

Copper (II) Remediation Using Novel Ironphosphate Nanoparticles

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Soils at current or previously mined and smelter sites normally contain higher concentrations of heavy metals such as Pb, Cu, Cd, and Hg exceeding the current regulatory levels [1]. Engineered nanoparticles have been found to offer great promise for remediation of contaminated soils and groundwater [2]. General mechanisms of remediation using engineered nanoparticles are induction of various sorption processes (e.g., adsorption to Fe₂O₃ nanoparticles), reductive immobilization (e.g., EZVI for reduction of chlorinated solvents), or surface precipitation of new contaminant phases with much reduced mobility such as Pb immobilization via addition of apatite resulting in precipitation of recalcitrant pyromorphite [3,4]. Phosphate can effectively capture metal cations including those of heavy metal contaminants, and phosphatemetals precipitates are typically very stable over a wide range of environmental conditions [4]. Therefore, metalphosphate nanoparticles hold promise for effective remediation of contaminated sites. Our main objective was to characterize copper remediation using ironphosphate nanoparticles in the presence of common soil ligands using transmission electron microscopy and energy dispersive xray analysis.

An understanding of metal transformation processes and their kinetics using 'direct' solid state speciation is lacking and is critical to accurately predict contaminant stabilization. Nanoparticle dissolution and the stability of heavy metalphosphate phases can be affected by pH, their size and by the presence of common soil ligands such as metal chelating (siderophores, e.g., Desferrioxamine B) and phosphorus solubilizing ligands such as carboxylate based organic acid anions [5,6]. Here, nitrate salt of copper was added to pH adjusted (6.0) fixed suspension volumes (30 ml) containing 1.5 g/L nanoparticles and 10 mM KCl FePO₄ nanoparticles while stirring at moderate speeds to have a starting concentration of 1 mM Cu(II) in the sample. The experiment was performed in duplicates and the samples were equilibrated on a reciprocating water bath shaker at 25°C; sample aliquots were drawn at 24, and 336 hrs and centrifuged to remove the supernatants and refrigerated. Samples were prepared for TEM analysis by diluting the solid sample with supernatant and mounted on a holey carbon Ni coated grid. TEM data were collected on FEI Titan 80300 microscope equipped with 4kx4k Gatan CCD camera and energy dispersive xray spectrometer (Oxford Inca EDS, with spectral resolution of ~130 eV). Gatan doubletilt Be holder has been used to avoid Cu signal that may arise from the holder.

Figures 1a and 1b show TEM images of pristine ironphosphate nanoparticles. The TEM images showed ~10 nm irregularly shaped particles with poorly defined boundaries. TEM data suggest that the nanoparticles are mostly amorphous (noncrystalline). The EDS results evidenced that the variation in

the composition of nanoparticles are very small (Table 1). Figure 1b shows the TEM image of Cu(II) reacted iron-phosphate nanoparticles at 336 hrs. Since TEM images (compare e.g. Figs. 1a and 1b) did not indicate the formation of a new phase, the results are consistent with surface complexation of Cu(II) on iron-phosphate nanoparticles. In addition, the EDS results (Table 1) showed that $4\pm 2\%$ Cu(II) was associated with the nanoparticles at 24 hr and 336 hr indicating that complexation of Cu(II) was stable and the nanoparticles show great potential for in-situ remediation of Cu(II) contaminated ground and surface waters.

References:

- [1] Diawara et al., 2006.
- [2] Karn et al., 2009
- [3] Kumpiene et al., 2008;
- [4] Knox et al., 2006.
- [5] Scheckel and Ryan, 2002;
- [6] Manecki and Maurice, 2008
- [7] We acknowledge funding from the National Research Council of the National Academies, and support from Dr.Chunming Su of the EPA research office in Ada, OK.

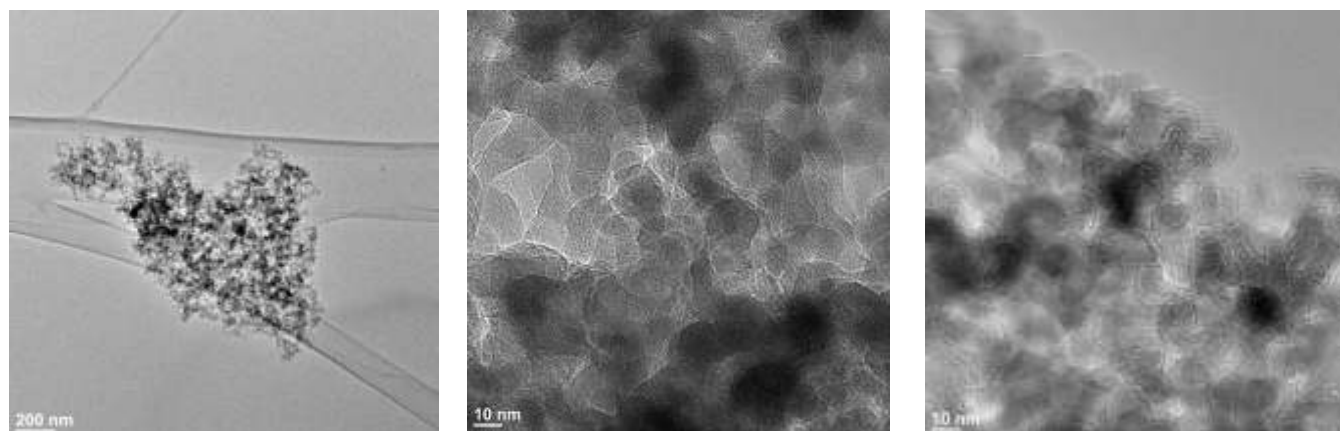


Figure 1. TEM images of pristine iron-phosphate nanoparticles (a,b) and nanoparticles reacted with Cu(II) at pH 6 in the presence of citrate and DFO-B.

Concentration (%)	Pristine nanoparticles	Nanoparticles reacted with Cu(II) at 24 hr	Nanoparticles reacted with Cu(II) at 336 hr
P	51 ± 3	48.7 ± 0.6	48.7 ± 0.6
Fe	49 ± 3	47.7 ± 1.1	47.7 ± 1.1
Cu	0	4 ± 2	4 ± 2

Table 1: Concentration of phosphate, iron, and copper in nanoparticles calculated from EDS results. Data from three points was averaged for each sample.