

Effect of Organic Acids on Cr(III) Oxidation by Mn-oxide

Jong-Bae Chung*

Department of Agricultural Chemistry, College of Natural Resources,
Taegu University, Kyongsan, 712-714 Korea

Received February 21, 1998

Two oxidation states of chromium commonly occur in natural soil/water systems, Cr(III) and Cr(VI). The oxidized form, Cr(VI), exists as the chromate ion and is more mobile and toxic than Cr(III). Therefore oxidation of Cr(III) by various Mn-oxides in natural systems is a very important environmental concern. Organic substances can inhibit the Cr(III) oxidation by binding Cr(III) strongly and also by dissolving Mn-oxides. Most of Cr(III) oxidation studies were carried out using *in vitro* systems without organic substances which exist in natural soil/water systems. In this study effect of organic acids – oxalate and pyruvate – on Cr(III) oxidation by birnessite (δ -MnO₂) was examined. The two organic acids significantly inhibited Cr(III) oxidation by birnessite. Oxalate showed more significant inhibition than pyruvate. As solution pH was lowered in the range of 3.0 to 5.0, the Cr(III) oxidation was more strongly depressed. Addition of more organic acids reduced the Cr(III) oxidation more extensively. Different inhibition effects by the organic acids could be due to their ability of reductive dissolution of Mn-oxides and/or Cr(III) binding. Organic acids dissolved Mn-oxide during the Cr(III) oxidation by the oxide. Dissolution by oxalic acid was much greater than that by pyruvate, and the dissolution was more extensive at lower pH. Inhibition of Cr(III) oxidation was parallel to the dissolution of Mn-oxide by organic acids. Although the effect of Cr(III) binding by organic acids on Cr(III) oxidation is not known yet, Mn-oxide dissolution by organic acids could be a main reason for the inhibition of Cr(III) oxidation by Mn-oxide in presence of organic acids. Thus oxidation of Cr(III) to Cr(VI) by various Mn-oxides in natural systems could be much less than the oxidation estimated by *in vitro* studies with only Cr(III) and Mn-oxides.

Key words: *birnessite, chromium oxidation, manganese oxide, oxalate, pyruvate.*

Trivalent and hexavalent Cr, the two environmentally significant oxidation states, behave very differently. Chromium(VI) is present as a chromate anion which can move through the soil and vadose zone. On the other hand, cation Cr(III) is strongly adsorbed on soil constituents and is highly immobile. The mechanisms which control interconversions of Cr between the two oxidation states in the soil have a major influence on the transport and toxicity of Cr in terrestrial systems and on transfers to groundwater or surface water systems.¹⁾

Although Cr reduction can occur via many pathways in soil systems below pH 9.0, the only known oxidants of Cr(III) are Mn-oxides.²⁾ Manganese oxides, widely distributed as suspended particles in surface waters and coatings in soils and sediments, are potential oxidizing agents of natural and xenobiotic organic compounds. The oxidant strength and reactivity of Mn-oxides make them important participants in environmental oxidation-reduction

reactions. Both the highly crystalline pyrolusite and the disordered birnessite Mn-oxides are capable of oxidizing Cr(III) to Cr(VI).^{2,3)} Manganite, buserite and hausmanite also have strong oxidizing capacities.⁴⁻⁶⁾

However, in natural waters, Cr(III) oxidation is much slower than could be expected from the laboratory studies.⁷⁾ Inorganic and organic compounds can affect the rate of Cr(III) oxidation by competition with and binding of Cr(III). Some organic substances can also dissolve Mn-oxides.⁸⁾ Manganese oxide particles and crusts in natural waters and soils can be reduced and dissolved by organic compounds, increasing the mobility of manganese.⁸⁾ Laboratory experiments showed that synthetic Mn-oxides are reduced and dissolved at appreciable rates by the microbial metabolites such as oxalate and pyruvate. Root exudates are also very effective in the dissolution of hydrous MnO₂ through chemical reduction and chelation.⁹⁾

In this study, the effect of organic acids on Cr(III) oxidation by birnessite (δ -MnO₂) was examined to explain the restricted oxidation of Cr(III) in natural soil/water systems comparing to the oxidation evaluated in laboratory studies.

