

## Effects of Organic Matter and pH on Chromium Oxidation Potential of Soil

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(Received November 19, 2001. Accepted December 8, 2001)

**Abstract :** Oxidation of Cr(III) to Cr(VI) can increase availability and toxicity of chromium. In this study, possible mechanisms by which pH and organic matter can control the chromium oxidation and reduction in soil system were examined using four soils of different pHs and organic matter contents. Reduction of Mn-oxides occurred in the soils of higher organic matter content (4.0%), but Mn-oxide was quite stable during the incubation in the soil of pH 7.0 and 0.5% organic matter content. Manganese oxides can be reductively dissolved at lower pH and higher organic matter conditions. The soil of pH 7.0 and 4.0% organic matter content showed the highest Cr-oxidation potential. Reduction of soluble Cr(VI) was observed in all the soils examined. The most rapid reduction was found in soil of pH 5.5 and 4.0% organic matter content, but the reduction was slow in soil of pH 7.0 and 0.5% organic matter content. Thus, the reductive capacity of organic matter added soils was much higher as compared to other two soils of lower organic matter content. In all the soils examined, the reductive capacity of soluble chromium was much higher than the oxidative capacity. Organic matter was found to be the most important controlling factor in the chromium oxidation and reduction. Reduction of Cr(VI) to Cr(III) could be a potentially useful remediation or detoxification process, and availability and toxicity of chromium in soil would be controlled by controlling organic matter content and pH of the soils.

**Key words :** chromium, Mn-oxide, organic matter, oxidation, reduction, soil pH

### INTRODUCTION

In general sludge application in agricultural lands is prohibited because of potential pathogene and heavy metal hazards to human health. Also there is concern that application of heavy metals from municipal sludges, and other materials such as hog and poultry wastes, may result in phytotoxic accumulation of these metals in soils. For proper and safe disposing of sludges and recycle of these materials as organic matter, we must understand bioavailability of metals and potential harmful effects to the soil-crop system.

Chromium is one of the heavy metals commonly found in sludges. Chromate is the thermodynamically stable chromium form at moderate pH and oxidizing conditions; however, in soil systems the vast majority of chromium is in the Cr(III) state as  $\text{Cr}_2\text{O}_3$ . Low solubility, strong adsorption of Cr(III) and a number of possible reductants combine to keep chromium in

the less stable Cr(III) state. Chromium(VI) added to soils is converted to Cr(III) and only low concentrations of Cr(VI) are normally present. Therefore, the presence of elevated Cr(VI) levels in soils is generally unexpected. The mechanisms that control interconversions of chromium between the two oxidation states in the soil have a major influence on the transport and toxicity of chromium in terrestrial systems. Although chromium reduction can occur via many pathways in soil systems below pH 9.0, the only known oxidants of Cr(III) are Mn-oxides. Both the highly crystalline pyrolusite and the disordered buserite Mn-oxides are capable of oxidizing Cr(III) to Cr(VI)<sup>1-3</sup>. Manganite and buserite also have strong oxidizing capacities<sup>4,5</sup>.

Bartlett and James found that oxidation of Cr(III) could occur readily under conditions prevalent in many field soils<sup>6</sup>, and the key to the oxidation was suggested to be the presence of oxidized Mn in the soil, which serves as the electron acceptor in the reaction. Since Mn-oxides are the only known oxidants of Cr(III), qualitatively, it is clear that the rate of Cr(VI) formation in soil is positively related to Mn-oxide con-

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**Table 1. Selected properties of soil used in the experiment**

pH (1:5 H <sub>2</sub> O)	OM	CEC	Oxide-Mn	Cr(VI)	Texture
	%	cmol/kg	mg/kg	mg/kg	
5.12	0.51	5.80	75.2	0.21	Sandy loam

nts<sup>6-8)</sup>.

The presence of soil organic matter brought about spontaneous reduction of Cr(VI) to Cr(III) and oxidation of added soluble chromium did not occur in peat soil<sup>8,9)</sup>. Oxidation of Cr(III) was not shown in acid soils in which the predominant manganese species apparently was in the reduced form<sup>6)</sup>. Chung and Sa found that chromium oxidation potential of arable upland soils was directly related with Mn-oxide content in the soils and pH and organic matter content had a very significant relationship with chromium oxidation in soil; as pH was higher and organic matter content lower, chromium oxidation potential was higher<sup>7)</sup>. Soil pH and organic matter seem to be important controlling factors for Mn-oxide content in soils. Manganese oxides can be reductively dissolved at lower pH and higher organic matter conditions<sup>10,11)</sup>.

