Adsorption and redox reactions of heavy metals on synthesized Mn oxide minerals

Xiong Han Feng a, Li Mei Zhai a, Wen Feng Tan a, Fan Liu a, *, Ji Zheng He b

a Key Lab of Subtropical Agriculture Resource & Environment, Ministry of Agriculture, Huazhong Agricultural University, Wuhan, 430070, China
b Research Centre for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

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The characteristics of heavy metal adsorption and Cr(III) oxidation on Mn oxide minerals are determined by their structure, composition, surface property and crystallinity.

Abstract

Several Mn oxide minerals commonly occurring in soils were synthesized by modified or optimized methods. The morphologies, structures, compositions and surface properties of the synthesized Mn oxide minerals were characterized. Adsorption and redox reactions of heavy metals on these minerals in relation to the mineral structures and surface properties were also investigated. The synthesized birnessite, todorokite, cryptomelane, and hausmannite were single-phased minerals and had the typical morphologies from analyses of XRD and TEM/ED. The PZCs of the synthesized birnessite, todorokite and cryptomelane were 1.75, 3.50 and 2.10, respectively. The magnitude order of their surface variable negative charge was: birnessite > cryptomelane > todorokite. The hausmannite had a much higher PZC than others with the least surface variable negative charge. Birnessite exhibited the highest adsorption capacity on heavy metals Pb2+, Cu2+, Co2+, Cd2+ and Zn2+, while hausmannite the smallest one. Birnessite, cryptomelane and todorokite showed the greatest adsorption capacity on Pb2+ among the tested heavy metals. Hydration tendency (pKf) of the heavy metals and the surface variable charge of the Mn minerals had significant impacts on the adsorption. The ability in Cr(III) oxidation and concomitant release of Mn2+ varied greatly depending on the structure, composition, surface properties and crystallinity of the minerals. The maximum amounts of Cr(III) oxidized by the Mn oxide minerals in order were (mmol/kg): birnessite (1330.0) > cryptomelane (422.6) > todorokite (59.7) > hausmannite (36.6).

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Keywords: Mn oxide mineral; Heavy metal; Adsorption; Redox; Surface properties

1. Introduction

Mn is one of oxyphile elements. Mn(II) is easily depleted from igneous and metamorphic rocks by weathering. It is highly mobile and easily oxidized to form a variety of Mn hydroxide/oxide (denoted as Mn oxide in following) minerals near surface of the Earth. These Mn oxide minerals widely exist in upper crust, such as soils and sediments in various forms of scattered weak crystallized aggregates, nodules, coatings, sediments, etc. They commonly have a lower PZC (point of zero charge), large surface area and strong acid sites, allowing high adsorption capacity, and excellent oxidation and catalysis activity (Post, 1999). To a large extent they influence and control the release, transfer, availability and toxicity of many nutrient elements, heavy metals and organic contaminants in soils and sediments (Oscarson et al., 1981; Pan, 1990; Stepniewska et al., 2004; Lu, 2004).

More than 15 known Mn oxide minerals occur in soils. Because of their easily changeable valent states, low contents in soils, co-existence of different phases, and finely crystalline or poorly ordered forms, separation, identification and direct investigation of naturally occurring Mn oxide minerals are...
always difficult. Structures and characteristics of many Mn oxide minerals are also poorly known (Mckenzie, 1989; Post, 1992). Syntheses of common Mn oxide minerals and further investigation of interaction between them and contaminants are usually adopted as an important route to study their structures, origination mechanisms and environmental geochemical behaviors. However, single-phased Mn oxide minerals are not easy to synthesize due to their non-stoichiometric composition, various species and close formation conditions. Many studies have focused on the surface properties, interactions with pollutants and mechanisms of a few Mn oxide minerals or aggregates of Mn oxides in soils, such as birnessite, cryptomelane, Mn coatings, and Mn nodules (Mckenzie, 1980; Oscarson et al., 1981; Shindo and Huang, 1984; Matucha et al., 2001; Larson et al., 2002; Manceau et al., 2002; Weaver et al., 2002; Shaughnessy et al., 2003; Stepniewska et al., 2004; Tan et al., 2005). However, information on comparison of properties for such Mn oxide minerals or aggregates of Mn oxides is limited. Recent EXAFS (extended X-ray absorption fine structure spectroscopy) studies indicated that surface chemical properties (such as adsorption-desorption) for Mn oxide minerals with different crystallographic structures were very different (Pan et al., 2004; Li et al., 2004). Their diverse environmental behaviors could also be expected. Comparison of properties for different Mn oxide minerals and the relevance with their structures is essential for the understanding of their behaviors in the environments.

