Efficient removal of arsenic species by green rust sulfate (GR_{SO4})

J.P.H. Perez^{1,2}, H.M. Freeman¹, J.A. Schuessler¹ & L.G. Benning^{1,2}

¹Helmholtz Centre Potsdam – GFZ German Research Centre for Geosciences, Potsdam, Germany

²Institute of Geological Sciences, Department of Earth Sciences, Free University of Berlin, Berlin, Germany

ABSTRACT: The interfacial reactivity between green rust sulfate (GR_{SO4}) and arsenic (As) species were investigated using batch adsorption experiments. GR_{SO4} is capable of adsorbing up to 155 and 88 mg g⁻¹ of As(III) and As(V), respectively. The value of pH greatly affects adsorption, with As(III) removal 2.5 times higher at alkaline pH, while As(V) removal higher at circum-neutral conditions. Competing groundwater species such as magnesium (Mg²⁺) or phosphate (PO₄³⁻) reduce removal efficiency. Our results show that GR_{SO4} is a stable, efficient and environmentally-relevant mineral substrate for As sequestration in anoxic groundwater systems.

1 INTRODUCTION

Due to its wide-spread distribution, toxicity and mobility, arsenic (As) contamination of groundwater resources remains a significant problem worldwide. Although conventional remediation techniques (e.g., oxidation, coagulation-flocculation, ion exchange) are widely employed for clean up, they are often too costly and environmentally unsuitable (Nicomel *et al.*, 2016).

In contrast, adsorption-based strategies are promising alternatives for groundwater treatment due to their facile implementation, cost-effectiveness and high removal efficiency (Leus *et al.*, 2017). However, interfacial reactions between (redox-active) mineral surfaces and contaminants such as As need to be quantitatively assessed in order to maximize their potential for subsurface remediation. Moreover, there is an imminent challenge regarding the development and testing of adequate (redox-active) mineral phases that have high metal-specific uptake capacities, strong binding affinities and excellent stabilities.

Herein, we report an in-depth investigation on the interfacial interactions between freshly precipitated green rust sulfate (GR_{SO4}) and aqueous As species. We tested the influence of pH, adsorbent loading, ionic strength and presence of potentially interfering ions and evaluated the performance of GR_{SO4} for the removal of As(III) and As(V).

2 EXPERIMENTAL SECTION

2.1 Synthesis and characterization of GR_{SO4}

GR_{SO4} was synthesized in an anaerobic chamber (95% N₂, 5% H₂) by co-precipitating stoichiometric amounts of (NH₄)₂Fe(SO₄)₂·6H₂O and Fe₂(SO₄)₃ with NaOH (Géhin *et al.*, 2002). The obtained

GR_{SO4} was characterized by X-ray powder diffraction (XRPD), inductively coupled plasma optical emission spectroscopy (ICP-OES), transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS).

2.2 Adsorption experiments

Batch adsorption experiments were done at room temperature, with GR_{SO4} suspensions reacted at pH 7 to 9 with 10 mg L⁻¹ aqueous As(III) and As(V) through shaking at 250 rpm for 24 h. The resulting samples were filtered, supernatants acidified and the separated solid and aqueous phased stored at 4°C until analysis.

3 RESULTS AND DISCUSSION

3.1 Influence of adsorption parameters

As(V) was efficiently removed (>99%) at all tested pH values. However, the As(III) removal increased significantly from 50 at pH 7 to 95% at pH 9, likely due to the possible formation of multi-nuclear As(III) complexes on the GR_{SO4} surface (Ona-Nguema *et al.*, 2009; Wang *et al.*, 2010).

Removal efficiency decreased as ionic strength increased from 0.005 to 0.5 M, with As(V) removal dropping by ~10% at high ionic strength (from >99 to 90%). On the other hand, inhibition of As(III) removal was more apparent, with removal efficiency decreasing from 59 to 38%. This reduction in As removal may be caused by the presence of potentially interfering species in the bulk solution. Hence, competitive adsorption experiments were conducted using binary solutions of As with calcium (Ca²⁺), magnesium (Mg²⁺) and phosphorous (PO₄³⁻).

The competitive adsorption results suggest that Mg^{2+} and PO_4^{3-} can inhibit the adsorption of As on the GR_{SO_4} surface, while Ca^{2+} is not affecting As adsorption. In the presence of Mg^{2+} , As(III) and As(V) removal decreased by ~ 7 and $\sim 22\%$, respectively. Mg^{2+} can block the access of As to the surface active sites of GR_{SO_4} due to the formation of outer-sphere hydrated complexes (Lightstone *et al.*, 2001). On the other hand, co-existing PO_4^{3-} species resulted in the reduction of the removal efficiency by ~ 7 and $\sim 25\%$ for As(III) and As(V), respectively. This is a consequence of the competition between PO_4^{3-} and As species for surface binding sites due to their similar structure (Bocher *et al.*, 2004).

3.2 Adsorption kinetics and isotherms

Adsorption kinetic data showed that a pseudo-2nd order kinetic model gives the best fit ($R^2 \geq 0.9990$) and that the uptake rate of As(III) and As(V) were 4 and 11 times faster at alkaline conditions compared to circum-neutral pH.

