

Metal Speciation in Particulates in the Mississippi River in Louisiana

Basic Information

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Problem and Research Objectives

The levels of some toxic heavy metals in the Mississippi River have increased over the last several decades due to anthropogenic input, one of them being storm water. Storm water run off from the nation's highways often contains toxic heavy metals at high concentrations. They are derived from various sources such as automobiles, atmospheric deposition, and construction materials. The levels of heavy metals in stormwater can exceed EPA's safe drinking water criteria.

Sansalone and others (Liu *et al.* 2001; Liu *et al.* 2001a) have developed filter media which will remove heavy metals by adsorption on MnOx minerals in a very small space. Recent work, which included application of the MnOx (x depends on Mn charge) coating on concrete (MOCM) granules, showed that it is an effective medium in the removal of heavy metals from synthetic stormwater. Experiments in the laboratory showed that compared to ordinary concrete, the breakdown curve of the coated media was extended by several hours.

The basic building block of MnOx minerals is the MnO₆ octahedron. These can share edges to form sheets, and corners to form tunnel-like structures. Depending on the number of octahedra on each side of the tunnel, a MnOx structure can be 1x1, 2x3, etc., where each unit refers to one octahedron. The MnOx minerals are very fine grained and poorly crystalline, which result in a very high surface area (Post 1999). MnOx minerals are ubiquitous in soils and ocean floors. They possess very high adsorption capacity and selectively remove large amounts of heavy metals from these surroundings. They are highly charged, with the point of zero charge depending on the pH. Most of the adsorption of metal ions occurs at the surface of the MnOx minerals due to unsatisfied oxygen or hydroxyl bonds and only a minor amount enters the layers in between sheets (Taylor 1986).

The low crystallinity, small grain size and a high degree of mixing at the micrometer scale, makes characterization of MnOx minerals difficult. For example, single crystal X-ray structure analysis has not been performed for most MnOx minerals. Concrete itself is a multi-phase material, with the dominant phase the calcium silicate hydrate being a very poorly crystalline phase. X-ray absorption spectroscopy (XAS) was one of the several techniques used to investigate the properties of these media.

Chromium contamination is present in more than half of all EPA superfund sites (http://es.epa.gov/ncer_abstracts/sbir/91/phase1/topicf13.html). One of the problems associated with chromium contamination is that chromium has little or no interaction with the surrounding soil. The weak chromium soil interaction can result in wide spread groundwater contamination. It has been shown that strip mining, tanneries, and other industrial processes cause chromium contamination (Khan, 2001). Chromium in the hexavalent form is highly toxic and is a known cancer causing agent (Proctor et al. 2002). The current method of cleaning up a contaminated site is costly and time consuming. These technologies require continual monitoring to ensure public health. Phytoremediation can play an important role in cleaning up these sites. Instead of moving and processing the contaminated soil, it is possible to plant specific types of plants to clean the soil. Other plants have been shown the ability to uptake and sequester chromium. Mesquite (*Prosopis spp.*), sunflowers, soybeans, clover (*Trifolium*

bracycalynum), and creosote bush (*Larrea tridentate*) have the ability to remove chromium contamination from the soil. Watercress has been shown to have the ability to uptake Thallium without harming the plant and is an ideal candidate for more phytoremediation experiments. Watercress, as the name suggest, grows best near a stream or other bodies of water. It also grows well in cold climates. All these factors make watercress a perfect candidate for extracting metals out of a contaminated stream or river.

Methodology

Manganese oxide media

The manganese oxide media preparation techniques have been outlined in a series of publications by Sansalone and others (Liu et al. 2001a,b). In brief, two preparation methods were used to precipitate a birnessite-like MnOx and a cryptomelane-like MnOx. These coating were also applied to millimeter-size grains obtained from portland cement concrete.

Bioremediation

The watercress was grown in a water culture hydroponics system for two weeks. Each of the two ten-gallon glass aquariums was filled with 30 liters of distilled water. Both aquariums were given the proper amount of hydroponics fertilizer to maintain the watercress. To one aquarium 15 grams of Na₂CrO₄ was added, to obtain a final chromium concentration of 500 ppm. The watercress was obtained from a local grower and was grown in soil for seven days before selected cuttings were placed in a perlite medium. The watercress in the perlite medium was suspended in the aquarium so that 3 inches of the perlite was submerged into the water culture system. After two weeks, the watercress was extracted and left to dry for a week. The dried watercress was then separated into two sections, the stems and the leaves. Both stems and leaves were ground up to achieve homogeneity.

