

Arsenic removal in manganese-containing groundwater

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Arsenic (As) can occur naturally in groundwaters worldwide (e.g., Bangladesh, India, Amazon region, etc.). Because of this large-scale contamination and its high toxicity and carcinogenicity, exposure to As leads to millions of deaths worldwide. Therefore, strategies to remove As from water using efficient and cheap treatment systems are critically needed. Iron(0) electrocoagulation (EC) has gained attention as a low-cost method for As removal because it has short supply chain and low energy requirements and, importantly, is easy to operate. In EC, a current is passed through an Fe(0) electrode, such that Fe(0) is oxidized to Fe(II). The production of Fe(II) generates reactive oxidants that oxidize As(III) to form As(V) – a less dangerous form of As, and Fe(II) to Fe(III), which forms nanoscale iron precipitates that remove arsenic from solution (van Genuchten et al. 2012, Nidheesh et al. 2017). However, the mechanism and efficiency of As removal depend strongly on the chemical composition of the groundwater. Thus, successful implementation of EC requires systematic chemical and mineralogical studies under varying operating conditions and groundwater chemistry.

In some waters, As and Mn co-occur at high concentrations (Gillispie et al. 2016, de Meyer et al. 2017). Recent work shows that Mn(II) can also be removed from water using an EC system. Moreover different oxidants are responsible for the oxidation of Fe and Mn at different pH and the greatest Mn removal occurs at pH 8.5 (van Genuchten et al. 2017). Combined, these studies suggest that As and Mn compete for the same pool of oxidants in an EC system and therefore that the efficiency of As removal may be influenced by the presence of Mn. The main goal of this work is thus to understand the extent to which As and Mn are removed during EC when aqueous As(III) and Mn(II) are initially present in the groundwater. In addition, knowledge of the speciation of As and Mn in the solid phase is needed in order to understand the mechanism of contaminant removal (oxidation and sorption) under varying conditions (concentrations of Mn, As, pH, and presence or absence of H₂O₂).

Analysis of aqueous and solid phase samples showed that the kinetics of As and Mn oxidation and mechanism of removal to the solid phase vary strongly according to the type of oxidant present in the system (e.g., $\cdot\text{OH}$ and Fe(IV), respectively). At acidic pH, As concentrations were less than the 10 $\mu\text{g L}^{-1}$ (WHO recommendation) in the presence of H₂O₂ after 30 min, but at basic pH the concentrations of As were higher than the WHO recommendation. In the O₂ system, As concentrations decreased over time, but did not attain the 10 $\mu\text{g L}^{-1}$ target. Solution pH, the initial oxidant (O₂ vs. H₂O₂) and Mn concentration influenced significantly the extent of As and Mn removal. The speciation of As and Mn in the solid phase, as determined by X-ray absorption spectroscopy (Stanford Synchrotron Radiation Lightsource, BL 4-1), showed greater As oxidation at pH 4.5 than at pH 8.5 and in the presence of Mn. On the contrary, greater Mn oxidation was observed at pH 8.5 than at pH 4.5. Moreover, in the

O₂ system, Mn and As were mainly present in reduced form in the solid phase. Then, the acidic pH are the most favorable pH to remove As from water because of favorable oxidation of As(III) and sorption of As(V), but this pH is not practical for water treatment. The other best pH to remove As depends on Mn concentrations in waters. Determine water matrix is then a very critical point to improve the performances of the system.

REFERENCES

Gillipsie, E.C., Andujar, E., Polizzotto, M., 2016. Chemical controls on aiotic and biotic release of geogenic arsenic from Pleistocene aquifer sediments to groundwater. *Environmental Science Processes & Impacts*, 18, 1090-1103.

de Meyer, C. M. C., Rodríguez, J. M., Carpio, E. A., García, P. A., Stengel, C. & Berg, M. 2017: Arsenic, manganese and aluminum contamination in groundwater resources of Western Amazonia (Peru). *Science of The Total Environment*, 607-608, 1437-1450.

Nidheesh, P. V. & Singh, T. S. A. 2017: Arsenic removal by electrocoagulation process: Recent trends and removal mechanism. *Chemosphere*, 181, 418-432.

van Genuchten, C. M., Addy S.E.A., Peña, J., Gadgil, A.J. 2012: Removal Arsenic from Synthetic Groundwater with Iron Electrocoagulation: An Fe and As K-edge EXAFS Study. *Environmental Science & Technology*, 51, 2982-2991.

van Genuchten, C. M. & Peña, J. 2017: Mn(II) Oxidation in Fenton and Fenton Type Systems: Identification of Reaction Efficiency and Reaction Products. *Environmental Science & Technology*, 46, 986-994.