

Catalytic Transformations of Chromium on Mn Substituted Goethite

Goethite is one of the common iron oxide minerals in soils. Our previous studies showed that goethite is capable of reducing toxic Cr(VI) to less toxic Cr(III) under sunlight. However, natural goethite is rarely stoichiometric and usually contains certain substitutional cations, such as Mn(III) or Mn(IV), which, on the other hand, is an oxidant for Cr(III). In order to provide more insight into the fate of Cr(VI) in the environment, the influence of Mn-substitution in goethite on its Cr(VI) photoreduction capability was further clarified in this study. Experiments were conducted to investigate the adsorption and photo-transformations of Cr on Mn-substituted goethite with Mn/(Mn + Fe) molar ratios ranging from 0 to 0.1. The results showed that Cr(VI) photo-reduction was decreased with increasing Mn-substitution in goethite. The re-oxidation of photo-reduced product, i.e., Cr(III), at the Mn sites on the surface of goethite is responsible for the lower Cr(VI) photo-reduction capacity of Mn-substituted goethite. Thus, the role of goethite in the reduction of Cr(VI) may be overestimated unless its Mn-substituted counterparts are considered. The effectiveness of Mn sites in goethite to increase toxic Cr(VI) has important implications in determining the fate and threat of Cr(VI) contamination.

Chromium (Cr) is one of the priority contaminants of major concern in the environment. In the environment, Cr exists in two common oxidation states, Cr(VI) and Cr(III), depending on pH and redox conditions. Cr(VI) is highly toxic, whereas Cr(III) is less harmful to humans and an essential nutrient for living organisms. Due to the significant differences in the toxicities and mobilities of Cr(III) and Cr(VI), understanding the redox transformations between Cr(VI) and Cr(III) is of great importance in determining their fates and potential threat to the ecosystem.

Our previous study showed that photo-reduction Cr(VI) to Cr(III) can occur on the surface of goethite (α -FeOOH, a common mineral in soils) in aqueous solutions without the addition of any reductants. Since Fe(III) sites in goethite cannot provide electrons to reduce Cr(VI), water molecules were suggested to be the electron donor. However, pure goethite is rare in the environment and natural goethite usually contains a number of substitutional cations such as Al³⁺, Mn³⁺ and Mn⁴⁺. The effects of metal-substitution on the surface properties of goethite on the adsorption and oxidation/reduction of Cr on goethite need to be further clarified in order to understand the role of goethite on the redox transformation of Cr. In this study, Cr(VI) reduction on Mn-substituted goethites was investigated. Chromium(VI) can be photo-reduced to Cr(III) by pure goethite, but co-existent Mn in the same structure may potentially oxidize Cr(III). The competition of these two reactions was demonstrated in this work.