Therefore, considering the widely existing soil conditions favorable for chromium oxidation, we must understand the soil characteristics related in chromium oxidation and reduction before application of Cr-containing sludges in soils. Also interactions of those soil characteristics in relation to the chromium oxidation and reduction should be further elucidated. In this study, we investigated the effects of organic matter and pH on chromium oxidation and reduction potential of soil.

## MATERIALS AND METHODS

### Soils and Soil Characterization

To study the redox processes of chromium in soil, four soils of different pHs and organic matter contents were prepared. An acidic soil of pH 5.1 collected from A horizon of the experimental field of Taegu University was air-dried and passed through a 2-mm sieve. Several physical and chemical characteristics were measured and the results are summarized in Table 1. pH and organic matter content were adjusted using Ca(OH)<sub>2</sub> and a commercial compost, and pH

**Table 2. pH and organic matter content of soils prepared for the experiment**

Soil	pH (1:5 H <sub>2</sub> O)	Organic matter, %
1	5.1	0.5
2	5.1	4.0
3	7.0	0.5
4	7.0	4.0

**Table 3. Some characteristic properties of the  $\delta$ -MnO<sub>2</sub>**

ZPC	Surface area, m <sup>2</sup> /g	O/Mn ratio
2.9	263.3	1.94

and organic matter content of the prepared four soils are presented in Table 2. pH was measured using combination glass electrode in 1:5 water suspension. Organic carbon was measured by dichromate oxidation<sup>12)</sup>. Oxide-Mn was measured by ICP (Varian Liberty Series II) after extraction with hydroxylamine hydrochloride<sup>13)</sup>. Soil texture was determined from particle size distribution measured by the micro-pipette method of Miller and Miller<sup>14)</sup>. Cation exchange capacity at pH 7.0 was measured using 1 N ammonium acetate extraction. Chromium(VI) in soil was extracted with 0.5 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and quantitated using the s-diphenyl carbazide method<sup>6)</sup>.

### Preparation of Birnessite( $\delta$ -MnO<sub>2</sub>)

Birnessite was prepared by adding HCl to an excess of KMnO<sub>4</sub> as described by McKenzie<sup>15)</sup>. The resulting oxide was washed with deionized water and 0.5 N HClO<sub>4</sub> alternatively until the residual K content was less than 1%. After drying at 40°C, the oxide was ground to pass through an 80-mesh sieve. To identify the prepared  $\delta$ -MnO<sub>2</sub>, zero point of charge (ZPC), surface area and O/Mn ratio were measured using a salt titration method<sup>16)</sup>, the iodometric method<sup>17)</sup>, and the ethylene glycol monoethyl ether method<sup>18)</sup>, respectively. The ZPC, surface area and O/Mn ratio were presented in Table 3 and corresponded very well with published criteria<sup>15)</sup>.

### Stability of Mn-oxide in Soils

One kg of each prepared soil was thoroughly mixed with 475 mg of the  $\delta$ -MnO<sub>2</sub>, so that the final concentration of total Mn added in the mixture was 300 mg/kg. The mixture with

0.03 MPa moisture retention was incubated in polyethylene film bag at 25°C in dark condition for 30 days. Changes of the Mn-oxide content were determined by periodical measurement of oxide-Mn in the soil.

### Chromium Oxidation in Soils

Chromium oxidation in the prepared soils was tested. One kg of each prepared soil containing 475 mg of the  $\delta$ -MnO<sub>2</sub> was mixed with Cr(NO<sub>3</sub>)<sub>3</sub>, so that the final concentration of Cr(III) added in the mixture was 30 mg/kg. The mixture with 0.03 MPa moisture retention was incubated in polyethylene film bag at 25°C in dark condition for 30 days. To determine oxidation of Cr, Cr(VI) was extracted with 0.5 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> periodically, and quantitated as described above.