*Corresponding author

Phone: 82-53-850-6755; Fax: 82-53-850-6709

E-mail: jbchung@biho.taegu.ac.kr

Abbreviation: ZPC, zero point of charge.

Materials and Methods

Preparation and characterization of birnessite. Birnessite was prepared by adding HCl to an excess of KMnO_4 as described by McKenzie.¹⁰ The resulting oxide was washed with deionized water and 0.5 N HClO_4 alternatively until the residual K content was less than 1% and then dried at 40°C, and ground to pass through an 80-mesh sieve.

To identify the prepared Mn-oxide, ZPC, O/Mn ratio, and surface area were measured using a salt titration method,¹¹ the iodometric method,¹² and the ethylene glycol monoethyl ether method¹³ respectively. It was also characterized by X-ray powder diffraction¹⁴ and transmission electron microscopy.

The birnessite prepared in this study was poorly crystalline and considered of characteristic clumps or balls of needle. Electronmicrograph of the prepared birnessite is available in the author's previous publication.¹⁵ Zero point of charge, surface area and O/Mn ratio determined for the synthesized oxide corresponded very well with published criteria of birnessite preparation.¹⁶ The data are summarized in Table 1. In X-ray diffraction analysis, four broad peaks characteristic of birnessite were observed: the most intense peak was at 0.75 nm with weaker signals at 0.33, 0.25 and 0.14 nm.

Cr(III) oxidation experiments. Manganese oxide was suspended in 250 mL 0.001 M NaNO_3 solution in 300 mL erlenmeyer flasks to yield an initial solid surface area to solution volume ratio of $25 \text{ m}^2\text{L}^{-1}$. Solution pH was adjusted to 3.0 and 5.0 with 0.5 M HNO_3 . Chromium nitrate was used as a Cr(III) source. The initial Cr(III) concentration in the suspension was 50 μM . Sodium salts of organic acids were added to give the concentration of 0.2 and 1.0 mM for oxalate and 0.2 mM for pyruvate. Prior to the studies at pH 5.0, the solution was purged of CO_2 with N_2 gas. The suspensions were stirred using a magnetic stirring plate at 25°C, and 3 mL samples were taken during the reaction period ranged from 0.5 to 50 min. The samples were centrifuged at 8,000 g for 20 min and filtered using 0.45 μm pore membrane filter. Chromium(VI) was determined by *s*-diphenyl carbazide procedure¹⁷ and solution Mn(II) was determined by using atomic absorption spectrophotometry.

Results and Discussion

Birnessite is a naturally occurring, poorly crystalline

Table 1. Some characteristic properties of the prepared birnessite.

ZPC	Surface area, m^2/g	O/Mn ratio
2.9	263.3	1.94

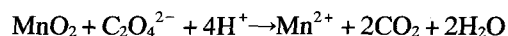
oxide of tetravalent manganese and very effective oxidant of Cr(III). Chromium(III) oxidation by birnessite has been examined by several researchers.^{3,15,18} The oxidation reaction occurs over a range of pH values and Cr(III) concentrations. The reaction stoichiometry of Mn(II) to Cr(VI) appears to be 1.5 : 1. Chromium(III) concentration, pH and the amount of initial available surface are the parameters controlling the degree of oxidation. Although thermodynamic calculations indicate that the reaction should continue until reactants are limiting, the reaction is limited as pH and Cr(III) concentration increase.¹⁹ Fendorf *et al.* proposed that surface nucleation could explain the inhibition on birnessite surface at pH 4.0–5.0 with high initial Cr(III) addition.¹⁹

In this study a kinetic method was used to elucidate Cr(III) oxidation by birnessite and effect of organic acids on the reaction. A relatively low initial Cr(III) concentration was used to avoid inhibitions of the reaction by Cr(III) nucleation on Mn-oxide surface. Cumulative Cr(VI) produced during the oxidation reaction as a function of time was determined. With 50 μM of initial Cr(III), most of the added Cr(III) was oxidized within the 50 min reaction period at both pH 3.0 and 5.0 (Fig. 1 and 3; no addition of oxalate or pyruvate). The rate of reaction at pH 3.0 was slower, but continued for prolonged times relative to that at pH 5.0. Oxidation was extremely rapid at pH 5.0 in the early reaction period.