In this work, several single phased Mn oxide minerals with different structures commonly distributed in soils and sediments were synthesized through improved or optimized methods. Their morphologies, structures and chemical compositions were characterized. Adsorption of heavy metals and redox reactions of Cr(III) on them and the association with their structures and surface properties were investigated.

2. Materials and methods
2.1. Syntheses of Mn oxide minerals
Birnessite was synthesized by the modified procedure (Feng, 2003) of Mckenzie (1971): 500 mL of 0.4 mol/L KMnO₄ was heated and kept boiling in an oil bath with stirring. The mixture solution of 35 mL concentration hydrochloric acid and 15 mL water was added dropwise to the above KMnO₄ solution at a speed of 0.7 L/min. After reacting with boiling for a further 30 min, the mixture solution was cooled, aged for 12 h at 60 °C and centrifuged at 2.54 × 10⁴ g in a Beckman Super-speed refrigerated centrifuge. The yielded mineral was washed with distilled deionized water (DDW, from Labconco Water Pro Ps, used throughout the experiments) until no chlorine ion could be detected by 0.1 mol/L acidic silver nitrate solution, the volatilized CH₃COOH during the reaction. The suspension was cooled, centrifuged at 2.54 × 10⁴ g for 20 min. A suitable amount of 2 mol/L CH₃COOH was added to make up concentration of 35 mL solution. Then, 1 mL mineral suspensions were mixed with 14 mL heavy metal solutions with a certain concentration in 25-mL polyethylene centrifuge tubes. The pH of the mixture was adjusted to 4.5 by adding 0.01 mmol/L NaOH or HNO₃. After reaction, the reaction mixtures were centrifuged before the precipitate was washed until the conductance of the supernatant was below 2 μS/cm. The product was then aged in water at 50 °C for 24 h, separated and freeze-dried.

Hausmannite was synthesized by a modification (Feng, 2003) of the procedure of Mckenzie (1971): DDW pretreated by bubbling N₂ (>99.9%) was used throughout this synthesis. Under stirring and bubbling of N₂, 100 mL 0.5 mol/L NaOH solution was slowly poured into 100 mL 0.2 mol/L MnSO₄. The mixture was kept reacting for 10 ~ 20 min. The hydroxide precipitate was washed by repeated decantation in the funnel, keeping the funnel completely filled to prevent oxidation. When pH of the filtrate was less than 8.5, the precipitate was suspended in 100 mL water and oxidized by bubbling O₂ at room temperature for 5 h. The product was fully washed and freeze-dried.

2.2. Characterization
X-ray diffraction (XRD) analyses were performed with FeKα radiation generated at a tube voltage of 40 kV, a tube current of 20 mA, and at a step scanning rate of 0.02° per 0.5 s. Philips-CMI2 Analytic Transmission Electron Microscopy (TEM) operated at 120 kV was used for TEM analyses. The TEM images and electron diffraction (ED) patterns of the samples were taken. Samples were analyzed for elemental composition using Varian Vizia-MPX ICP-OES. The general molecular formulas of the Mn oxide minerals were determined according to the method described by Kijima et al. (2001). All chemical analysis for each sample was repeated three times and the mean was recorded. Specific surface area measurements were done using a ST-08 Surface Area Analyzer. Fast potentiometric titration method was used to determine PZC (Laverdiere and Weaver, 1977). Surface charge was measured by a back titration method (Quockett and Hendershot, 1993).