### Chromium Reduction in Soils

Chromium reduction in the prepared soils was tested. One kg of each prepared soil containing 475 mg of the  $\delta$ -MnO<sub>2</sub> was mixed with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, so that the final concentration of Cr(VI) added in the mixture was 30 mg/kg. The mixture with 0.03 MPa moisture retention was incubated in polyethylene film bag at 25°C in dark condition for 30 days. To determine reduction of Cr, Cr(VI) was extracted with 0.5 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> periodically, and quantitated as described above.

## RESULTS AND DISCUSSION

### Stability of Mn-oxide in Soils

Since the only known oxidants of Cr(III) are Mn-oxides,

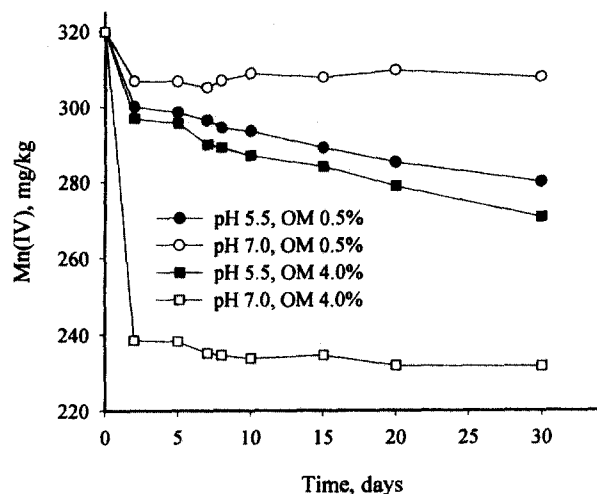


Fig. 1. Stability of Mn-oxide in soils of different pHs and organic matter contents.

content of Mn-oxides is the most important factor for chromium oxidation-reduction in soils. Therefore, chromium oxidation potential of soils could be directly related with Mn-oxide content. Stability of Mn-oxide in soil is controlled by various conditions, but soil pH and organic matter are such important controlling factors in the persistence or abundance of Mn-oxides<sup>7</sup>. Stability of  $\delta$ -MnO<sub>2</sub> in soils of different pHs and organic matter contents were determined and the results are shown in Fig. 1.

The reductive dissolution of Mn-oxide was observed in all four soils investigated. The reactions are characterized by a nonlinear loss of the added Mn-oxide with time. The reduction of Mn-oxide was rapid at the beginning and much slower in the following days. The change of the reduction rate was probably due to the oxidation of a larger fraction of the most reactive organic matter. The reductive dissolution was most significant in the soil of pH 7.0 and 4% organic matter content. And Mn-oxide was most stable in the soil of pH 7.0 and 0.5% organic matter content. Since reduction and dissolution of Mn-oxides by organic matter are rapid in lower pH<sup>10,11</sup>, we expected that the dissolution would be more significant in the soil of lower pH. But Mn-oxide was more stable in the soil of pH 5.1 at 4% organic matter content. The reason for this result is not clear at this point. Comparing the reductive dissolution of Mn-oxide at pH 7.0, the dissolution was significantly higher in the soil of higher organic matter content. It can be concluded that soil organic matter is such an important controlling factor in the persistence or abundance of Mn-oxides in soils of near the neutral pH. Our findings are in good agreement with the results of other investigations<sup>7,10,11,19</sup>.

In the manganese cycle in soil involving divalent, tetravalent, and probably other oxidation states of the element, the favored form depends on the acidity, the microbial community, the presence of O<sub>2</sub>, and the availability and abundance of organic matter. In soils of pH below 5.5, Mn(II) predominates because of the chemical equilibrium. Increasing pH brings biological forces into play, and the microbiological production of Mn-oxides and other oxides becomes apparent. In the same general pH range, biological reduction regenerates divalent manganese. And at reactions higher than pH 8.0, chemical auto-oxidation favors the oxidized states of the element. Although pH can control the persistence of Mn-oxides in soils, if soils contain relatively higher content of organic matter, Mn-oxides are expected to be not stable even in higher pH and easily dissolved by the organic matter. Manganese-oxides can

be dissolved reductively by various organic substances in soil and water environments<sup>10,11,19</sup>. Therefore, Mn-oxide content in soil can be lower in soils of high organic matter content, and then the Cr-reduction capacity can be higher in this soil condition, since Mn-oxides are the oxidant and organic matters are the reductant.