Addition of organic acids showed significant inhibition effects in the Cr(III) oxidation (Fig. 1 and 3). The inhibition effect was more significant at lower pH. With increasing organic acid addition, Cr(III) oxidation was further inhibited. At pH 3.0 the oxidation was almost completely inhibited by 1.0 mM of oxalate addition. Although pyruvate could also inhibit Cr(III) oxidation by birnessite, the inhibition was much less than that by oxalate.

Such inhibition of Cr(III) oxidation by organic acids can be attributed to; (1) dissolution of Mn-oxides by organic acids, (2) Cr(III) complexation by organic acids, and (3) adsorption of organic ligands on the oxide surface. Since various aromatic and nonaromatic compounds are known to dissolve Mn-oxides,⁸ in this study the effect of Mn-oxide dissolution by organic acids on Cr(III) oxidation was examined and discussed. Oxalate and pyruvate are microbial metabolites found in natural soil/water systems and they participate in many oxidation-reduction reactions.

Manganese(IV) oxide undergoes reductive dissolution in the presence of organic acids. The following stoichiometric reaction can be written for the dissolution of Mn-oxide by oxalate.



Xyla *et al.* compared oxalate and dissolved Mn(II) concentration during the dissolution reaction, and found that

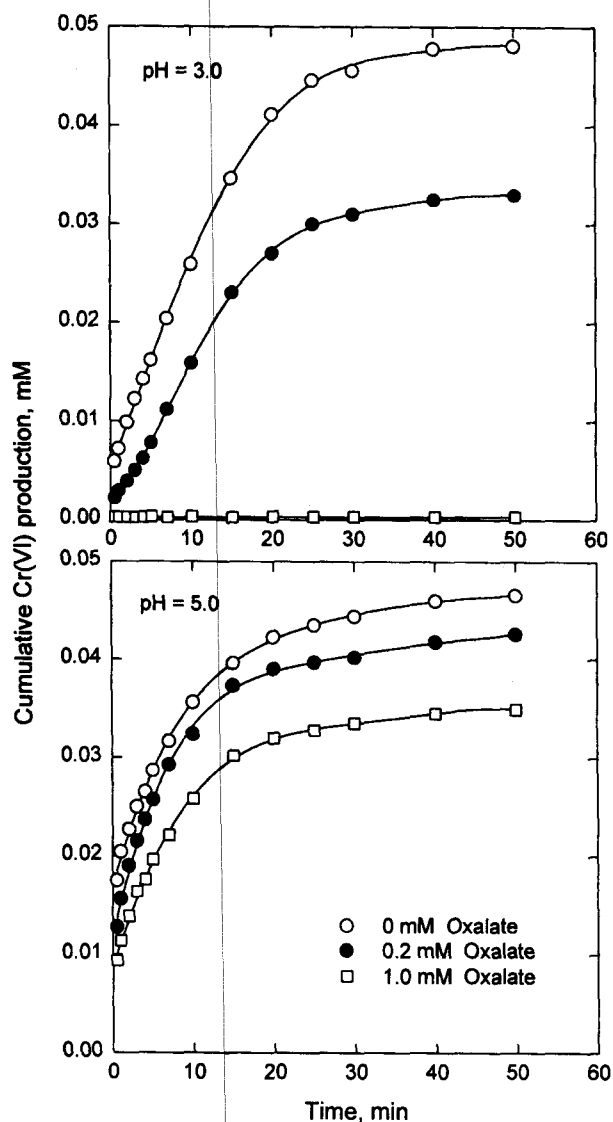


Fig. 1. Effects of oxalate on Cr(III) oxidation by birnessite at pH 3.0 and 5.0. Initial birnessite surface area to solution volume ratio was $25 \text{ m}^2\text{L}^{-1}$.