2.3. Adsorption experiments
Isothermal adsorption of Pb²⁺, Cu²⁺, Cd²⁺, Co²⁺, Zn²⁺ on the tested minerals: Firstly, 20 mg/mL mineral suspensions with pH 4.5 and a series concentration of Pb²⁺, Cu²⁺, Cd²⁺, Co²⁺, Zn²⁺ solutions with pH 4.5 were prepared. Then, 1 mL mineral suspensions were mixed with 14 mL heavy metal solutions with a certain concentration in 25-mL polyethylene centrifuge tubes. The pH of the mixture was adjusted to 4.5 by adding 0.01 mmol/L NaOH or HNO₃. The tubes were then stoppered, shaken for 2 h, equilibrated for 24 h at 25 ± 1 °C, and centrifuged at 7800 × g for 10 min in a Beckman Super-speed refrigerated centrifuge. The supernatants were collected and analyzed for heavy metal concentration on Varian Vista-MPX ICP-OES. Each run was made in duplicate.

2.4. Redox experiments
Oxidation of Cr(III) with different concentrations on the tested minerals: The oxidation reactions were performed in 25-mL polyethylene centrifuge tubes by shaking at 25 ± 1 °C for 4 h. Reactions were initiated by mixing an aliquot of the above mineral suspensions (1 mL) with a known volume of freshly prepared 4 mmol/L Cr(NO₃)₃ at pH 2.0 and a certain volume of DDW. The total volume of the reaction mixtures were 12 mL. The pHs of the mixtures were then immediately switched to 4.5 by adjusting with 0.1 and 0.01 mmol/L NaOH or HNO₃. After reaction, the reaction mixtures were filtered and ten milliliters of 0.04 mol/L K₂HPO₄ was used to release the adsorbed Cr(VI) on the minerals’ surfaces by decantation washing the residues several times. The filtrates were also collected and volume to 50 mL. Each run was made in duplicate. Manganese and total chromium were determined by atomic adsorption spectroscopy. Cr(VI) was determined using the diphenylcarbazide colorimetric method (Bartlett and James, 1979).

3. Results and discussion
3.1. Characterization of the synthesized Mn oxide minerals
According to the crystal structures, Mn oxides can be classified into three types: layer structures, tunnel structures and
lower oxides (Mckenzie, 1989). Todorokite is a large tunnel structured Mn oxide with a $3 \times 3$ array of edge shared MnO$_6$ octahedra chains. Diffraction data from the synthesized todorokite (Fig. 1) matched well with those of the natural todorokites (JCPDS 13–164 and JCPDS 38–475) and the synthetic sample with hydrothermal method (Golden et al., 1986). The todorokite consisted of fibers with different length extended from a platy trilling matrix, 1 ~ 5 $\mu$m in length, and about 20 nm in width (Feng et al., 2004a).

Hausmannite, spinel structured, is one of two important Mn lower oxides in soils (McKenzie, 1989; Post, 1992). The synthesized hausmannite was darkly yellow powder, darkened to black after being heated at 100 ~ 200 $^\circ$C. All of the diffraction peaks at 0.494, 0.309, 0.289, 0.277, 0.250, 0.237, 0.205, 0.183, 0.180, 0.170, 0.164, 0.158, 0.154 and 0.144 nm in its XRD pattern (Fig. 1b) were due to hausmannite (JCPDS 24–734). From the TEM image (Fig. 2a), hausmannite had a typical cubic morphology with different crystal sizes, 0.3 ~ 0.8 $\mu$m for the large particles and 40 ~ 100 nm for the small ones. The small particles were possibly yielded from the large ones by cleavage during sampling. The [100] ED pattern (Fig. 2b) was indexed with the parameters: tetragonal unit cell, $a = 0.576$, $b = 0.947$, indicating that it has a structure of tetragonal crystal system and its morphology belong to pseudocubic symmetry.