### Chromium Oxidation in Soils

Chromium oxidation is known to be dependent to the pH directly. Fendorf and Zasoski found that chromium oxidation is rapid and extensive in low pH in the mixture of birnessite Mn-oxide and soluble Cr(III)<sup>3</sup>. The solution pH controls various surface characteristics of Mn-oxide and interaction of soluble ionic species on the surface. However, in acidic soils generally the intrinsic Mn-oxide content is already low and the oxidation of added Cr(III) can be limited in field conditions. Manganese-oxides, the only known oxidants of chromium, are not stable in organic soils and also Cr(VI) is being reduced to Cr(III) with organic matter serving as the reductant<sup>7,20</sup>. Therefore, the oxidation processes would take place generally in soils high in Mn-oxides and low in organic matter content<sup>6,21</sup>. Effect of organic matter content and pH of soil on the oxidation of Cr(III) was tested and the results are presented in Fig. 2.

The oxidation of soluble Cr(III) occurred in all soils containing Mn-oxide. The concentration of Cr(VI) achieved its maximum within 5 days after addition and then decreased with time. A decrease in the concentration of Cr(VI) 5 days after add-

ition could be the consequence of competition between the oxidation and reduction processes of chromium in soils. Another explanation for the limited oxidation of added Cr(III) is possible by the fact that soluble Cr(III) added to the soil is either quickly complexed with organic substances or adsorbed and precipitated as  $\text{Cr}(\text{OH})_3$  species<sup>20</sup>. Considering these results, the reduction of Cr(VI) could dominate over possible oxidation of Cr(III) in soils of low Mn-oxides and high organic matter. On the basis of data in Fig 2, the oxidation capacity of soils for soluble Cr(III) was found to be higher for soils of lower organic matter content. More oxidation was observed in soils of higher pH, but the pH effect on the chromium oxidation was less significant than that of organic matter. Milacic et al. found that the oxidation of chromium was negligible in peat soil amended with tannery waste<sup>22</sup>. Wickliff et al. also found that the amount of chromium available to plants decreased significantly in tannery sludge-treated soil that was rich in organic matter<sup>23</sup>.

Bartlett and James found that 100 mg/kg of oxidized Mn reduced by hydroquinone in soil sample was enough for efficient oxidation of Cr(III) to Cr(VI)<sup>6</sup>. Although this suggestion could be true, Chung and Sa found very low Cr(III) oxidation potential in soil containing 223 mg/kg of oxide-Mn<sup>7</sup>. Such low oxidation potential could be attributed to the high organic matter content in the soil. These results agree very well with those reported by Kozuh et al. who observed oxidation of chromium in soils with low content of organic

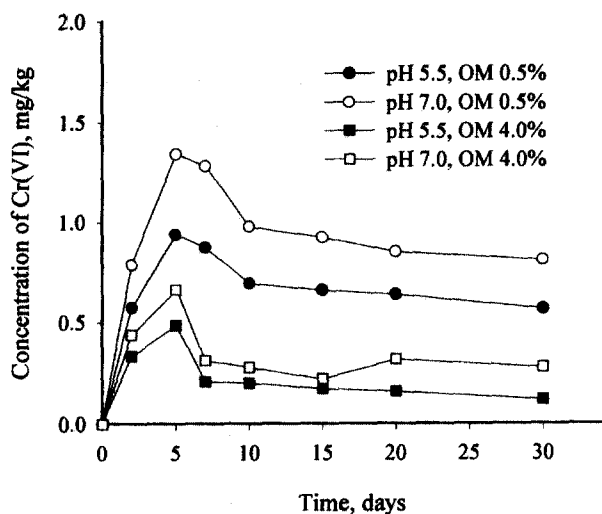


Fig. 2. Kinetics of oxidation of soluble Cr(III) added in soils of different pHs and organic matter contents.