The equilibrium adsorption data were fitted to the Langmuir and Freundlich isotherms. Based on the model fits, As adsorption onto GR_{SO_4} can be best described by a Langmuir model, a result that supports previous X-ray absorption spectroscopic studies (Jönsson and Sherman, 2008; Wang *et al.*, 2010) that suggested that As species form monodentate mononuclear and bidentate binuclear inner-sphere complexes at GR particle edges.

Using the Langmuir isotherm model, the maximum adsorption capacity (q_{max}) for As onto GR_{SO_4} at pH 7 and 8–9 was evaluated. Our results show that at alkaline pH, GR_{SO_4} can adsorb up to 155 mg As(III) per g of solid, a value 2.5 times higher than at neutral pH. On the contrary, a higher adsorption capacity was observed for As(V) at neutral pH (88 mg g^{-1}) compared to alkaline pH (67 mg g^{-1}).

3.3 Environmental implications on the fate and mobility of As

We show that GR_{SO_4} has an excellent ability to adsorb As species and has the highest sorption capacity of any iron (oxyhydr)oxides found in surface and near-surface environments, including ferrihydrite, goethite, hematite, maghemite and magnetite. In terms of surface coverages, GR_{SO_4} outperforms all of these phases (Fig. 1), and more importantly, it is also one of the very few redox active mineral phases that exhibits unusually high As(III) coverage.

Finally, we show that GR_{SO_4} remains stable post-As adsorption at typical contaminated groundwater conditions ($\sim 10 \text{ mg L}^{-1}$). Long term monitoring (three months) of GR_{SO_4} samples showed no structural and morphological changes, as confirmed by XRD analysis and TEM imaging. This was supported by analyses of aqueous As in the reacting supernatant, which showed no significant re-release of adsorbed As into the aqueous phase.

Figure 1. Comparison of As surface coverages of GR_{SO_4} (this study) with other iron (oxyhydr)oxides.

4 CONCLUSIONS

We quantified the interfacial reactivity between GR_{SO_4} and As species. Using batch adsorption experiments, we examined the influence of various critical environmental parameters on As removal. We successfully demonstrated that GR_{SO_4} is a highly effective and stable mineral adsorbent compared to other iron (oxyhydr)oxide phases at the concentration of As-contaminated groundwater ($\sim 10 \text{ mg L}^{-1}$). GR_{SO_4} demonstrated an exceptional As sorption reactivity which makes it a potentially novel and environmentally-relevant mineral substrate for the sequestration of As in reduced groundwater systems. Overall, our results provide important insights as to how uptake and release of As in contaminated groundwaters can be influenced by the presence of redox-active GR phases.

ACKNOWLEDGEMENTS

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 675219 and the German Helmholtz Recruiting Initiative funding to LGB and HMF.

REFERENCES

- Bocher, F., Géhin, A., Ruby, C., Ghanbaja, J., Abdelmoula, M. & Génin, J.-M.R. 2004. Coprecipitation of Fe(II–III) hydroxycarbonate green rust stabilised by phosphate adsorption. *Solid State Sci.* 6(1): 117–124.
- Géhin, A., Ruby, C., Abdelmoula, M., Benali, O., Ghanbaja, J., Refait, P. & Génin, J.-M.R. 2002. Synthesis of Fe(II–III) hydroxysulphate green rust by coprecipitation. *Solid State Sci.* 4(1): 61–66.
- Jönsson, J. & Sherman, D.M. 2008. Sorption of As(III) and As(V) to siderite, green rust (fougerite) and magnetite: implications for arsenic release in anoxic groundwaters. *Chem. Geol.* 255(1–2): 173–181.

- Leus, K., Perez, J.P.H., Folens, K., Meledina, M., Van Tendeloo, G., Du Laing, G. & Van Der Voort, P. 2017. UiO-66-(SH)₂ as stable, selective and regenerable adsorbent for the removal of mercury from water under environmentally-relevant conditions. *Faraday Discuss.* 201: 145–161.
- Lightstone, F.C., Schwegler, E., Hood, R.Q., Gygi, F. & Galli, G. (2001). A first principles molecular dynamics simulation of the hydrated magnesium ion. *Chem. Phys. Lett.* 343(5–6): 549–555.
- Nicomel, N.R., Leus, K., Folens, K., Van Der Voort, P. & Du Laing, G. 2016. Technologies for arsenic removal from water: current status and future perspectives. *Int. J. Environ. Res. Publ. Health* 13(1): 62.
- Ona-Nguema, G., Morin, G., Wang, Y., Menguy, N., Juillot, F., Olivi, L., Aquilanti, G., Abdelmoula, M., Ruby, C., Bargar, J.R., Guyot, F., Calas, G. & Brown, Jr, G.E. 2009. Arsenite sequestration at the surface of nano-Fe(OH)₂, ferrous-carbonate hydroxide, and green-rust after bioreduction of arsenic-sorbed lepidocrocite by *Shewanella putrefaciens*. *Geochim. Cosmochim. Acta* 73(5): 1359–1381.
- Wang, Y., Morin, G., Ona-Nguema, G., Juillot, F., Guyot, F., Calas, G. & Brown, G.E. 2010. Evidence for different surface speciation of arsenite and arsenate on green rust: an EXAFS and XANES Study. *Environ. Sci. Technol.* 44(1): 109–115.