the ratio of oxalate consumed to Mn(II) produced was 1:1 for the Mn(IV)-oxide.¹⁹⁾

As expected, inhibition of Cr(III) oxidation had a good correlation with Mn-oxide dissolution by organic acids. When 1.0 mM of oxalate was added at pH 3.0, nearly 80% of the added Mn-oxide was dissolved during the reaction period and the dissolution was found to be directly proportional to oxalate concentration (Fig. 2). This behavior indicates that surface coverage by oxalate is below saturation with the concentration range (0.2~1.0 mM) employed. This dissolution could be one of the main reasons for the decreased Cr(III) oxidation under such reaction conditions in Fig. 1.

The different inhibition of Cr(III) oxidation by organic acids at different solution pHs in Fig. 1 and 3 would be due to the pH-dependence of reductive dissolution of Mn-oxide. pH had a substantial impact on rates of reduc-

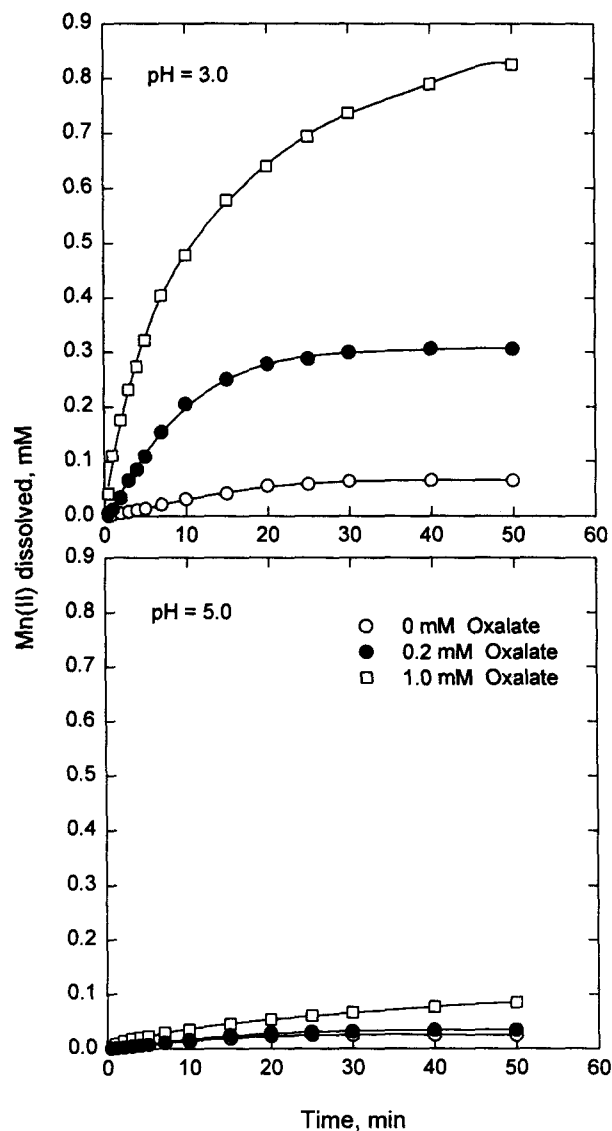


Fig. 2. Dissolution of birnessite by oxalate at pH 3.0 and 5.0. Initial birnessite surface area to solution volume ratio was $25 \text{ m}^2\text{L}^{-1}$.