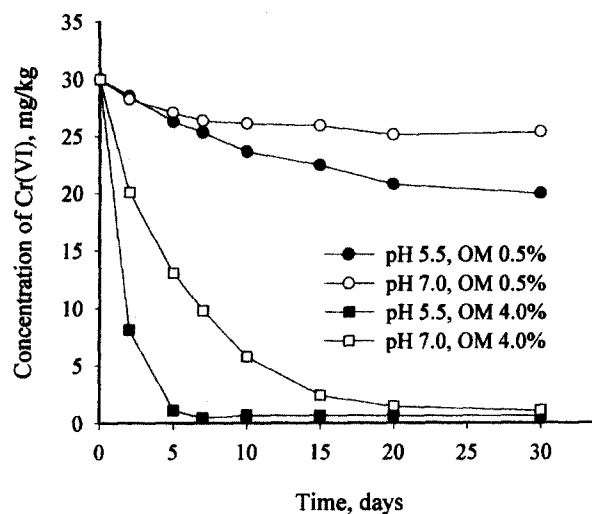


Fig. 3. Kinetics of reduction of soluble Cr(VI) added in soils of different pHs and organic matter contents.

matter and high content of Mn-oxide<sup>9)</sup>. The oxidation of Cr(III) to Cr(VI) can also be limited indirectly in soils of higher organic matter, since the oxidant Mn-oxides cannot be accumulated in such soils.

### Chromium Reduction in Soils

The reduction of soluble Cr(VI) requires the involvement of available solid organic matter in soils<sup>8)</sup>. It could depend primarily on the amount of organic matter and on its accessibility to Cr(VI), although the rates of Cr(VI) reduction are highly dependent on the specific organic compound. Also the rates of Cr(VI) reduction are strongly pH dependent, the rate increasing with decreasing pH<sup>24)</sup>. Effect of organic matter content and pH of soil on the reduction of Cr(VI) was tested and the results are presented in Fig. 3.

The reduction of soluble Cr(VI) added to the soils was found to be faster in the soils of higher organic matter content. After 5 days, all the added Cr(VI) was reduced in the soil of pH 5.1 and 4% organic matter. Although the reduction rate was slower, all the added Cr(VI) was also reduced after 20 days in the organic matter added soils of pH 7.0. Thus, the reductive capacity of organic matter added soils was much higher as compared to other two soils of lower organic matter content. In the soils of lower organic matter content, the reductions of Cr(VI) were less than 30% of the Cr(VI) added initially. The addition of organic matter to soils increased the Cr(VI) reductive capacity of the soils. Deng and Stone have shown that unlike Cr(VI) reduction in bulk solution<sup>25)</sup>, mineral surfaces common to soils and sediments catalyze the reduction of Cr(VI) by organic compounds. Jardine et al. found that the reduction of Cr(VI) to Cr(III) is dramatically more significant on soils with higher levels of surface-bound organic matter<sup>20)</sup>. These results indicate that organic matter is serving as a suitable reductant for Cr(VI).

As shown in Fig 3, the reduction of soluble Cr(VI) added to the soils was found to be faster at lower pH. Wittbrodt and Palmer also found that rates of Cr(VI) reduction increase strongly with decreasing pH<sup>24)</sup>. But the effect of pH on the reduction of Cr(VI) was less significant than that of organic matter content. It is generally known that Cr(III) forms various Cr(OH)<sub>3</sub> species in the pH range from 3.8 to 11.5. These species could be more easily formed after Cr(VI) reduction in the soil of higher pH. They could block active organic sites and decrease the accessibility of the organic matter for further reduction of Cr(VI).

On the basis of the experiments presented in Fig. 3, it can be concluded that the reduction of the added soluble Cr(VI) takes place rapidly in soils high in organic matter content.

## CONCLUSIONS

Our experiments confirm that oxidation of Cr(III) to Cr(VI) can occur in most of soils. However, the oxidation of chromium depends mostly on content of organic matter. Organic matter is directly the reductant of Cr(VI) and also determines the persistence of Mn-oxides in soil. The effect of pH on the stability of Mn-oxide was relatively significant, but the effect of pH on the oxidation and reduction of chromium was small. Soils that are low in organic matter and high in Mn-oxides deserve a special attention in applications of Cr-containing wastes. These types of soil might be well able to oxidize chromium despite the fact that this process is generally known to be very slow. The reduction of Cr(VI) could dominate over possible oxidation of Cr(III) in soils of higher organic matter content.

Since the concentration and toxicity of soluble chromium and its mobility in terrestrial environments depend on its oxidation state, reduction of Cr(VI) to Cr(III) could be a potentially useful remediation or detoxification process. Chromium (VI) generation in soils of high Cr-oxidation potential can be reduced by increasing of organic matter content in the soils.

## ACKNOWLEDGEMENT

This research was supported by the Daegu University Research Fund in 2000.