Cryptomelane is a $2 \times 2$ tunnel-structured manganese oxide. 0.701, 0.492, 0.344, 0.311, 0.247, 0.220, 0.193 and 0.164 nm peaks in the XRD pattern (Fig. 1c) of the synthesized sample can all be attributed to cryptomelane (JCPDS 20–908). It consisted of single phased and needle shaped crystals with 50 ~ 250 nm in length and 30 nm in width (Fig. 2c). Its ED pattern (Fig. 2d) was indexed with the parameters: tetragonal unit cell, $a = 0.984$ nm, $b = 0.285$ nm. The diffraction points are very weak around unclear polycrystalline rings, indicating its low crystallinity and small particle size similar to natural aphanitic cryptomelane.

Birnessite, the most common Mn oxide mineral in soils, is constructed of layers of edge sharing MnO$_6$ octahedra separated by a layer of water molecules (Post and Veblen, 1990). The prepared birnessite were single phased mineral, indicated by four characteristic peaks (JCPDS 23–1239) at 0.739, 0.366, 0.246, 0.142 nm in its XRD pattern (Fig. 1d) and its micro-morphology (Fig. 2e). It consisted of cluster or ball like aggregates with a size of 0.5 ~ 1 $\mu$m, in good agreement with the morphology of balls of needles as described by Mckenzie (1989). The balls were actually random stacked thin plate aggregates from being observed in high multiple (Feng, 2003). They were composed of many fine crystals rather than a coherent twin crystal, which could also be testified by its ED patterns (Fig. 2f). It displayed diffuse polycrystalline rings. The $d$ spacings for the first and second ring were 0.246 and 0.142 nm, which were attributed to (100) and (110) plane, respectively. The ring for the basic plane (001) was more diffuse and unclear.

Thus, the synthesized Mn oxide minerals were confirmed to be single crystalline phases. The basic properties of the tested
Table 1
Basic properties of the synthesized Mn oxide minerals

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical composition</th>
<th>AOS of Mn</th>
<th>Specific surface area m²/g</th>
<th>Crystallinity</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Birnessite</td>
<td>K₀.₀₅MnO₂₀.₀₁(H₂O)₀.₆₅</td>
<td>3.₉₆</td>
<td>4₈.₉</td>
<td>Weak</td>
<td>Layer</td>
</tr>
<tr>
<td>Todorokite</td>
<td>M₀.₁₇MnO₂₀.₀₆(H₂O)₀.₈₈</td>
<td>3.₈₂</td>
<td>₉₈.₅</td>
<td>High</td>
<td>Tunnel</td>
</tr>
<tr>
<td>Cryptomelane</td>
<td>K₀.₂₄MnO₂₀.₀₇(H₂O)₀.₄₈</td>
<td>3.₉₀</td>
<td>₁₃₀.₇</td>
<td>Weak</td>
<td>Tunnel</td>
</tr>
<tr>
<td>Hausmannite</td>
<td>MnO₁.₁₆(H₂O)₀.₁₄</td>
<td>2.₆₆</td>
<td>₉₈.₅</td>
<td>High</td>
<td>Low oxide</td>
</tr>
</tbody>
</table>

*Calculated from elemental composition and AOS of Mn (Feng, 2003).*  
*b Determined by the strength of the XRD peaks.*

Manganese oxide minerals are listed in Table 1. The average Mn oxidation states (AOS) for the birnessite, todorokite, and cryptomelane were very high, being 3.96, 3.82, and 3.90, respectively. Their PZCs were very low, being 1.75, 3.50 and 3.90, respectively. Conversely, hausmannite had a low PZC, being 2.66 and >10 (Shaughnessy et al., 2003), respectively. The birnessite and cryptomelane were poorly crystallized, but the todorokite and hausmannite were well crystallized. The variable surface negative charge for the birnessite, todorokite, and cryptomelane increased with pH (Fig. 3). Its magnitude sequence was: birnessite > cryptomelane > todorokite. When pH was above 4.5, the hausmannite suspension was not stable during determination of PZC and surface charge, possibly due to its disproportionation reaction (Feng et al., 2005). Thus, no accurate PZC and surface charge data were recorded for the hausmannite.