X-ray absorption spectroscopy

The XAS spectra were collected at the J. Bennett Johnston Sr., Center for Advanced Microstructures and Devices (CAMD), Baton Rouge, Louisiana, Double Crystal Monochromator beamline. The ring operated at 1.3 GeV. The current in the ring typically ranged between 130 to 60 mA. The experiments were conducted in air. The concentrated specimens were analyzed in transmission and those with low concentrations were analyzed in fluorescence by a thirteen-element high purity germanium detector. Specimens were prepared by smearing a very thin layer of the powder onto a Kapton tape. Ge 220 crystals were used in the monochromator. For chromium, the dried watercress samples were placed on Kapton tape for XAS analysis.

The XANES spectra for manganese were collected from 200 eV below the edge to up to 20 eV blow the edge in 3eV steps; from – 20 eV to 60 eV above the edge in 0.3 eV steps; and 60 eV above the edge to 300 eV above the edge in 3 eV steps. For manganese EXAFS, the range over which data could be collected was limited by the iron K edge at 7112 eV. Thus only several hundred eV of data could be collected. The steps

were 3 eV below the edge and 2 eV above the edge up to 7112 eV. The data was reduced by Athena written by Bruce Ravel.

The XANES spectra for chromium were collected from 200 eV below the edge with 3 eV steps, from 20 eV from the edge to 40 eV above the edge with 0.3 eV steps, and up to 300 eV above the edge with 2 eV steps. The counting time at each step was determined in inverse proportion to the number of counts in that region.

Principal Findings and Significance

Manganese-coated cementitious media for wastewater treatment

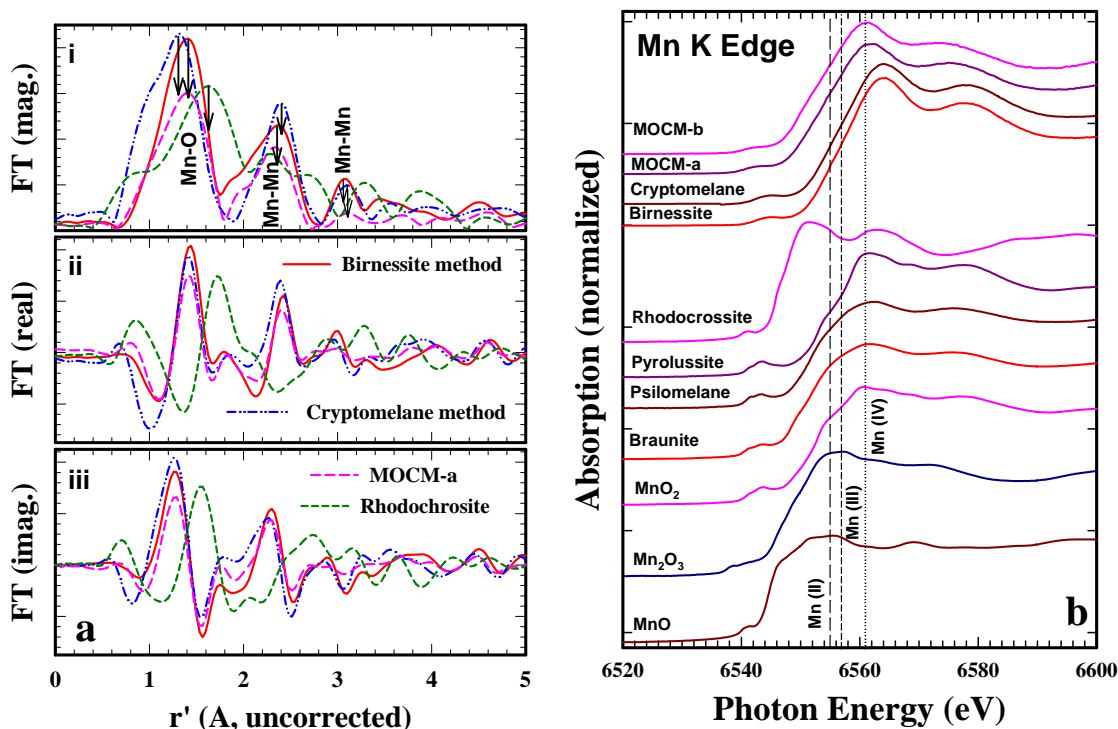


Figure 1: i: EXAFS spectra; ii: XANES spectra

Figure 1a shows the EXAFS spectra of the coating media. Broadly, there are three main peaks (Figure 7i), corresponding to Mn-O, Mn-Mn (edge-sharing), and Mn-Mn (double-corner sharing) distances (Manceau and Combes 1988). The double-corner sharing shell is absent in manganese phyllosilicates (birnessite in this study), where only edge-sharing between Mn-O octahedra occurs. The todorokite structure, in contrast, has both edge-sharing and corner sharing tetrahedra. Thus, while only two MnO distances occur in birnessite, 2.85 and 2.95 Å, four Mn-O distances occur in todorokite. These are 2.84 Å, 2.93 Å, 3.46 Å, and 3.56 Å. The former two correspond to edge sharing distances, while the last two correspond to double-corner sharing distances. The EXAFS spectra of both the MnOx coatings show a strong Mn double corner peak.

