Reaction of aqueous Cu–Citrate with MnO₂ birnessite: Characterization of Mn dissolution, oxidation products and surface interactions

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HIGHLIGHTS

- Cu–Citrate can be oxidized at the MnO₂ interface.
- Adsorbed ionic Cu(II) exhibits isomorphic substitution with Mn(II).
- Initial surface coordination may take place through a Cu(II) ternary Type A complex.
- Acetonedicarboxylate may decarboxylate through MnO₂–Cu surface catalysis.
- XPS results show MnO₂ surface hydration and interfacial Copper redox activity.

GRAPHICAL ABSTRACT

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ABSTRACT

Citric acid, a widespread soil rhizosphere plant/microbe carboxylic acid exudate can easily form chelates with heavy metals, increasing their availability in the environment. When Cu(II) from algal control in water bodies or reservoirs and fungicides, such as the Bordeaux mixture, and citrate interact, solubilization through chelation is a possible outcome. Manganese (hydr)oxides represent a significant portion of the subsurface environment and can affect the fate and transport of chemical species through adsorption and oxidation. This study explores the possible interaction between MnO₂ and Cu–Citrate under ambient oxic conditions. The calculated Mn(II) dissolution rates during the initial 1 h of reaction followed the series Cu(II) > Cu–Citrate 1:0.5 > Cu–Citrate 1:1_(oxic) > Citrate > Cu–Citrate 1:1_(anoxic), reinforcing the central role of (complexed or un-complexed) Cu(II) during the initial surface-coordination instead of following the s-shaped auto-catalytic curves of Mn(II) dissolution in citrate solution. The use of capillary electrophoresis allowed the detection of an intermediate Cu(II)Acetonedicarboxylate complex and the oxidation products acetonedicarboxylate, acetoacetate, acetone and acetic acid. The mass balance analysis of Cu–Citrate 1:1 suggests the partial adsorption of Cu–Citrate(ads) and catalytic degradation of acetonedicarboxylate through a MnO₂–Cu surface sorbed complex. Lastly, XPS analysis confirmed the MnO₂ surface Cu(II) reduction along with an outer-hydration layer at the MnO₂ interface, where electron transfer and aquo ligand exchange may lead to the oxidation of Cu–Citrate.

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1. Introduction

Initially assumed to lead to minor deleterious environmental effects, the widespread application of copper for algal bloom control in reservoirs and recreational open water bodies, along with fungicide treatment in orchards and vineyards, has inadvertently led to the persistent accumulation and transport of copper wastes. The addition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ to a reservoir for algal control over a period of 15 yrs has led to $100\text{--}500 \mu\text{g g}^{-1}$ Cu accumulation in the top 5 cm of the soils (Haughey et al., 2000). Application of the Bordeaux mixture ($\text{Ca}(\text{OH})_2 + \text{CuSO}_4$) fungicide in vineyards has led to long-term soil storage, with on-site grown maize root concentrations of Cu between 90 and 600 mg kg^{-1} (Brun et al., 2001). Although relatively “trapped” by soil, the unwanted transport of Cu through solubilization remains a problem. In a large survey of urban, rural and forest soils, including orchards to which Cu pesticides have been applied since the 1900s, 98% of the soluble copper was bound to organic ligands (Sauve et al., 1997). Evidence from X-Ray Absorption Near Edge Structure (XANES), X-ray Fluorescence (XRF) and Extended X-Ray Absorption Fine Structure (EXAFS) data has provided confirmation that over 90% of the Cu in the soil samples is present as Cu–SOM (soil organic matter) complexes as opposed to ionic forms (Strawn and Baker, 2009). Citric acid is ubiquitous in the natural environment and can be released as a rhizosphere microbial or plant root exudate that can form equimolar coordination compounds with heavy-metals. Although citrate complexation may alleviate soils with high Cu contamination, membrane permeation of Cu–Citrate leads to visibly stunted growth and chlorosis in *Lolium perenne* (Johnson and Singhal, 2013). Various metal hydroxides (FeOOH , MnO_2 , Al_2O_3 , etc.) are primary components of rhizosphere soils. In a study of Cd–citrate adsorption to Al_2O_3 , low pH enhanced ternary surface complex formation (=Al-Cit-Cd^0) whereas alumina deprotonation at a higher pH led to decreased citrate adsorption and competition with the aqueous (Cd-citrate^{-1}) complex (Boily and Fein, 1996). Manganese hydr(oxides) are powerful oxidants and effective natural cation-exchange sinks, and they can be reduced by organic acid carboxyl or hydroxyl functional groups (Stone and Morgan, 1984). In a study of the citric acid $\delta\text{-MnO}_2$ reaction, an induction period and s-shaped Mn(II) dissolution curves led to the proposal of a special auto-catalytic Mn(II)–Mn(III)–citrate cycle (Wang and Stone, 2006a). Although some amount of foundational work on the interactions of citrate under different conditions has been laid, questions remain regarding the Cu–Citrate reactions with subsurface (hydr)oxides or other Cu-coordination complexes.