### 3.2. Isothermal adsorption of heavy metals

Adsorption isotherms (Fig. 4) of different heavy metals were similar in shape, could be attributed to L type (Giles et al., 1960). When the equilibrium concentration of heavy metal ions was increased from the lowest value, the adsorption amount firstly increased sharply, then increased slightly, and tended to keep stable and approached a maximum. All of the adsorption isotherms were fitted well by the Langmuir model with highly significant correlations (r = 6, R₀.₀₁ = 0.917). The equation is \[ Y = A_{\text{max}}KC/(1 + KC) \], where \( Y \) is adsorption amount per unit weight (mmol/kg), \( A_{\text{max}} \) represents the maximum adsorption amount, \( C \) is equilibrium concentration of heavy metals and \( K \) denotes a constant related to adsorption energy being a function of adsorption enthalpy and temperature (Kinniburgh, 1986).

The Langmuir parameters, calculated by non-linear least squares analysis (Kinniburgh, 1986), were shown in Table 2. The adsorption capacity of heavy metals for the tested Mn oxide minerals differed greatly from each other. Among them, birnessite exhibited the greatest adsorption capacity on the heavy metals and hausmannite exhibited the weakest one. Except hausmannite, the Mn oxide minerals adsorbed the greatest amount of Pb²⁺. The sequence of maximum capacity for heavy metals by birnessite was Pb²⁺ > Cu²⁺ > Zn²⁺ > Co²⁺ > Cd²⁺, that by cryptomelane was Pb²⁺ > Cu²⁺ > Cd²⁺ ≈ Zn²⁺ > Co²⁺, and those by todorokite and hausmannite were Pb²⁺ > Cu²⁺ > Co²⁺ > Cd²⁺ > Zn²⁺ and Cu²⁺ > Pb²⁺ > Co²⁺ ≈ Zn²⁺ > Cd²⁺, respectively. Hausmannite is the only mineral having the less adsorption for Pb²⁺ than that for Cu²⁺. The first order hydrolysis constants (\( K_{\text{f}} \)) for Pb²⁺, Cu²⁺, Zn²⁺, Co²⁺ and Cd²⁺ decrease in turn, they are 10⁻⁷.⁷, 10⁻⁷.⁹, 10⁻⁹.⁰, 10⁻⁹.⁷ and 10⁻¹⁰.¹, respectively (Baes and Mesmer, 1976). The maximum adsorption amounts for the heavy metals by birnessite were in the same sequence to that of their hydrolysis constants. Other minerals exhibited the maximum adsorption amounts with similar but not identical sequence. A similar sequence was also reported elsewhere for the Mn oxides or Mn oxide aggregates (Mckenzie, 1989; Parida et al., 1996; Tan et al., 2005). Therefore, the heavy metal ions may be adsorbed by the Mn oxide minerals mainly in form of hydroxylation cations. pH in the experiments (4.5) is greatly less than pKᵣ of the heavy metals, indicating that the hydroxylation cations were formed via hydrolysis induced by the surfaces of the Mn oxide minerals (Yu et al., 1996; Weaver et al., 2002). The energy barriers for specific adsorption of heavy metals were thus lowered and adsorption was improved. Such effect was more significant for the heavy metals with lower hydrolysis constants. Moreover, the radii of the heavy metal ions, coordination forms and mineral structures would also influence adsorption of heavy metals (Mckenzie, 1989; Parida et al., 1996; Lanson et al., 2002; Pan et al., 2004; Li et al., 2004), and those could cause non-identical sequence as mentioned above.

