Oxidation of Cr(III)-citrate/tartrate complexes by δ-MnO$_2$: Production of Cr(VI) and its impact factors

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ABSTRACT

Cr(III)-cit and Cr(III)-tar were synthesized and purified, and then their stability in the presence of δ-MnO$_2$ was further investigated in batch experiments under different conditions to predict the potential oxidation behaviors of Cr(III)–organic acid complexes in the environment. The results indicated that although the rates and extents of Cr(III)-cit and Cr(III)-tar oxidation by δ-MnO$_2$ were much lower than those of aqueous Cr(III), Cr(VI) could be gradually released through the whole reaction. The oxidations of Cr(III)-cit and Cr(III)-tar were affected by the initial concentrations of δ-MnO$_2$, pH and co-existing ions. Lower pH and higher concentrations of δ-MnO$_2$ markedly enhanced the production of Cr(VI). Ammonium ions significantly improved the oxidation of Cr(III)-cit and Cr(III)-tar, but phosphate ions demonstrated an opposite effect due to the formation of more stable CrPO$_4$. The oxidation process of Cr(III)-cit and Cr(III)-tar by δ-MnO$_2$ can be divided into two phases. At the initial phase, a relatively rapid reaction obeyed the first-order model, and then a zero-order one was followed. It was observed that in all the cases the extent of Cr(III)-cit oxidation was lower than that of Cr(III)-tar. Thus, it was concluded that the stability of Cr(III)-cit was higher than that of Cr(III)-tar.

1. Introduction

Chromium (Cr), from natural sources (Oze et al., 2004) and anthropogenic discharge (Brandt and Elding, 1998), found its way into the environment and posed a serious threat to both animals and plants. It exists in numerous valence states in natural environments, but the most common and stable states are Cr(III) and Cr(VI) with different toxicity, mobility and bioavailability. Cr(III) is less mobile and approximately 100 times less toxic than Cr(VI) (Max, 2003).

Thus, the research to enhance the immobilization of Cr(VI) for site remediation of Cr(VI)-contaminated water and soil has been widely conducted. Zero valent iron, divalent iron and sulfide are the common reductants for the conversion of Cr(VI) into Cr(III) and frequently reported in literature (Lan et al., 2005, 2006; Melitas et al., 2001; Seaman et al., 1999). Organic acids containing α-OH groups, such as citric acid and tartaric acid, are also very efficient in the reduction of Cr(VI) to Cr(III), especially in the presence of Mn(II) or Fe(III) with irradiation (Lan et al., 2008; Li et al., 2007; Tian et al., 2010).

Because less toxic Cr(III) species can be potentially transformed into harmful Cr(VI) in the presence of certain oxidants, the oxidation of Cr(III) has been an increasing concern. Schroeder and Lee (1975) investigated the effect of dissolved oxygen in soil on Cr(III) oxidation. Their results indicated that dissolved oxygen had exiguous contributions to

the oxidation of Cr(III). An extremely small amount of Cr(III) oxidation by dissolved oxygen was observed over a 2-week period. Eary and Rai (1987) also reported that no aqueous Cr(VI) was detected in a 19 μM Cr(III) solution with approximately 8 ppm dissolved oxygen at pHs from 4 to 12.5 even after 24 days.

Photo-oxidation is another possible pathway of converting Cr(III) to Cr(VI) (Ciesla et al., 2004; Zhang and Bartlett, 1999). Ciesla et al. (2004) observed that Cr(III)–EDTA could be oxidized to Cr(VI) in alkaline solutions. Dai et al. (2010, 2011) investigated the photo-oxidation of Cr(III)-citrate and Cr(III)-tartrate (hereinafter abbreviated as Cr(III)-cit and Cr(III)-tar, respectively) and pointed out that the oxidation rates of both Cr(III)-cit and Cr(III)-tar were much faster than that of aqueous Cr(III).