This study aims to characterize the interaction between MnO_2 and Cu citrate. Cu(II) adsorption was examined, dissolved Mn(II) retained in solution was plotted as a function of time, and capillary electrophoresis allowed the identification of the reaction intermediates. Finally, zeta potential measurements, XPS analysis and in situ ATR-FTIR allowed analysis of the reactions occurring at the MnO_2 solid/water interface.

2. Materials and methods

All of the stock and experimental solutions and the solutions were prepared from reagent grade chemicals using de-ionized water (DDW). When cleaning glassware for use in the experiments, it was first soaked overnight in 4 M HNO_3 and then rinsed using deionized water.

2.1. Chemicals

Citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$), CuCl_2 , MnCl_2 , potassium permanganate (KMnO_4), NaOH and NaCl were purchased from

Sinopharm Chemical Reagent Co., Ltd., Beijing. The oxidation product “acetonedicarboxylate” was purchased from the Tokyo Chemical Industry Co., Ltd., The additional oxidation products, “acetoacetate” (lithium acetoacetate) and acetone, were purchased from Sigma Aldrich. For the capillary electrophoresis buffer, 1-tetradecyl trimethyl ammonium bromide (TTAB) was purchased from Alfa Aesar, Beijing.

2.2. Manganese dioxide preparation and characterization

MnO_2 was synthesized using the stoichiometric oxidation of Mn(II) by Mn(VII) (Stone, 1987). The XRD analysis yielded *d*-spacing patterns located at 7.23, 3.66, 2.57 and 1.69 Å. These patterns are consistent with the literature (Wang and Stone, 2006a). The BET analysis of the solid yielded a surface area of $74 \text{ m}^2 \text{ g}^{-1}$, with an average pore size of 114.68 Å and a single-point total pore volume of $0.21 \text{ cm}^3 \text{ g}^{-1}$. The zeta potential analysis indicated a pH_{pzc} at approximately 3.0 (Fig. 3). Further details of the MnO_2 preparation can be found in the Supporting Information.

3. Experimental setup

Experiments on the effect of the Cu:Citrate ratio were conducted in Al-foil-wrapped 500 mL glass beakers. Cu(II) and citrate were prepared (in 1:1, 1:0.5 and 1:0 molar ratios) and later diluted to a final concentration of 0.25 mM. The ionic strength was 0.01 M NaCl, and the pH (5.5 ± 0.03) was adjusted with 0.1 M NaOH and HCl during dilution to a final solution volume of 500 mL. The temperature ($25 \pm 0.5^\circ\text{C}$) was controlled by a heated magnetic stirrer. The MnO_2 concentration employed in all of the experiments was 0.1 g L^{-1} . For anoxic conditions, N_2 gas was purged before and continuously during the reaction, whereas oxic conditions were conducted under ambient lab conditions. After MnO_2 addition, the reaction pH was tested at various time intervals and adjusted accordingly. At predetermined times, 5 mL samples were withdrawn, passed through a $0.45 \mu\text{m}$ filter and acidified to a pH value ≤ 3 for total dissolved Cu(II) and Mn(II) quantification by ICP–OES (Inductively Coupled Plasma Spectroscopy, Agilent, U.S.A.).

