for such studies in porous media due to their reduced complexity that allows

to unravel the coupling between water-solid reactions, despite they do not represent the whole complexity of natural systems (Wielinski et al., 2022). Therefore, as a second part of our research, we mimic those systems via the use of PEGDA/chitosan nanomagnetite aggregates and microfluidic setups, ideal to study time-dependent Sb reduction reactions. We combine microfluidic sorption experiments, synchrotron X-ray spectroscopy, and reactive transport modelling with the aim to bridge the gap between spatially and temporally resolved sorption process in complex porous media.

2. Results and Discussion

2.1. As, Sb and U sorption by 'green'-synthesized magnetite

We have taken advantage of a concept of the circular economy, exploiting an existing waste from the steel industry that HYMAG'IN company has transformed into magnetite (Cruzet et al., 2017), to study the immobilisation of As, Sb, and U and provide new insights into a new 'green' route for the decontamination of water. The results showed up to 98% U removal under controlled pH conditions, while phosphate did not hinder this immobilization. In contrast, the results confirmed the limited uptake of As and Sb oxyanions by magnetite in presence of phosphate as the competing anion, displaying only 7-11% removal. To limit this wastewater problem, raw ZVI anaerobic oxidation was examined as mechanism to increase the pH and as a source of Fe^{2+} in a first step, and in a second step to remove phosphate via vivianite precipitation, therefore prior to the reaction with magnetite. UV-Vis, XRD and SEM-EDS showed that vivianite precipitation is feasible at $\text{pH} > 4.5$, mainly depending on the phosphate concentration. The higher the $[\text{PO}_4^{3-}]$, the lower is the pH at which vivianite precipitates and the higher the % removal of phosphate from solution. It is anticipated that an optimum 3-steps design with separate reactors controlling the conditions of ZVI oxidation, followed by vivianite precipitation and finally, reaction with magnetite (Fig. 1), can achieve high contaminant uptake in field applications.

2.2. Sb retention by hydrogel nanomagnetite aggregates: a novel approach using microfluidic models

We performed a series of flow-through controlled experiments through aggregates in a microfluidic set up involving cylindrical structured PEGDA/nanomagnetite aggregates to obtain Break Through Curves (BTC) of Sb species. The cylinders were made using an emulsion of PEGDA with magnetite nanoparticles (i) coated with chitosan and (ii) without chitosan. The microfluidic devices consisted of flow-channel cells made of Norland Optical Adhesive 81, which is impermeable to gases (Fig. 1a). Antimony solution made with $\text{KSb}(\text{OH})_6$ at various concentrations was used as the input solution. The effluent solution was collected regularly for Sb(V) and Cl^- (as the tracer) measurement by Ion Chromatography (Fig. 1b). According to the results, a mean retardation time of about 200 min was estimated for Sb immobilization, and the system reached maximum efficiency for Sb removal after about 480 min. In general, we showed the efficiency of the system and a significant retention of Sb depending on the initial concentration and the material of the aggregates.

Once each flow-through experiment was over, the cylinder transects were analysed by x-ray micro-fluorescence (μ -XRF) and X-ray absorption near-edge structure (XANES) while sitting inside the microfluidic device. We performed microfocus elemental and redox mapping of Sb on these aggregates, measuring its diffusion, and reduction particularly in their core to investigate the temporal distribution and the oxidation state of the reduced aqueous species of Sb produced by nanomagnetite reduction. The resulted spectra point to a reduction of Sb(V) by magnetite when $[\text{Sb}]$ is low, i.e. twice the magnetite surface site for chitosan-free magnetite. In presence of chitosan, reduction is observed at lower $[\text{Sb}]$. We have probably two population of Sb. The one sitting on magnetite surface, and the one bonded to (slightly positively charged) chitosan chains. More specifically, Sb(V) was reduced to Sb(III) at 100% and 200% NPs reactive sites coverage at the absence of chitosan, while only at 100% coverage at the presence of chitosan. On the contrary, Sb(V) adsorption appeared to be more efficient at the presence of chitosan and at higher initial concentrations, i.e. at 500% coverage of the nanomagnetite reactive sites. This work provides insights into the role of nanomagnetite aggregates into the immobilization of Sb, as a novel remediation strategy for the drinking and waste waters.