![Fig. 3. Surface negative charge (a); and charge density (b) of the synthesized Mn oxide minerals versus pH.](image-url)
The adsorption sequences for the same heavy metal ions by the different minerals varied slightly. The sequence for Pb\(^{2+}\), Zn\(^{2+}\) and Cd\(^{2+}\) was birnessite > cryptomelane > todorokite > hausmannite, the same as that of surface variable charge at pH 4.5 (Fig. 3). The sequence for Cu\(^{2+}\) and Co\(^{2+}\) were birnessite > todorokite > hausmannite > cryptomelane and birnessite > todorokite > cryptomelane > hausmannite, respectively. Except that hausmannite had the extra high adsorption capacity of Cu\(^{2+}\), the adsorption sequences for Cu\(^{2+}\) and Co\(^{2+}\) were also close to that of surface negative charge because the charge on the surfaces of todorokite and cryptomelane had little difference. Mn oxide minerals adsorb heavy metals primarily in form of specific adsorption (Mckenzie, 1980, 1989; Parida et al., 1996; Manceau et al., 2002; Pan et al., 2004; Li et al., 2004). Though specific adsorption is a chemical adsorption and surface charge has little direct effect on it, surface negative charge of the Mn oxide minerals still enhance the adsorption of heavy metals. The possible reason is that more surface negative charge makes the surface induced hydrolysis stronger. In this case the more hydroxylation cations with lower charge and hydration degree (hydration free energy is in direction proportion to the square of charge) were produced, the higher specific adsorption capacity was thus obtained. The adsorbed heavy metal ions on the mineral surfaces were assumed to array in mono molecular layer and hexagonal closest package, surface area occupied by the adsorbed heavy metal ions could be denoted as \(2 \sqrt{3} \pi r^2\) (Chen et al., 2001). As for first hydration ions, \(r = r_{ion} + 2r_{H_2O}, r_{H_2O} = 0.138 \text{ nm (Mckenzie, 1980).}\) The ionic radii (\(r_{ion}\)) for Pb\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\), Co\(^{2+}\) and Cd\(^{2+}\) with octahedral coordination are 1.20, 0.73, 0.74, 0.74 and 0.95 nm, respectively (Shannon, 1976). The theoretic maximum adsorption amounts calculated with the monolayer cover of first hydration ion are shown in Table 3. Except that the maximum adsorption amount of Cu\(^{2+}\) by hausmannite was a bit greater than the theoretic one, those of all heavy metals by cryptomelane, todorokite and hausmannite were less than the corresponding theoretic values. However those of all heavy metals by birnessite were much greater (5.7 \~{} 12.4 times) than the corresponding theoretic values. That of Pb\(^{2+}\) by birnessite was very close to the theoretic maximum adsorption calculated with the monolayer cover of non-hydration ion radius of Pb\(^{2+}\). It was reported that no evidence was found for the oxidation of lead and formation of Pb-Mn minerals after Pb\(^{2+}\) was adsorbed by the Mn oxide minerals.

Fig. 4. Isotherms of the heavy metals adsorption on the synthesized Mn oxide minerals at a temperature of 25 \(^\circ\)C and pH of 4.5.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Parameters</th>
<th>Heavy metal types</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pb</td>
</tr>
<tr>
<td>Birnessite</td>
<td>(A_{max}/\text{mmol/Kg})</td>
<td>1832</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>25.9</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>0.995</td>
</tr>
<tr>
<td>Todorokite</td>
<td>(A_{max}/\text{mmol/Kg})</td>
<td>284.3</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>214.6</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>0.999</td>
</tr>
<tr>
<td>Cryptomelane</td>
<td>(A_{max}/\text{mmol/Kg})</td>
<td>292.8</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>292.3</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>0.982</td>
</tr>
<tr>
<td>Hausmannite</td>
<td>(A_{max}/\text{mmol/Kg})</td>
<td>105.3</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>196.5</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>0.949</td>
</tr>
</tbody>
</table>

The Langmuir equation is \(Y = A_{max}KC/(1 + KC)\), where \(Y, A_{max}, C\), and \(K\) represent adsorption amount per unit weight (mmol/kg), maximum adsorption amount, equilibrium concentration of heavy metal ions and a constant.