Beamlines

17A X-ray Powder Diffraction
17C EXAFS

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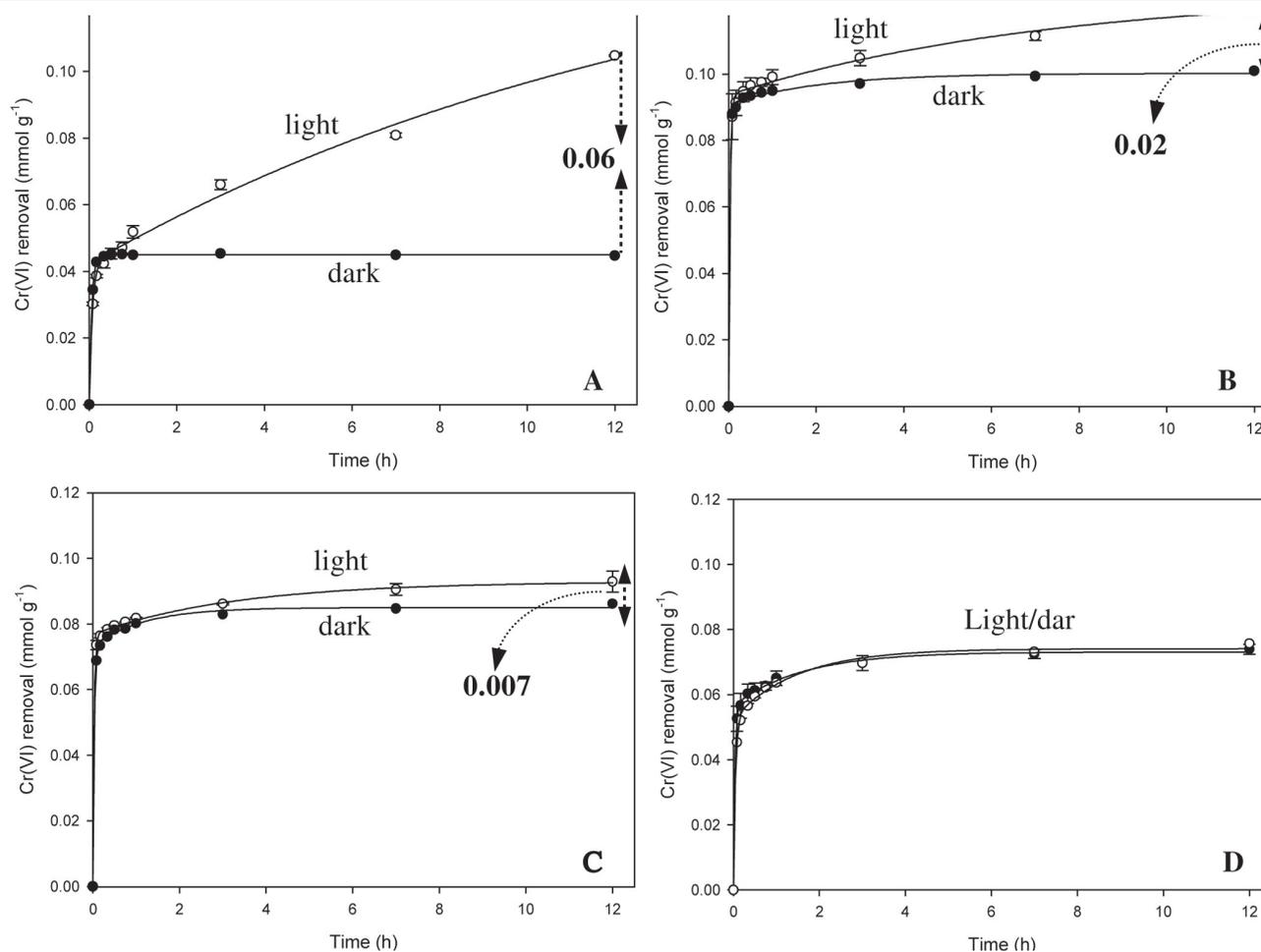


Fig. 1: The enhancement of Cr(VI) removal on pure and Mn-substituted goethite in the presence of light as a function of time. The goethite concentration is 1 g L⁻¹, and the initial Cr(VI) concentration is 0.192 mM. A: pure goethite; B: 1% Mn-goethite; C: 5% Mn-goethite; D: 10% Mn-goethite.

Mn-substituted goethite samples were synthesized with the Mn/(Mn+Fe) molar ratios of 0, 0.01, 0.05, and 0.10 (denoted as FeMn₀, FeMn₁, FeMn₅ and FeMn₁₀, respectively). Fig. 1 shows the Cr(VI) removal kinetics on pure and Mn-substituted goethite samples with and without UV illumination. The term "removal" is used here to describe the overall loss of Cr(VI) from the solution due to the adsorption and photoreduction of Cr(VI) that are concurrent in the system. The results showed that the rates of Cr(VI) removal by the goethite samples were significantly enhanced when the Cr(VI)/ goethite systems were exposed to the UV light. The enhancement in the removal rate was most significant in the system of pure goethite and gradually decreased with increasing Mn content in the samples. In this system, UV illumination resulted in an increase of 0.06 mmol g⁻¹ in Cr(VI) removal after 12-h reaction (Fig. 1a). Comparatively, in the systems of FeMn₁ and FeMn₅, the increases in Cr(VI) removal due to UV illumination was only 0.02 and 0.007 mmol g⁻¹, respectively (Figs. 1b and 1c). As the Mn substitution was further increased to 10% (i.e., the sample

of FeMn₁₀), the influence of light exposure on the reaction rate of Cr(VI) removal became insignificant (Fig. 1d). These results showed that an increase in the Mn substitution results in a less discrepancy between the Cr removal rates with and without light exposure. Therefore, the presence of Mn in goethite structure suppresses the Cr(VI) photo-reduction rate on goethite.