The capillary electrophoresis experiments were conducted in 300 mL glass beakers following a similar preparation of the Cu–Citrate 1:1 and Citrate from the “Cu:Citrate ratio experiments” under ambient oxic conditions. Aliquots (1 mL) were withdrawn at specified times and passed through a $0.22 \mu\text{m}$ filter for direct analysis by capillary electrophoresis. Additional experimental details can be found in Fig. 2.

Zeta potential experiments were conducted (in triplicate) in 50 mL lysing test tubes placed on an end-over-end rotator in the lab at 25°C with rotation at 140 rpm to ensure an even suspension. The experimental conditions were as follows: 0.1 g L^{-1} of MnO_2 , temperature of 25°C , ionic strength of 0.01 M NaCl, Cu(II) concentration of 0.25 mM, Cu–Citrate 1:1 concentration of 0.25 mM. The solution pH varied as follows: Cu(II) solution (pH 4–7), Cu–Citrate 1:1 (pH 5–8) and MnO_2 (pH 3–10). Dilute NaOH and HCl were used for the pH adjustments. The samples were withdrawn after 48 h of reaction time and analyzed using a Beckman Coulter (Delsa Nano C Particle and Zeta Potential Analyzer).

XPS and in situ ATR-FTIR experiments were completed following the same conditions as the ratio experiment with 500 mL beakers, whereas in situ ATR-FTIR was conducted using 300 mL beakers at 25°C . For the XPS experiments, 10 mL samples were removed at 1 h, 6 h, 12 h and 24 h reaction times and passed through a $0.2 \mu\text{m}$ filter to capture the reacted solid MnO_2 particles, which were then placed directly into a lyophilizer to dry/store the samples for XPS analysis. Information on the analytical machines and the data processing can be found in the Supporting Information.

4. Analysis methods

Capillary electrophoresis: Cu–Citrate complex and citric acid. To monitor the oxidation pathway and the oxidation products, we elected to use a capillary electrophoresis unit (Beckman Coulter P/ACE MDQ Capillary Electrophoresis System). The methods by Theobald and Dunemann (1996) for Cu–citrate and by (Wang et al. (2003)) were slightly modified (see Supporting Information) in this study for the determination of the oxidation intermediates and products.

5. Results and discussion

5.1. Effect of the copper-to-citrate ratio on Mn(II) dissolution

The speciation of ionic Cu(II) and Cu–Citrate 1:1 (the primary species in this study) is shown in Figs. S5 and S4, respectively. At pH 5.5, which was employed in our study, Cu^{2+} is the primary species in the absence of Citrate but, in a 1:1 Cu: Citrate molar ratio, the speciation at pH 5.5 changes in favor of a majority $\approx 96\text{--}98\%$ of Cu–Citrate with 2–4% H-Citrate^{2-} . At a ratio of 1:0.5, there is approximately a 50–50% balance between Cu–Citrate and H-Citrate^{2-} .

Increasing the molar ratios of Cu: Citrate from ionic Cu(II), 1:0.5 and 1:1 ($_{(\text{oxic})}/_{(\text{anoxic})}$) led to an overall increase in the amount of time required to achieve the dissolved Cu equilibrium. The ionic Cu(II) solution reached equilibrium at approximately 4 h versus nearly 48 h in the 1:0.5 and 1:1 ($_{(\text{oxic})}$) solutions, as shown in Fig. 1A. Under anoxic conditions (Cu–Citrate 1:1 ($_{(\text{anoxic})}$)), equilibrium was reached more quickly than under oxic conditions (i.e., 12 h versus 48 h in Cu–Citrate 1:1 ($_{(\text{oxic})}$)), although in the former, the dissolved Cu concentrations at 48 h of reaction time were higher than in Cu–Citrate 1:1 ($_{(\text{oxic})}$).

Fig. 1A and B shows that the values for MnO_2 sorbed ionic Cu(II) and the corresponding Mn(II) dissolution appear to share a close relationship. After plotting the total dissolved Cu(II) concentration as a function of the total dissolved Mn(II), we found a direct positive correlation ($r^2 = 0.98716$), as shown in Fig. S3. This phenomenon, also known as “isomorphic substitution”, has been encountered by other researchers (Kanungo et al., 2004). Divalent cations, such as Ni(II) or Cu(II), can readily substitute for Mn(II) in the manganese oxide lattice to counterbalance the charge that develops during dissolution of Mn(IV) to Mn(III) and (II)

(Nicolas-Tolentino et al., 1999). Although divalent heavy metals may follow this rule, the plots of Cu–Citrate complexes were non-linear.