* Calculated by non-linear least squares analysis (Kinniburgh, 1986).
Therefore if the Mn oxides mineral adsorbed heavy metal ions with a cover of monomolecular layer, Pb\(^{2+}\) was adsorbed by birnessite possibly in a main form of non-hydration ion, but as for cryptomelane, todorokite and hausmannite the adsorbed Pb\(^{2+}\) existed possibly in a primary state of hydration ion. The distinct surface sites with different affinity on the surfaces of the different Mn oxide minerals may possibly account for the different forms and coordination states of the adsorbed heavy metals (Pan et al., 2004; Li et al., 2004).

### 3.3. Cr(III) oxidation by the synthesized Mn oxide minerals

Fig. 5 shows the curves of the Cr(III) oxidized to Cr(VI) by the Mn oxide minerals. The curves are similar in shape, resembling the Langmuir adsorption isotherm. When the concentration of Cr(III) was below 5 mmol/L, the amount of Cr(VI) produced by the Mn oxide minerals increased sharply, then increased slightly, eventually kept stable and approached a maximum value with increase of added Cr(III) concentration. The Mn oxide minerals differed greatly in oxidation ability. Birnessite showed the strongest oxidation capacity, followed by cryptomelane, todorokite and hausmannite. The magnitude sequence of the maximum amount of Cr(III) oxidation calculated with Langmuir model fitting was: birnessite (1330.0 mmol/kg) > cryptomelane (422.6 mmol/kg) > todorokite (59.7 mmol/kg) > hausmannite (36.6 mmol/kg).

The Mn\(^{2+}\) released during redox reaction is shown in Fig. 6. It increased with increase of Cr(III) oxidation, and was different in amount and amplitude. Birnessite, cryptomelane and todorokite released little Mn\(^{2+}\) to solution. The yielded Mn\(^{2+}\) during oxidation was re-adsorbed on the negatively charged surfaces of the above three minerals (pH > PZC). In contrast, hausmannite released much more Mn\(^{2+}\) to the solution. Because hausmannite is a low oxide mineral (Table 1), in which Mn was consisted of Mn\(^{2+}\) and Mn\(^{3+}\), hausmannite would produce more Mn\(^{2+}\) at the same oxidation amount. Furthermore, hausmannite possessed much positive charge under the experimental system (pH < PZC) and thus weak ability on Mn \(^{2+}\) adsorption. The released Mn\(^{2+}\) amounts to the solution are in the following sequence: hausmannite > todorokite > cryptomelane > birnessite.

The properties of minerals are determined by both their compositions and crystal structures. The disordered H\(_2\)O/K sheets in birnessite are sandwiched between the MnO\(_6\) octahedral layers. They are combined by van der Walls force and hydrogen bonds between hydroxyl in H\(_2\)O/K sheets and O atoms in MnO\(_6\) octahedral layers. Cryptomelane and todorokite were constructed by covalent-bond linked MnO\(_6\) octahedral chains (Post, 1992) and are more stable and exhibit weaker activity on Cr(III) oxidation than birnessite (Tan et al., 2005). Compared with todorokite, weakly crystallized cryptomelane possessed more growth defects in its crystal lattice, higher surface area and greater amount of active oxygen in its tunnel structure (Yin et al., 1994). These may account for its stronger oxidization of Cr(III) than todorokite. Hausmannite had a much lower Mn AOS than the other minerals (Table 1). It is the most thermally stable Mn oxide mineral, having a spinel-like structure with Mn\(^{2+}\) in the octahedral and Mn\(^{4+}\) in tetrahedral sites (Post, 1992). This may result in its the least Cr(III) oxidation capacity.