tive dissolution of Mn-oxide (Fig. 2 and 4). Rates of reductive dissolution increased as the pH was decreased for both oxalate and pyruvate. The effect of pH on dissolution rate is more pronounced for oxalate than for pyruvate. Linear regression of Mn(II) produced as a function of time up to where 10% of the oxide has been dissolved was used to calculate initial rates of reductive dissolution. For oxalate (0.2 mM), in the early stage of the reaction, the rate of reductive dissolution at pH 3.0 was 10 times faster than at pH 5.0. For pyruvate (0.2 mM), on the other hand, a similar change in pH only increased the reaction rate by a factor of 5. The proposed dissolution mechanism includes the formation of a precursor surface complex with oxalate followed by electron transfer and release of the reduced metal center into the solution.¹⁹⁾ pH influences rates of reductive dissolution through its impact on the chemical speciation of reductant molecules,

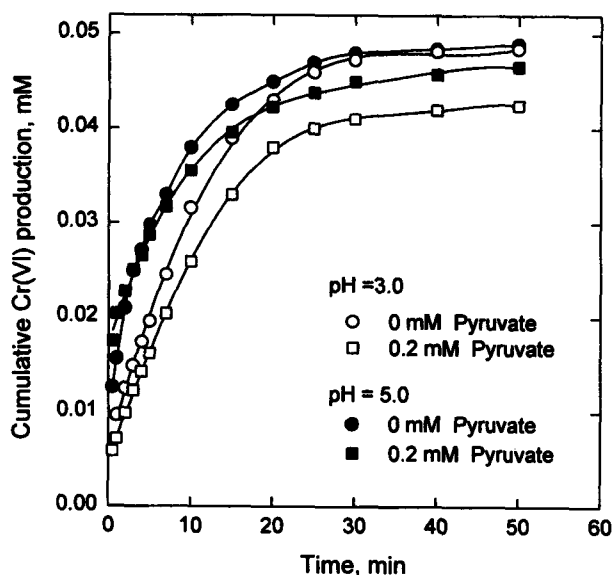


Fig. 3. Effects of pyruvate on Cr(III) oxidation by birnessite at pH 3.0 and 5.0. Initial birnessite surface area to solution volume ratio was $25 \text{ m}^2\text{L}^{-1}$.

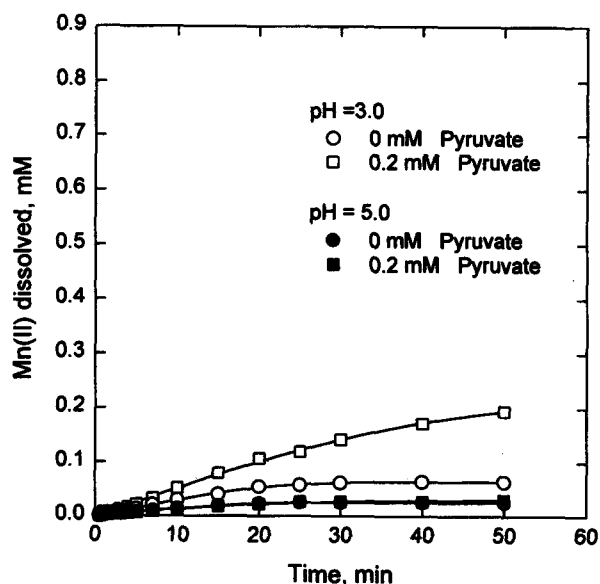
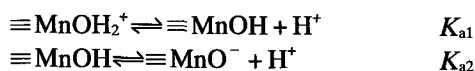


Fig. 4. Dissolution of birnessite by pyruvate at pH 3.0 and 5.0. Initial birnessite surface area to solution volume ratio was $25 \text{ m}^2\text{L}^{-1}$.

oxide surface sites, and reaction intermediates. Protonation equilibria on Mn-oxide surfaces can be represented by the following reactions:



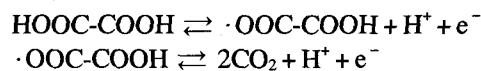
Surface of oxides can carry no net charge when the pH is equal to the pH_{zpc} value. Since the pH_{zpc} of birnessite is 2.9, the oxide surface can carry a net negative charge in the pH range 3.0 to 5.0 used in this study. Therefore the pH dependence of dissolution parallels the pH dependence of the adsorption of oxalate on the surface. Pro-

tonation of the oxide surface could accelerate the non-reductive dissolution of oxide minerals, and may, similarly, accelerate the detachment of reduced surface manganese ions. Readsorption of Mn(II) becomes more important with increasing pH and may at higher pH, block the oxide surface, thus limiting adsorption of oxalate or pyruvate.