Cryptomelane, a 1x1 MnOx structure (Post 1999), has both edge sharing and double cornering sharing octahedra like todorokite. Considering that TEM observations show only one MnOx phase in the birnessite-type coating, EXAFS suggest that the “birnessite” method coating has more of a tunnel-like structure. The ratio of the peak heights of Mn-Mn(edge) to Mn-Mn(corner) suggests that the “birnessite” method product is similar to nsutite, while the cryptomelane product is similar to ramsdellite. However, the cryptomelane precipitate is not a single phase but a mixture of MnOx phases.

The Mn K edge XANES spectra of the coating media are shown in Figure 1b. Several standard mineral spectra are also shown. A comparison of the birnessite method Mn XANES spectrum with the birnessite synthesized by Guest et al. 2002 (Guest *et al.* 2002) shows a substantial difference. A comparison among these spectra shows the following: the coating media have little Mn²⁺, most of the Mn being in the 4+ state. A least squares fitting of the birnessite method residue by pyrolusite and synthetic Mn₂O₃ showed it to be 80% Mn⁴⁺. However, the residual is somewhat high indicating that these are not the most appropriate standards to fit. Still, the fit provides an indication of the proportions of different oxidation states.

The EXAFS data of MOCM-a are shown in Figure 7a. The figure (Figure 7ai) shows a distinct bulge around 1.9 Å in the pseudo-radial distance of the MOCM compared to those of the MnOx coatings. A comparison of the real and imaginary parts of the Fourier transforms suggests that the bulge is due to Mn-O shell in rhodochrosite which occurs at a much larger distance than the Mn-O shell in the MnOx coatings. Some manganese is thus entering the calcium carbonate structure. A comparison of the edge-sharing and corner sharing peak heights suggest that lesser corner sharing occurs in MOCM compared to the coatings themselves. Thus the MOCM MnOx has more birnessite-like structure.

The Mn K edge XANES spectra of MOCM-a and -b are shown in Figure 7b. Least squares fitting of the Mn spectra of MOCM-a showed that it contains more Mn³⁺ and possibly a minor amount of Mn²⁺. Qualitatively, these spectra occur at lower energy compared to the MnOx coatings, indicating they have less Mn⁴⁺. MOCM-b absorption edge occurs at slightly lower energy compared to MOCM-a, indicating it has lower overall oxidation state. The addition of rhodochrosite to the fit did not decrease the residual suggesting either its absence or its presence in a very small amount.

XANES spectroscopy of the coatings shows that very little of the Mn is present in the +2 oxidation state, if any. Assuming that only one type of MnOx is present in the birnessite-like coating, an assumption supported by TEM observations, the MnO₆ octahedra in the phase has both edge-sharing and corner-sharing octahedra. Thus the structure is unlike that of birnessite, which has only edge-sharing octahedra.

Hyperaccumulation, and Reduction of Cr (IV) to Cr (III) From a Hydroponics Solution by Watercress (Nasturtium officinal)

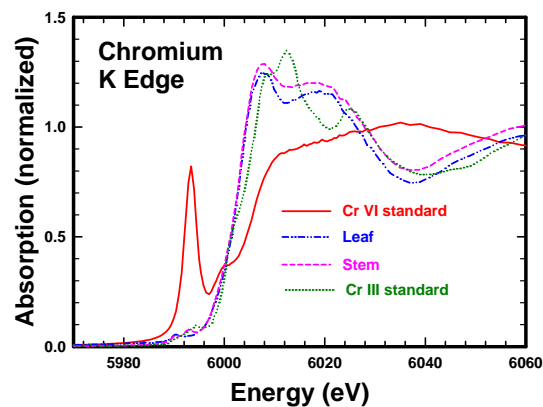


Figure 2

Figure 2 shows the XAS spectra of the leaf and stem samples of the watercress used in remediation treatment, along with that of sodium chromate, a standard.

First, the strong chromium peak in both the leaf and the stem indicates that watercress contains chromium and is capable of removing it from solution. Second, the hexavalent strong pre-edge peak of chromium at 5993.4 eV is completely reduced in the leaf, whereas some Cr VI remains in the stem. This pre-edge peak is absent in Cr III.

Flame atomic absorption spectroscopic analysis of the stem and leaf samples of the watercress was performed to obtain their chromium content. The concentrations of chromium in the stem and leaf samples were 400 ppm and 5,400 ppm, respectively. Watercress is thus a hyper accumulator of Cr.

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