The corresponding Mn(II) dissolution kinetics for ionic Cu(II), Cu–Citrate 1:0.5, 1:1 ($_{(\text{oxic})}/_{(\text{anoxic})}$) and citrate are shown in Fig. 1B. The dissolution kinetics within the first hour shown in Fig. 1B inset may help characterize the underlying mechanisms during the initial surface reaction. Focusing on the initial 0–1 h portion, linear regression was conducted to obtain the initial dissolution rates. The results are shown graphically in Fig. 1B inset graph, in which the dashed lines represent the linear regression fittings ($r^2 = 0.96\text{--}0.98$). We elected to use Eq. (1), previously employed by Wang and Stone in their comparison between MnO_2 and MnOOH , to correct for the differences in the manganese oxide surface area. The calculation is as follows:

$$R_A = \frac{R_0}{BET \times FW \times C} \quad (1)$$

where R_A ($\text{mM m}^{-2} \text{h}^{-1}$) is the surface area corrected rate, R_0 (mM h^{-1}) is the Mn dissolution rate calculated through linear regression, BET ($\text{m}^2 \text{g}^{-1}$) is the MnO_2 surface area, FW (g M^{-1} of MnO_2) is the formula weight followed by C (moles of MnO_2), the suspension concentration employed (Wang and Stone, 2006b). The parameters used in the calculations can be found in Table S1. The rates of dissolution can be ordered as follows: ionic Cu(II) > Cu–Citrate 1:0.5 > Cu–Citrate 1:1 ($_{(\text{oxic})}$) > Citrate > Cu–Citrate 1:1 ($_{(\text{anoxic})}$), with corresponding rates of $0.0118 \pm 10 \times 10^{-4}$, $0.0114 \pm 6.3 \times 10^{-4}$, $0.0077 \pm 3.5 \times 10^{-4}$, $0.0058 \pm 2.8 \times 10^{-4}$ and $0.00494 \pm 4.0 \times 10^{-4} \text{ mM m}^{-2} \text{h}^{-1}$, respectively. Through a simple unit conversion, the calculated R_A values are of the same magnitude for structurally similar α -hydroxy acids and ketones (Wang and Stone, 2006a,b).

Perhaps most interesting was that the initial Mn(II) dissolution from the Cu–Citrate 1:0.5 and 1:1 ($_{(\text{oxic})}$) solutions followed the ionic Cu(II) curve, in contrast to the s-shaped induction curves of Mn(II) dissolution mediated by citrate found in this study and in Wang and Stone, 2006a. This similarity suggests that Cu–Citrate 1:1 ($_{(\text{oxic})}$) may form initial ternary surface complexes through the octahedral coordination sphere of the citrate coordinated Cu instead of through the citrate ligand. Additional support for this hypothesis is provided by the calculated values for $[\text{Cu–Citrate 1:1}]_{(\text{adsorbed})}$ in the mass balance discussion of Text S4. Cu (complexed or non-complexed) may coordinate to MnO_2 through an initial aquo ligand

Fig. 1. Time-course plots of Cu(II) and Mn(II) during the reaction of ionic Cu, Cu–Citrate and citrate (A) total dissolved Cu(II) plotted as a function of time (B) Mn(II) dissolution plotted as a function of time (Inset graph is the Mn(II) dissolution within the first hour of reaction time with linear fitting curves); the solid lines represent the trend lines for the data.

exchange with surface oxygen or hydroxyl groups, similar to other (hydr)oxides, such as alumina (McBride, 1985). An illustration of this process can be observed in Fig. 1A. In the Cu(II)Glutamate reaction with Al_2O_3 , a 1:2 ratio Type B surface complex with long-range forces was responsible for binding under acidic conditions, whereas under alkaline conditions, a 1:1 Type A complex was the dominant species (Fitts et al., 1999). A comparison of the calculated Mn(II) dissolution rates also shows that Cu–Citrate 1:1_(oxic) falls between citric acid and ionic Cu(II). During the initial 0–1 h of reaction, the Mn(II) dissolution follows the order: Cu(II) > Cu–Citrate 1:0.5 > Cu–Citrate 1:1_(oxic) > Citrate > Cu–Citrate 1:1_(anoxic). Between 1 and 48 h of reaction time, the order becomes Citrate > Cu–Citrate 1:1_(oxic) > Cu–Citrate 1:0.5 > Cu–Citrate 1:1_(anoxic) > Cu(II), as shown in Fig. 1B. As indicated, over extended periods, non-complexed organic ligands may be more available to promote dissolution of subsurface mineral phases compared with their complexed analogues.