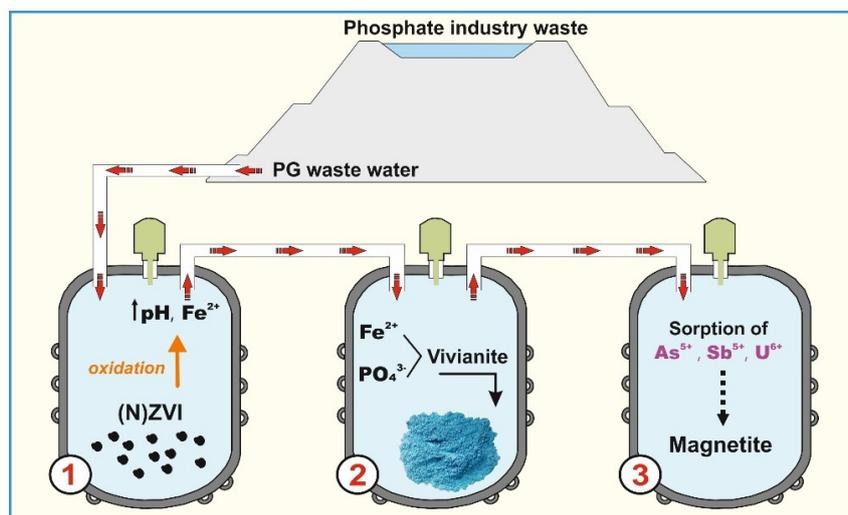


Figure 1. Schematic depiction of the 3-steps remediation approach to phosphate-rich waste leachates model solution (i.e. phosphogypsum (PG) effluents)

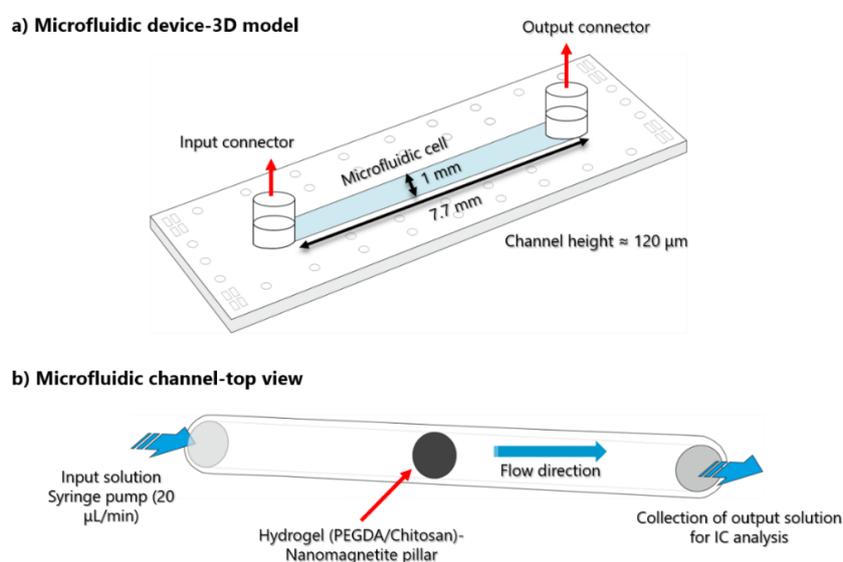


Figure 2. Schematic depictions of (a) the microfluidic device made of NOA channel (light blue) fixed on glass slide, and (b) the microfluidic channels, including the polymer nanomagnetite cylindrical aggregate, and the connectors.

References

- Crouzet, C., Brunet, F., Recham, N., Auzende, A. L., Findling, N., Magnin, V., ... & Goffé, B. (2017). Hydrothermal steel slag valorization—Part II: Hydrogen and nanomagnetite production. *Frontiers in Earth Science*, **5**, 86.
- Gorski, C. A., Nurmi, J. T., Tratnyek, P. G., Hofstetter, T. B., & Scherer, M. M. (2010). Redox behavior of magnetite: Implications for contaminant reduction. *Environmental science & technology*, **44**, 55-60.
- He, J., Bardelli, F., Gehin, A., Silvester, E., & Charlet, L. (2016). Novel chitosan goethite bionanocomposite beads for arsenic remediation. *Water research*, **101**, 1-9.
- Kirsch, R., Scheinost, A. C., Rossberg, A., Banerjee, D., & Charlet, L. (2008). Reduction of antimony by nanoparticulate magnetite and mackinawite. *Mineralogical Magazine*, **72**, 185-189.
- Pan, Z., Bártová, B., LaGrange, T., Butorin, S. M., Hyatt, N. C., Stennett, M. C., ... & Bernier-Latmani, R. (2020). Nanoscale mechanism of UO₂ formation through uranium reduction by magnetite. *Nature communications*, **11**, 1-12.
- Wielinski, J., Jimenez-Martinez, J., Göttlicher, J., Steininger, R., Mangold, S., Hug, S. J., ... & Voegelin, A. (2022). Spatiotemporal Mineral Phase Evolution and Arsenic Retention in Microfluidic Models of Zerovalent Iron-Based Water Treatment. *Environmental Science & Technology*, **56**, 13696-13708.
- Zhang, M., Wang, Y., Zhao, D., & Pan, G. (2010). Immobilization of arsenic in soils by stabilized nanoscale zero-valent iron, iron sulfide (FeS), and magnetite (Fe₃O₄) particles. *Chinese Science Bulletin*, **55**, 365-372.