Investigation of magnetite-Co interactions by soft XAS and XMCD

LAURA FABLET[1,2], MATHIEU PÉDROT[3], REMI MARSAC[2] AND FADI CHOUEIKANI[1]

[1]SOLEIL Synchrotron
[2]Univ Rennes, CNRS, Géosciences Rennes, UMR 6118
[3]Université de Rennes 1, CNRS, Géosciences Rennes, UMR 6118

Presenting Author: laura.fablet@univ-rennes.fr

Magnetite (Fe_3O_4) nanoparticles (MNs) are largely known as strong adsorbents for dissolved contaminants such as divalent transition metals (e.g. Co^{2+}). Therefore, MNs play an important role on the behaviour and fate of trace contaminants, and are commonly used in wastewater treatment technologies, for instance. In addition, surface modification of MNs using Co^{2+} (either adsorbed ions or surface $CoO_{(s)}$ precipitates) affects MNs magnetic properties, which leads to a broad range of high technology applications. However, the mechanisms involved between magnetite and transition metals are still poorly understood in aqueous solution.

Stoichiometric MNs (i.e. with Fe(II)/Fe(III) = 0.5) were synthesized by co-precipitation and adsorption studies were performed with different Co concentrations at pH = 8 and [NaCl] = 0.01 M. The Co adsorption isotherm was found non-linear over the 5 orders of magnitude in aqueous [Co] investigated. This could tentatively be modelled assuming the formation of (i) adsorbed or incorporated of Co^{2+} at loadings ($[Co]_s \leq 1$ Co/nm²), (ii) small Co polymers at intermediate loadings ($1 \leq [Co]_s \leq 10$ Co/nm²) and (iii) precipitation of $Co(OH)_{2(s)}$ onto the magnetite surface for highest Co concentrations. Soft X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) at the Co and Fe $L_{2,3}$ absorption edges confirmed the occurrence of three types of surface modification. From low to high surface loadings, these techniques revealed (i) the presence of Co^{2+} in octahedral coordination environment with a similar magnetic behavior to cobalt ferrite ($CoFe_2O_4$) or adsorbed Co^{2+} ions, (ii) a magnetically-silent Co^{2+} species and (iii) an antiferromagnetic $Co(OH)_2$ phase, whose occurrence coincided with that of modelled species.

This study provides a detailed understanding of the Co sorption and surface precipitation mechanisms onto magnetite, as well as the chemical and magnetic properties of these particles. These results might not only be used to better understand the effect of magnetite on the behaviour and fate of metal contaminants in the environment, but also to optimize the synthesis procedures of Co-modified MNs using water as solvent for high technology applications.