5.1.1. Following the oxidation process with capillary electrophoresis

Fig. 2A shows that the tested initial concentrations for [Cu–Citrate] and [Free-Citrate] were in excellent agreement with the speciation calculations (Fig. S4). The initial oxidation product is acetonedicarboxylic acid (Wang and Stone, 2006a; Meichtry et al., 2011), as shown in Fig. 2A and B. Acetonedicarboxylate (Fig. 2A) reaches a concentration of 0.05 mM after 20 h of reaction time versus 40 h of reaction time in the citrate solution (Fig. 2B). The mass balance data and an acetonedicarboxylate concentration

higher than the [Cu–Citrate] initial concentration suggests that there is non-stoichiometric oxidation during the reaction. Similar to this phenomenon are results from a MnO_2 column experiment in which 3.5 times more Co(II)EDTA^{2-} was oxidized relative to the Mn reduced. The authors have suggested that ambient O_2 may regenerate Mn(II) to form fresh catalytic MnO_2 surfaces (Jardine and Taylor, 1995).

After reaching a peak, we suggested through our mass balance analysis of Cu–Citrate 1:1 that acetonedicarboxylate is degraded through a MnO_2 –Cu surface complex reaction (Text S4). An illustration of the proposed reaction can be found in Fig. S8. In solution, Cu(II) catalyzed decarboxylation of acetonedicarboxylate is known to occur through an intermediate enol ringed complex (Hay and Leong, 1971). Certain evidence in support of this intermediate can be found from isolation of the aqueous [Cu(II)Acetonedicarboxylate] in solution (Fig. 2A), a change in the Cu oxidation state (Fig. 4A) and the mass balance discussion in Text S4. Due to potential surface-mediated catalysis in the Cu–Citrate 1:1 solution, the oxidation reaction proceeds more to completion, leading to potentially higher amounts of acetone in solution. Acetone, the final oxidation product, is volatile, and detection of its concentration in solution may be lower than the actual concentration (Meichtry et al., 2011). In the citrate solution, due to much slower degradation of acetonedicarboxylate, the concentration of acetoacetate is significantly higher than in the Cu–Citrate 1:1 solution, as shown in Fig. 2B.

5.2. Processes at the solid/aqueous interface: the zeta potential, XPS and ATR-FTIR results

Focusing on the MnO_2 at 0 h versus the MnO_2 at 48 h, there is a decrease in the zeta potential with an increase in pH. We attribute this change to the hydration, protonation and de-protonation of the surface functional –OH groups, as shown in Fig. 3. Regarding Cu(II) at 48 h, there is an overall increase in the surface potential of MnO_2 . At pH values of 5 and 6, there is a difference of approximately 20 mV, whereas at pH 7.0, the difference increases to 25–50 mV. The formation of Cu(II) hydroxo species at neutral pH are believed to be more readily adsorbed due to faster rates of water loss (Stumm, 1992), and the Cu(OH)_x precipitates can form inner-spherically coordinated complexes closer to the MnO_2 surface. This surface aggregation translates to the positive increase in surface potential, as shown in Fig. 3.

Fig. 2. Time course plots of (A.) Cu–Citrate 1:1 (B) citrate (mass balance is [citrate] + [acetonedicarboxylate] + [acetoacetate] + [acetate] + [acetone]) and the oxidation products as a function of time. The experiments were conducted at 25 °C with a pH of 5.5 under “oxic” conditions. The initial concentration was Cu–Citrate 1:1 (0.25 mM) citrate (0.25 mM).

Fig. 3. Zeta potential results plotted at various pH values.