### Table 3

Hydration ion radii of the heavy metals and their maximum theoretic adsorption amounts with monolayer cover on the tested manganese oxides

<table>
<thead>
<tr>
<th>Samples</th>
<th>Pb (0.396)</th>
<th>Co (0.35)</th>
<th>Cu (0.349)</th>
<th>Cd (0.371)</th>
<th>Zn (0.35)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Birnessite</td>
<td>148</td>
<td>189</td>
<td>190</td>
<td>168</td>
<td>189</td>
</tr>
<tr>
<td>Todorokite</td>
<td>301</td>
<td>386</td>
<td>388</td>
<td>343</td>
<td>386</td>
</tr>
<tr>
<td>Cryptomelane</td>
<td>400</td>
<td>512</td>
<td>515</td>
<td>455</td>
<td>512</td>
</tr>
<tr>
<td>Hausmannite</td>
<td>116</td>
<td>149</td>
<td>150</td>
<td>132</td>
<td>149</td>
</tr>
</tbody>
</table>

\(^{a}\) Radius of hydrated ion was calculated by \(r_{\text{ion}}^{+} + 2r_{\text{H}_{2}\text{O}}\). \(r_{\text{ion}}^{+}\) was cited from Shannon (1976).
The redox reaction between Mn oxide minerals and Cr(III) occurred on the interface of minerals and solution. Adsorption of Cr(III) and desorption of Cr(VI) on the surface of minerals were two steps for the oxidation reaction before and after electrons transfer from Cr(III) to the minerals (Stepniawska et al., 2004). Adsorption of Cr(III) on the surface of Mn oxide minerals would enhance the oxidation of Cr(III), while adsorption of Cr(VI) would hamper adsorption and subsequent oxidation of Cr(III). Adsorption of Cr(III) and Cr(VI) is greatly influenced by the surface charge characteristics of the minerals and the chemical species of Cr(III) and Cr(VI). The first and second order hydrolysis constants ($pK_1$ and $pK_2$) are 3.57 and 6.28 (Rai et al., 1987). The first and second order dissociation constants ($pK_{a1}$ and $pK_{a2}$) of Chromic acid ($H_2CrO_4$) are 0.75 and 6.45 (Kotas and Stasicka, 2000). Therefore, in the experiment system (pH 4.5) the favoured species of Cr(III) was positively charged Cr(OH)$_2^{2+}$ (88.1%). Cr(VI) existed mostly in form of negatively charged HCrO$_4^-$(98.9%). According to the PZCs of the Mn oxide minerals (Table 1), birnessite, cryptomelane and todorokite possessed surface negative charge at pH 4.5, while the surface of the hausmanite was strongly positively charged. Thus, birnessite, cryptomelane and todorokite were preferable to adsorb Cr(III) and repel the oxidation product Cr(VI) to the solution, improving the oxidation of Cr(III). On the contrary, Hausmanite tended to repel Cr(III) and immobile Cr(VI), surface sites were easy to be blocked. Furthermore, it had a low specific surface area, providing small amount of surface sites per unit weight. These were against to Cr(III) oxidation. Consequently, surface charge property is a significant influencing factor on Cr(III) oxidation by Mn oxide minerals.

4. Conclusion

Based on the XRD and TEM/ED analyses, all of the synthesized Mn oxide minerals, birnessite, todorokite, cryptomelane and hausmanite were single phased and exhibited the typical morphologies. The PZCs of birnessite, todorokite and cryptomelane were 1.75, 3.50 and 2.10, respectively. Their surface negative charge was in the same sequence to their PZC. Comparatively, hausmanite had a much higher PZC and lower surface negative charge than the other three minerals. Hydration constants of the heavy metal and the surface variable charge of the Mn minerals greatly influenced the adsorption of heavy metals. Birnessite exhibited the greatest adsorption capacity on the heavy metals, while hausmanite exhibited the weakest one. Except that hausmanite had the extra high adsorption of Cu$^{2+}$, Mn oxide minerals possessed the greatest adsorption capacity on Pb$^{2+}$ among the tested heavy metals. The Mn oxide minerals differed greatly in Cr(III) oxidation capacity depending on their structure, composition, surface property and crystallinity. The maximum amount of Cr(III) oxidation decreased in following sequence: birnessite (1330.0 mmol/kg) > cryptomelane (422.6 mmol/kg) > todorokite (59.7 mmol/kg) > hausmanite (36.6 mmol/kg).

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