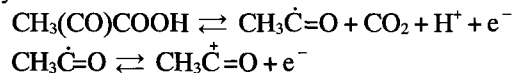
Oxalate (pK_a values of 1.26 and 3.82) is predominately a divalent anion at pH above 4.0, while pyruvate (pK_a of 2.35) is a monovalent anion. Protonated forms of either reductant are minor components above in the pH range used in this study, and their concentrations decrease by an order of magnitude for every one-unit increase in pH.

Oxalic and pyruvic acids are oxidized by metal ion complexes in two one- equivalent steps.^{20,21)}

Oxalic acid:



Pyruvic acid :



As mentioned above, the observed dependence of dissolution rates on the initial organic acid concentration suggests that the dissolution rates are directly related to the surface concentration of organic acid. This is very common observation in dissolution studies of sparingly soluble minerals in the presence of ligands. The general mechanism for the reductive dissolution of a metal oxide includes the following steps: (1) surface complex formation between the adsorbed ligand and the surface metal center; (2) electron transfer within the surface complex, resulting in a reduced surface metal center and the oxidized ligand; and (3) detachment of the reduced surface metal center. At pH 3.0, between the first and second pK_a of oxalate, some of the added oxalate will be protonated to form the species HC_2O_4^- . If, however, most of the added oxalate is consumed in the reaction, the protonation of oxalate will have little effect on the overall stoichiometry expressed above.

The rate of dissolution depended quite strongly upon the organic reductant employed (Fig. 2 and 4). Thus steps that do not involve the organic substrate such as desorption of Mn(II) cannot be rate limiting. Two mechanisms have been postulated for the oxidation of organic compounds by metal complexes in homogeneous solution: bonded and nonbonded electron transfer.²²⁾ Reaction via a bonded mechanism involves direct bonding between the metal center and organic reductant (inner sphere complex formation) prior to electron transfer. If this mechanism is correct, an organic reductant with high affinity for surface sites will react more quickly than one with low affinity. Reaction via nonbonded mechanism, in con-

trast, involves outer-sphere complex formation prior to electron transfer. In this case the inner coordination sphere of the metal ion remains intact, and no direct bond between oxidant and reductant is formed. Rates of reaction for different organic reductants may vary considerably, however, because of differences in the activation energy required for electron transfer. The differences in Mn-oxide dissolution by different organic acids can be elucidated by considering above reaction mechanisms. At this point the reason for the different dissolution of Mn-oxide by different organic substances is not clear.

Although dissolution of Mn-oxide would be a main reason for the depression of Cr(III) oxidation by organic acids, metal binding capacity of organic acids should be also considered as another factor for the inhibition. To address this issue, further researches are needed.

In conclusion, the inhibition effect must be taken into account in the assessment of whether the Cr(III) oxidation reaction on Mn-oxides plays an important role in the Cr cycle in natural soil/water systems.

Acknowledgments. This research was supported in part by the Taegu University Research Grant, 1997.