Interestingly, changes to the zeta potential of MnO_2 after reaction with Cu–Citrate 1:1 is not as pronounced as the Cu(II) solution, as shown in Fig. 3. At the initial portion of the reaction in the Cu–Citrate 1:1 solution, $[\text{Cu–Citrate}]_{\text{(adsorbed)}}$ is adsorbed by MnO_2 . Over time, the concentration of the oxidation products increases in solution, which may resolubilize previously adsorbed Cu as labile aqueous complexes (Text S4). The increase in the zeta potential at pH 8 of the Cu–citrate 1:1 solution may be due to the formation of hydrolyzed Cu species (Fig. S4).

5.2.1. XPS surface analysis of interfacial reactions

The results from the X-ray photoelectron spectra of the Cu 2p, Mn 2p and O 1s shells are illustrated in Fig. 4A–C. Within the Mn 2p 3/2 peak, there are three reference lines corresponding to the different valence states of Mn. These lines are binding energies of 642.8, 641.6 and 640.6 eV. for Mn(IV), Mn(III) and Mn(II), respectively (Wang et al., 2012). As the reaction progresses, the Mn2p 3/2 peak shifts more toward the Mn(III) and Mn(II) reference lines (Fig. 4B).

Focusing on Fig. 4A, there are certain data that may relate to the intermediate Cu(II) coordination-complex found during the CE analysis. Tridentate Cu–Citrate and bidentate Cu(II)Acetonedicarboxylate do not typically result in a valence change, but the additional electron density supplied by MnO_2 during surface complexation may lead to a change in valence $\text{Cu(II)} \rightarrow \text{Cu(I)}$. This change in the valence state may occur primarily at the $\text{MnO}_2/\text{MnOOH}$ surface where bridging allows the transfer of electron density from the solid surface to the Cu–Citrate or Cu(II)Acetonedicarboxylate complex. A peak at 932.43 eV corresponds to Cu(I)oxide, whereas peaks at 933.57 and 934.75 are assigned to Cu(II)oxide and Cu(II)hydroxide, respectively (Biesinger et al., 2010). To examine the change in Cu(II) and Cu(I) with time, we calculated the relative area differences between each peak to gain respective percentages of each during different sample times, employing Eq. (2) as follows:

$$\text{Cu}^{\text{I/II}}\% = \frac{\text{peak}_a}{\text{peak}_{932} + \text{peak}_{934}} \times 100 \quad (2)$$

where $\text{Cu}^{\text{I/II}}\%$ is the relative percentage of either peak, peak_a is the peak area of peak_{932} or peak_{934} , and the divisor is the sum of both peak areas. After 1 h of reaction time, 56% of the adsorbed Cu from Cu–Citrate 1:1 has already been reduced, as shown in the side chart of Fig. 4A. Increases in the Cu(OH)_2 peak area at 6 h and 12 h of reaction time to 60% and the subsequent decrease back to 46% after 24 h of reaction may suggest redox activity of surface adsorbed Cu(II) (Fig. 4A). This timing coincides well with the peak in the acetonedicarboxylate concentration in Fig. 2A and the subsequent degradation from there up to 24 h of reaction time. This result provides support to our postulation that acetonedicarboxylate degradation occurs as a MnO_2 –Cu surface sorbed intermediate coordination compound (see also Test S4 and Fig. S8). Inspection of Fig. 4C highlights the O 1s shell oxygen surface groups of MnO_2 and the shoulder peak, indicating surface hydration of the solid.

5.2.2. In situ ATR-FTIR analysis of reactions at the MnO_2 interface

In Fig. 5A and B, a broad peak present at 3330 cm^{-1} was assigned to the $-\text{OH}$ group of H_2O present in both solutions. During the reaction, evidence for CO_2 evolution can be observed in the growing bands at 2345 cm^{-1} in Fig. S2A (Citrate) and 2360 cm^{-1} in Fig. S2B (Cu–Citrate 1:1).

