

How biogenic nano-iron oxides can control the fate of pollutants

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Nanominerals have been the subject of extensive research for the last decade, especially because of their exceptional surface properties. These properties indeed confer to these nanoparticles an important role in pollutant dynamics via sorption and precipitation reactions, colloidal transport, and redox surface reactions (e.g. [1]).

In this communication we will present recent advances in the identification of such processes in impacted natural systems as contaminated soils and mining environments as well as in laboratory systems relevant of water treatment processes. Microscopic and spectroscopic investigations of these systems emphasize the role of nano – iron oxides [2, 3], oxyhydroxides [1], hydroxides [4, 5] and hydroxysulfates [6, 7] from abiotic or microbial origin. Particular attention will be paid to better understanding the respective roles of physico-chemical factors and microbial metabolisms in controlling the kinetics of nano-mineral nucleation and evolution, and the ability of these solids to scavenge inorganic pollutants, especially arsenic. Finally, recent evidence for surface redox reactions involving reactive oxygen species [8] will be discussed as a promising process for remediation of contaminated surface waters.

- [1] Charlet *et al.* (2011) *CR Geoscience* **343**, 123–139.
[2] Morin *et al.* (2009) *Langmuir* **25**, 9119–9128. [3] Wang *et al.* (2008) *GCA* **72**, 2573–2586. [4] Ona-Nguema *et al.* (2009) *GCA* **73**, 1359–1381. [5] Wang *et al.* (2010) *ES&T* **44**, 109–115. [6] Egal *et al.* (2009) *Chemical Geol.* **265**, 432–441. [7] Egal *et al.* (2010) *Appl. Geochem.* **25**, 1949–1957. [8] Ona-Nguema *et al.* (2010) *ES&T* **44**, 5416–5422.

Removal of fluoride on Mg–Al mixed oxides prepared at different temperatures

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Hydrotalcite is in layered double hydroxides (LDHs) structures, the general chemical formula is represented $[M_1(II)_{1-x}M_2(III)_x(OH)_2]A_{n-x/n} \cdot mH_2O$, where $M_1(II)$ = divalent cation (Mg^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} , Cd^{2+}), $M_2(III)$ = trivalent cation (Al^{3+} , Fe^{3+} , Cr^{3+}), A_n^- = interlayer anion with valence n , x is $M_2(III)/M_1(II) + M_2(III)$. In the present study Mg–Al mixed oxides, which were obtained by thermal decomposition of precipitated hydrotalcite-like compounds, were used as sorbents to remove fluoride in aqueous systems. Calcination temperatures were 873 K, 1073 K, and 1273 K.

The XRD peaks for co-precipitation products were assigned to hydrotalcite, but this pattern completely disappeared and assigned to MgO after calcination at each temperature, spinel phase was also observed at 1273 K. Higher calcination temperature provided higher crystallinities and larger crystal size of mixed oxide which was confirmed by TEM images. Fluoride sorption on mixed oxides can be mainly explained by ionic exchange of OH^- to F^- . Mg and Al ions were released during the sorption of fluoride; the behaviors of released Mg and Al during the sorption of fluoride have been affected by the elemental distributions of the surface on mixed oxides. The molar ratio of Al/Mg in hydrotalcite-like compounds before calcinations was determined to 0.33 after acid decomposition; however XPS results indicate that the molar ratio of Al/Mg on the surface of mixed oxide increased by the calcination temperatures. After sorption of fluoride, hydrotalcite have been reconstructed again with mixed oxide calcined at 873 K and 1073 K, however, less crystalline hydrotalcite, $Mg(OH)_2$, and spinel were observed on mixed oxides calcined at 1273 K. The lowest sorption efficiency of mixed oxide calcined at 1273 K probably due to the small amount of MgO by the phase transition to spinel because the spinel was stable in water and doesn't react with fluoride. On the other hand, removal of fluoride was more easily achieved in mixed oxides calcined at 1073 K than another mixed oxides; this may be caused by good correlation with lattice parameter of MgO. Mg–Al mixed oxides is one of promising products to remove anion including fluoride, but the sorption efficiency are affected by properties of the surface molar ratio and structures, therefore calcination temperatures must to be considered.