In comparison with dissolved oxygen and photo-oxidation, manganese oxides contribute dominantly to Cr(III) oxidation in natural environments (Brandt and Elding, 1998). Manganese oxides with outstanding adsorption capacity and strong oxidizing ability have been proved to be the only inorganic oxidants capable of oxidizing Cr(III) to Cr(VI) in the soil environment (Eary and Rai, 1987). However, the reaction is controlled by many factors, such as the surface characteristics of oxides, competitive ions, pH and the availability of dissolved Cr(III) to the surface of manganese oxides (Apte et al., 2006; Eary and Rai, 1987). Bartlett (1991) reported that a large portion of Cr(III) in soils even under the favorable conditions was not oxidized to Cr(VI) by manganese oxides due to the shortage of dissolved Cr(III). This result was also confirmed by Dai et al. (2009), who indicated that some insoluble forms of Cr(III) were quite stable. The role of Mn-oxidizing microorganisms in Cr(III) oxidation has attracted more attention (Emerson, 2000).

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Microorganisms mediate Mn(II) oxidation to form manganese oxides, which subsequently converts Cr(III) into Cr(VI) (Wu et al., 2005).

As mentioned previously, citric acid and tartaric acid, commonly present in soils, are often utilized for Cr(VI) reduction, and the complexes of Cr(III)-cit and Cr(III)-tar form subsequently. The formation of the complexes will enhance the possibility of Cr(III) oxidation by manganese oxides in soils owing to the higher solubility and mobility of Cr(III)–organic acid complexes than aqueous Cr(III) (Cao et al., 2011). However, up to now few attempts or deeper investigations into the oxidation of Cr(III)-cit and Cr(III)-tar by manganese oxides have been carried out but for the reports on photo-oxidation of Cr(III)–organic acid complexes (Ciesla et al., 2004; Dai et al., 2010, 2011). In this study, the oxidation of Cr(III)-cit/tar by δ-MnO$_2$ and its impact factors including reactants concentrations, pHs and coexisting ions were investigated. δ-MnO$_2$ was selected since it is a major manganese-bearing mineral found in many soils. Therefore, it is believed that this study can contribute to the comprehensive understanding of Cr(III) oxidation in soils.

2. Materials and methods

2.1. Chemicals

Stock solutions of citric acid (0.1 M) and tartaric acid (0.1 M) were prepared by dissolving reagent-grade citric acid and tartaric acid (Shanghai Chemical Co., Ltd.) in deionized water, respectively. Stock solution of Cr(III) (0.01 M) was obtained by dissolving CrCl$_3$·6H$_2$O(s) (Sinopharm Chemical Reagent Co., Ltd) in diluted HCl solution (pH < 2 in case of hydrolysis). Stock solution of DPC (1, 5-diphenylcarbazid, purchased from Sigma Aldrich Company) was prepared by dissolving 0.2 g DPC in 100 mL acetone and then put in a brown bottle and stored in a fridge prior to use. Acetate buffer solutions (0.1 M) with a pH range of 4 to 6 were obtained using CH$_3$COOH and NaOH. The solutions of Cr(III)-cit and Cr(III)-tar with desired pH for oxidation experiments were separately prepared by diluting synthesized Cr(III)-cit and Cr(III)-tar solutions (see Section 2.3) . All the other chemicals used in this study were at least of reagent grade.

2.2. Preparation of δ-MnO$_2$

δ-MnO$_2$ was prepared according to the method reported by Mckenzie (1971). Manganese oxide obtained in this study was examined by X-ray diffraction (XRD) (Rigaku Rotaflex D/max, Japan) using Cu Kα radiation (50 kV, 150 mA) at a rotation speed of 10° 2θ min^{-1} in the 2θ range of 5–75° and the XRD pattern (data not shown) suggested that the collected solid was pure δ-MnO$_2$ particles. The specific surface area of δ-MnO$_2$ was 22 m^2 g^{-1}, measured by BET (Brunauer-Emmett-Teller) adsorption isotherm technique on a JW-004 surface area analyzer (Beijing Jing Wei Gao Bo). The stock suspension of δ-MnO$_2$ with 0.1 M concentration was prepared by mixing δ-MnO$_2$ (s) in deionized water and then kept in the refrigerator. It must be evenly stirred by a magnetic stirrer simultaneously prior to use.