## REFERENCES

1. Kim, J. G., Dixon, J. B., Chusuei, C. C. and Deng, Y. (2002) Oxidation of chromium(III) to (VI) by manganese oxides, *Soil Sci. Soc. Am. J.* 66, 306-315.
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. E. and Zasoski, R. J. (1992) Chromium(III) oxidation by  $\delta$ -MnO<sub>2</sub> : 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 mang-

- anite(T-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. Bartlett, R. J. and James, B. (1979) Behavior of chromium in soils: III. Oxidation, *J. Environ. Qual.* 8, 31-35.
  7. Chung, J. B. and Sa, T. M. (2001) Chromium oxidation potential and related soil characteristics in arable upland soils, *Commun. Soil Sci. Plant Anal.* 32, 1719-1733.
  8. Kozuh, N., Stupar, J. and Gorenc, B. (2000) Reduction and oxidation processes of chromium in soils, *Environ. Sci. Technol.* 34, 112-119.
  9. Bartlett, R. J. and Kimble, J. M. (1976) Behavior of chromium in soils: II. Hexavalent forms, *J. Environ. Qual.* 5, 383-386.
  10. Stone, A. T. (1987) Microbial metabolites and the reductive dissolution of manganese oxides: oxalate and pyruvate, *Geochim. Cosmochim. Acta.* 51, 919-925.
  11. Xyla, A. G., Sulzberger, B. G., Luther, W., Hering, J. G., Cappellen, P. V. and Stumm, W. (1992) Reductive dissolution of manganese(III, IV) (hydr)oxides by oxalate: The effect of pH and light, *Langmuir.* 8, 95-103.
  12. Nelson, D. W. and Sommers, L. E. (1982) Total carbon, organic carbon, and organic matter, pp. 539-579. In Page, A. L. et al. (eds.), *Methods of Soil Analysis, Part 2: Chemical and Microbiological Properties*, Soil Science Society of America, Madison, WI.
  13. Gambrell, R. P. and Patrick Jr., W. H. (1982) Manganese, pp. 313-322 In Page, A. L. et al. (eds.), *Methods of Soil Analysis, Part 2: Chemical and Microbiological Properties*, Soil Science Society of America, Madison, WI.
  14. Miller, W. P. and Miller, D. M. (1987) A micro-pipette method for soil mechanical analysis, *Commun. Soil Sci. Plant Anal.* 18, 1-15.
  15. McKenzie, R. M. (1971) The synthesis of birnessite, cryptomelane, and some other oxides and hydroxides of manganese, *Mineralogical Magazine.* 88, 493-502.
  16. 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.
  17. 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.
  18. Carter, D. L., Mortland, M. M and Kemper, W. D. (1986) Specific surface, pp. 413-423, In Klute, A. (ed.) *Methods of Soil Analysis, Part I. Agronomy* 9, Am. Soc. Agron. Inc., Madison, WI.
  19. 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.
  20. Jardine, P. M., Fendorf, S. E., Mayes, M. A., Larsen, L. L., Brooks, S. C. and Bailey, B. (1999) Fate and transport of hexavalent chromium in undisturbed heterogeneous soil, *Environ. Sci. Technol.* 33, 2939-2944.
  21. Chung, J. B., Burau, R. G. and Zasoski, R. J. (2001) Chromate generation by chromate depleted subsurface materials, *Water Air Soil Pollut.* 128, 407-417.
  22. Milacic, R. and Stupar, J. (1995) Fractionation and oxidation of chromium in tannery waste- and sewage sludge-amended soils, *Environ. Sci. Technol.* 29, 506-514.
  23. Wickliff, C., Volk, V. V., Tingey, D. T., Griffis, W. L., Trunk, M. Y. and Witherow, J. L. (1982) Reactions of chrome tannery sludge in organic and mineral soils, *Water Air Soil Pollut.* 17, 61-74.
  24. Wittbrodt, P. R. and Palmer, C. D. (1995) Reduction of Cr(VI) in the presence of excess soil fulvic acid, *Environ. Sci. Technol.* 29, 255-263.
  25. Deng, B. and Stone, A. T. (1996) Surface-catalyzed chromium(VI) reduction: Comparisons of different organic reductants and different oxide surfaces, *Environ. Sci. Technol.* 30, 2484-2494.