References

1. Chung, J. B., Burau, R. G. and Zasoski, R. J. (1998) Chromate generation by chromate depleted subsurface materials. *Environ. Sci. Technol.* (Submitted)
2. Eary, L. E. and Rai, D. (1987) Kinetics of chromium(III) to chromium(VI) by reaction with manganese dioxide. *Environ. Sci. Technol.* **21**, 1187-1193.
3. Fendorf, S. and Zasoski, R. J. (1992) Chromium(III) oxidation by δ -MnO₂: 1. Characterization. *Environ. Sci. Technol.* **26**, 79-85.
4. Johnson, C. A. and Xyla, A. G. (1991) The oxidation of chromium(III) to chromium(VI) on the surface of manganite(γ -MnOOH). *Geochim. Cosmochim. Acta* **55**, 2861-2866.
5. Silvester, E., Charlet, L. and Manceau, A. (1995) Mechanism of chromium(III) oxidation by Na-buserite. *J. Phys. Chem.* **99**, 16662-16669.
6. Zasoski, R. J. and Chung, J. B. (1992) Chromium(III) oxidation by manganese oxides: Effect of manganese(III). *Agronomy Abstract* 247.
7. Nakayama, E. (1981) Chemical speciation of chromium in sea water: Part 2. Effects of manganese oxides and reducible organic materials on the redox processes of chromium. *Anal. Chim. Acta* **130**, 401-404.
8. Stone, A. T. and Morgan, J. J. (1984) Reduction and dissolution of manganese(III) and manganese(IV) oxides by organics: 2. Survey of the reactivity of organics. *Environ. Sci. Technol.* **18**, 617-624.
9. Godo, G. H. and Reisenauer, H. M. (1980) Plant effects on soil manganese availability. *Soil Sci. Soc. Am. J.* **44**, 993-995.
10. McKenzie, R. M. (1971) The synthesis of birnessite, cryptmelane, and some other oxides and hydroxides of manganese. *Mineral. Mag.* **88**, 493-502.
11. Sakurai, K., Ohdate, Y. and Kyuma, K. (1988) Comparison of salt titration and potentiometric titration methods for the determination of zero point of charge (ZPC). *Soil Sci. Plant Nutr.* **34**, 171-182.
12. Murray, J. W., Balistrieri, L. S. and Paul, B. (1984) The oxidation state of manganese in marine sediments and ferromanganese nodules. *Geochim. Cosmochim. Acta* **48**, 1237-1247.
13. Carter, D. L., Mortland, M. M. and Kemper, W. D. (1986) Specific surface. In *Methods of soil analysis, Part I. Agronomy 9*, Klute, A. (ed.) pp. 413-423, Am. Soc. Agron. Inc., Madison, WI.
14. Whittig, L. D. and Allardice, W. R. (1986) X-ray diffraction techniques. In *Methods of soil analysis, Part I. Agronomy 9*, Klute, A. (ed.) pp. 331-362, Am. Soc. Agron. Inc., Madison, WI.
15. Chung, J. B. (1998) Chromium speciation in Cr(III) oxidation by Mn-oxides: Relation to the oxidation mechanism. *Agric. Chem. Biotechnol.* **41**, (in print).
16. McKenzie, R. M. (1989) Manganese oxides and hydroxides. In *Minerals in soil environments*, Dixon, J. B. and Weed, S. B. (eds.) pp. 439-465, SSSA, Madison, WI.
17. Bartlett, R.J. and James, B. (1979) Behavior of chromium in soils: III. Oxidation. *J. Environ. Qual.* **8**, 31-35.
18. Chung, J. B., Zasoski, R. J. and Lim, S. U. (1994) Kinetics of chromium(III) oxidation by various manganese oxides. *Agric. Chem. Biotechnol.* **37**, 414-420.
19. Xyla, A. G., Sulzberger, B., Luther, G.W., Hering, J. G., Cappellen, P. V. and Stumm, W. (1992) Reductive dissolution of manganese(III, IV) hydroxides by oxalate: The effect of pH and light. *Langmuir* **8**, 95-103.
20. Davies, G. and Watkins, K. O. (1970) Inner-sphere mechanisms of oxidation: Stoichiometry and kinetics of the cobalt(III) oxidation of oxalic acid in acid perchlorate solution. *Inorg. Chem.* **9**, 2735-2739.
21. Drummond, A. Y. and Waters, W. A. (1995) Stages in oxidations of organic compounds by potassium permanganate: Oxidations of ketones and pyruvic acid. *J. Chem. Soc. (London)*, 497-504.
22. Littler, J. S. (1970) Spec. Publ.-Chem Soc., No. 24.