2.3. Preparation of Cr(III)-cit and Cr(III)-tar

As mentioned previously, citric acid and tartaric acid are frequently used for Cr(VI) reduction. Therefore, it is necessary to eliminate the impact of these free acids on the oxidation of Cr(III)-cit and Cr(III)-tar. Cr(III)-cit was prepared according to the method reported by Dai et al. (2010). Briefly, Cr(III)-cit was obtained by mixing 2:1 molar ratio of Cr(III) and citric acid solutions at pH 6 and 25 °C for 48 h. Excessive Cr(III) was used for complete chelation of citric acid. The mixture was then filtered and purified by 732 cation exchange resin to eliminate unchelated Cr(III). The effluent was collected and examined by HPLC and UV–Vis spectrophotometry, and no free Cr(III) and citric acid were found in the collected solution. The concentration of Cr(III)-cit

was finally measured by AAS, and the stock solution (1000 μM) was stored in the fridge prior to use. The procedures of Cr(III)-tar preparation were almost the same as above except for the optimal pH being 4 rather than pH 6.

2.4. Oxidation experiments

The oxidation of Cr(III)-cit and Cr(III)-tar was conducted in brown bottles to eliminate the interference of light. The desired stock solutions of Cr(III)-cit/tar and δ-MnO$_2$ were in turn introduced into the acetate buffer solution, and the final volume of the suspension was 100 mL. And then the reaction vessels were tightly sealed and immersed in Thermostat Water Bath Shaker at 180 rpm and 25 °C. At certain intervals (the intervals were also depended), about 3 mL sample was drawn out with a plastic syringe from the suspension and expeditiously filtered via a 0.22 μm membrane filter into a clean and dried glass tube. Aliquot of filtrate (1.0 mL) was drawn out with a pipette for the determination of Cr(VI) concentration. All the experiments in this study were performed in triplicate.

2.5. Analytical methods

The Cr(VI) concentration was measured by the DPC colorimetric method. Sulfuric acid, diluted 20 times by deionized water (v/v), was used to control pH for color development. The absorbance of each sample was determined by a 1-cm cell at 540 nm on a UV-9100 spectrophotometer (Beijing Ruili Co., Ltd). The concentration of total Cr was measured by AAS and those of Cr(III)-cit and Cr(III)-tar complexes were calculated by the difference of total Cr and Cr(VI). An Orion 868 pH meter, after three-point calibration, was used to determine pH values. The chromatographs of citric acid and tartaric acid were conducted by HPLC (Waters 2487). The mobile phase consisted of 25 mM NaH$_2$PO$_4$ with pH 2.4 and 10% (v/v) MeOH. LiChrospher C$_{18}$ (5 μm, 250 mm × 4.6 mm) was used as the separation column. The components in the effluent were detected at 214 nm for citric acid and 210 nm for tartaric acid.

3. Results and discussion

3.1. Effect of δ-MnO$_2$ concentration on the oxidation of Cr(III)-cit and Cr(III)-tar

The effect of δ-MnO$_2$ concentrations ranging from 500 to 2000 μM on the oxidation of Cr(III)-cit and Cr(III)-tar was investigated at pH 4 and 25 °C, and the results are shown in Fig. 1. Aqueous Cr(III) was rapidly oxidized to Cr(VI) and the oxidation rates increased with the initial concentrations of δ-MnO$_2$ at the beginning stage of the reaction (Fig. 1). However, during the period of 2 to 12 h, the reaction rates and extents in all the cases were almost the same and the oxidation percentages of Cr(III) were at approximately 96%, indicating that no Cr(III) was further converted to Cr(VI). Nevertheless, by the end of the reaction (24 h) the remaining Cr(III) was further transformed into Cr(VI) and the oxidation percentage reached approximately 100%. The results about aqueous Cr(III) oxidation were well supported by those in the literature. For example, Dai et al. (2009) observed that less than 90% Cr(III) was oxidized over δ-MnO$_2$ at pH 5 and pointed out that Mn(II) yielded from the reduction of manganese oxides competed with Cr(III) for adsorption sites on the surface of manganese oxides, inhibiting the Cr (III) oxidation in the later stage of the reaction. Ross and Bartlett (1981) also found that the adsorption of added Mn(II) on soil manganese oxides blocked Cr(III) oxidation until Mn(II) adsorbed on soil manganese oxides was re-converted to MnO$_2$. Taking all the facts into account, it is concluded that the further enhancement in Cr(III) oxidation after 12 h was ascribed to the re-oxidation of adsorbed Mn(II) by dissolved oxygen in the reaction system. However, the rates and extents of Cr(III)-cit and Cr(III)-tar by δ-MnO$_2$ were much lower than those of aqueous Cr(III).