The portion of Cr(VI) removal increased after light exposure was attributed to photo-reduction of Cr(VI) and formation of Cr(III) oxide on the surfaces of goethite, as indicated by the Cr K-edge XANES results. This was confirmed using the orthophosphate extraction method, with which adsorbed Cr(VI) can be desorbed from the surface while adsorbed Cr(III) cannot. The average recovery rate of Cr(VI) was determined to be 98.6% for Mn-substituted or pure goethite samples reacted with Cr(VI) in the dark. Thus, upon exposure to UV light, any decrease in the desorbed Cr(VI) by orthophosphate would be the result of the photoreduction of Cr(VI) to Cr(III) in the system.

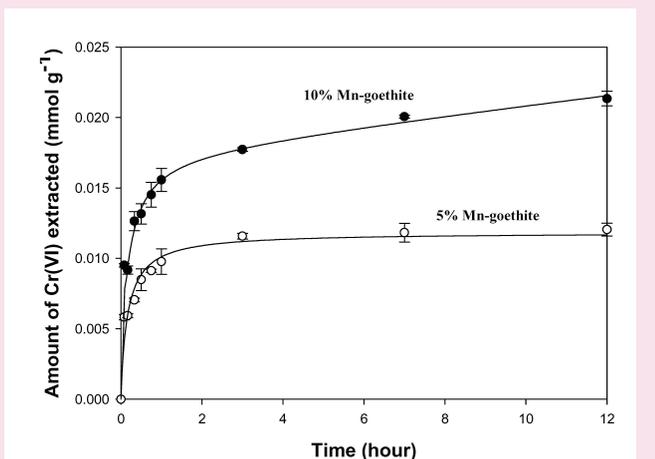


Fig. 2: The oxidation of Cr(III) to Cr(VI) on Mn-goethite at pH 4 as a function of time.

A decrease in Cr(VI) adsorption upon increasing the Mn content in goethite would consequently result in the decrease in the Cr(VI) photoreduction of the material. On the other hand, after adsorbed Cr(VI) was reduced to Cr(III), the Cr(III) species on the surface may be preferentially associated with the surface Mn sites due to the higher potential of proton dissociation on Mn-OH groups than that of Fe-OH groups. Subsequently, surface Cr(III) interacted with surface Mn sites may be re-oxidized to Cr(VI). To clarify whether Mn sites in goethite structure can oxidize Cr(III), Cr(III) adsorption was conducted for FeMn5 and FeMn10. As shown in Fig. 2, Cr(III) could be oxidized on Mn-substituted goethite, and the oxidation proceeded continuously with prolonged reaction time. Meanwhile, the oxidation rate increased with an increase in Mn substitution. For instance, 0.02 mmol g⁻¹ of Cr(III) was oxidized to Cr(VI) after reacting with 10% Mn-substituted goethite for 12 h, whereas only 0.007 mmol g⁻¹ of Cr(VI) was determined after 12 h for 5% Mn-substituted goethite (Fig. 1). These results provided evidence that the re-oxidation of Cr(III) to Cr(VI) on Mn-substituted goethite may occur after Cr(VI) is photo-reduced to Cr(III).

Under illumination, Cr(VI) can be adsorbed and reduced to Cr(III) on the surfaces of both goethite and Mn-substituted goethite. With an increase in the Mn content of goethite, the reduction rate of Cr(VI) significantly decreased, mainly resulting from a corresponding decrease in Cr(VI) adsorption. In addition, the re-oxidation of photo-reduced product, i.e., Cr(III), also cause the depression of Cr(VI) reduction in the Mn-substituted system under illumination. Since goethite and metal-substituted goethite are widely distributed in soils, the results of this work can provide more insight into Cr transport, transformation, and toxicity in the environment. ■

Experimental Stations

EXAFS end station
X-ray powder diffraction end station

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