Fully protonated $\text{C}=\text{O}$ stretches commonly occur at the 1700 cm^{-1} range but shift to lower bands upon complexation or deprotonation. We associate the band at 1743 cm^{-1} as the $\text{C}=\text{O}$ group valance vibration band of citric acid (Fig. 5A), whereas the

Fig. 4. XPS results from the reaction of 0.1 g L^{-1} MnO_2 with 0.25 mM Cu–Citrate 1:1 under oxidic conditions at $25\text{ }^\circ\text{C}$ and pH 5.5 with an ionic strength of 0.01 M NaCl. The samples were obtained using a syringe at 1, 6, 12 and 24 h of reaction time. (A) The Cu 2p spectra with the area calculated Cu(II)/Cu(I) percentages on the right (B) the Mn2p spectra (C) the O 1s spectra.

band at 1758 cm^{-1} (Fig. 5B) is associated with a metal-coordinated carboxyl group (Tsimbler et al., 1969). During bidentate/tridentate coordination, an increase in the ν_{asCOO} citrate band at 1635 cm^{-1} (Fig. 5A) is shifted to 1650 cm^{-1} (Fig. 5B) in Cu–Citrate 1:1 due to the electron withdrawing properties of bidentate/tridentate coordinated Cu(II) adjacent to the carboxyl groups of carboxylic acids (Hay and Myneni, 2007). A band at 1666 cm^{-1} in Fig. 5B is attrib-

Fig. 5. In situ ATR-FTIR spectra of (A) citric acid and (B) Cu-Citrate 1:1 oxidation; the range for 2000–2800 cm^{-1} can be found in Fig. S2A and B.

uted to labile aquo ligands in the octahedral coordination sphere of Cu-Citrate, similar to the bands at 1660–1666 cm^{-1} of the Ni(II), Al(III) and Ga(III)-Citrate complexes (Lindgren et al., 2009). If this band represents the octahedral coordination sphere of Cu-Citrate 1:1, this evidence supports our hypothesis of an initial reaction through a ‘Type A’ surface complex resembling the illustration in Fig. 1A. By 24 h of reaction time, new bands appear at 1527 cm^{-1} in the citric acid solution (Fig. 5A) and at 1542 cm^{-1} in the Cu-Citrate solution (Fig. 5B), representing the adsorbed β -keto acids acetonedicarboxylate and acetoacetate (Borer et al., 2007). Twin shoulder peaks that appear after 36 h of reaction time at 2946 and 2869 cm^{-1} in Fig. 5B correspond to the transitioning between a $\text{C}=\text{C}$ sp^2 and $\text{C}-\text{C}$ sp^3 state of either acetoacetate or the further oxidation products, acetate and acetone. The absence of the shoulder peaks in Fig. 5A (the Citrate solution) appears to support the idea that, in Fig. 2B, the concentration of acetate and acetone are lower compared with the Cu-Citrate 1:1 reaction with MnO_2 in Fig. 2A. The shoulder peaks at bands 3841 cm^{-1} and 3748 cm^{-1} may represent $-\text{OH}$ intermolecular bonding between enolic forms of acetonedicarboxylate or acetoacetate, whereas a band at 3625 cm^{-1} in the Cu-citrate solution represents conjugated $\nu-\text{OH}$ stretching vibrations (Gyliene et al., 2004; Wade, 2011). Finally, the peaks at 1481 cm^{-1} of the Cu-citrate solution and at 1465 cm^{-1} were ascribed to rocking of the CH_2 methyl groups, possibly in transition from intramolecular proton transfers common in tautomeric capable β -keto acids.

6. Conclusion

Similarities of the Mn(II) dissolution rates between ionic Cu(II) and Cu-Citrate 1:1 provide an indication of the importance of the coordination spheres in initial binding to solid surfaces. The isomorphic substitution relationship between Cu(II) and Mn(II) is also evident. Verification of the Cu(II)Acetonedicarboxylate intermediate enolic complex provides new insight into systems, including coordination compounds, in the environment. Surface reaction analysis through zeta potential, XPS and in situ ATR-FTIR suggests that the coordination sphere of Cu-Citrate plays a role in electron transfer, surface coordination and redox conditions at the MnO_2 surface.

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Appendix A. Supplementary data

MnO_2 preparation and characterization, Isomorphic substitution relationship graph, Cu-citrate and Cu(II) chemical speciation, capillary electrophoresis analytical method information and Cu-Citrate 1:1 mass balance discussion. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2014.04.039>.

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