The controlling effect of pH on oxidation of Cr(III) by manganese oxide minerals

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Abstract

Oxidation of Cr(III) by three types of manganese oxide minerals (birnessite I, birnessite II, and todorokite) and effects of pH were investigated by chemical analysis, equilibrium redox, X-ray diffraction (XRD), and transmission electron microscopy. The effects of pH in the reaction systems on the oxidation of Cr(III) were similar among the three manganese oxide minerals. As pH increased from pH 2.0, the amount of Cr(III) oxidized by the tested manganese oxide minerals first increased, and then peaked at pH 3.0–3.5. While pH continually increased from 3.0 to 3.5, the amount of Cr(III) oxidized by the manganese oxide minerals sharply decreased. Until pH was higher than 5.0–5.5, the Cr(III) oxidation amounts changed to a small extent or kept stable. pH influenced the oxidation of Cr(III) mainly by altering the redox potential in the system, i.e., the concentration of H^+ , the species of Cr(III), and their distributions in the system. However, the surface charge of the manganese oxide minerals, subjected to the pH in the system, was not found to greatly influence the extent of the oxidation. When pH was below 5.0, oxidation of Cr(III) by the manganese oxide minerals was (or tended to be) an equilibrium reaction and was controlled thermodynamically. When pH was above 5.0–5.5, $Cr(OH)_3$ precipitate was produced in the system and pH had little effect on the oxidation content of Cr(III).

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1. Introduction

There has been increasing concern over chromium (Cr) pollution in aquatic environments and soils. Chromium (Cr) exists in two most common stable oxidation states, Cr(III) and Cr(VI), in the natural water system [1,2]. Cr(VI) is more labile and 10–100 times more toxic than Cr(III), and carcinogenic even at low concentrations of 50 ppb [3,4]. Manganese oxide minerals are one of the most active constituents in soils and sediments with extraordinary sorption capacity and strong oxidizing ability [5–8]. The minerals have been demonstrated to be the only inorganic oxidants capable of oxidizing Cr(III) to Cr(VI) species in the surface environments [9–12]. To a large extent, the oxidation of Cr(III) by manganese oxides influences and/or controls the transport, transformation, bioavailability, and biotoxicity of

Cr in the environments [13–15]. Many factors, such as structure, crystallinity, and oxidation status of Mn minerals and environmental pH, temperature, and ionic strength, are credited with influencing the extent and rate of Cr(III) oxidation by the manganese oxide minerals [15–19]. Among these factors, pH likely has more complex effects on the interaction between Cr(III) and manganese oxides, because it determines not only the H^+ activity in the reaction system but also surface charge characteristics and the oxidation half-reaction potential of the manganese oxide minerals, as well as species of Cr(III) and their distribution [10,12,14,18,20,21].

It was reported that manganese oxides can strongly oxidize Cr(III) at low pH, due to their higher oxidation potential, and no Cr(III) precipitation occurs under this condition [12,21]. Risser and Bailey [22] showed a more complete oxidation of Cr(III) by synthetic δ - MnO_2 at pH 3.5–4.5 after fixed time period. At a pH range of 2.5–8.5, extent of Cr(III) oxidation by the Fe–Mn nodules increased with the decrease of pH due to consumption of H^+ , variations of surface charge properties of Mn

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oxides and redox potential during oxidation, and influence of coexisted iron oxides [18]. Cr(III) oxidation by γ -MnOOH was observed to be faster and more significant at pH 3.0–4.5, and when pH increased to 4.5–6.0 the reactions were minimized, due to blockage of reaction sites on the mineral surface by the produced multinuclear complexes or surface precipitation [12]. Cr(III) oxidation at pH 4 by several manganese oxides, todorokite, birnessite, lithiophorite, and pyrolusite, was much greater than that at pH 7 [14]. However, it was also reported that pH influenced oxidation of Cr(III) by manganese oxides in different ways in different pH range, and maximum oxidation appeared at a certain pH value or pH range [10,21]. pH effects on Cr(III) oxidation were attributed to two opposing processes. One was the attraction and adsorption of Cr(III) species by the surface of manganese oxides, which was advantageous for oxidation and was enhanced with increasing pH due to increase of surface negative charge. Another was complexing and precipitating of Cr(III) with OH^- , which was disadvantageous to the oxidation and also promoted by increasing pH. Amacher [10] observed faster and stronger Cr(III) oxidation by manganese oxides with increasing pH from 1.0 to 5.5 but little change happened in rate and extent of the reaction from 5.5 to 7.0. The amount of Cr(III) oxidized by α -MnO₂ and γ -MnOOH varied with pH in the range from 2.0 to 7.0, with the largest value at pH 4.5–6.0 [21]. Otherwise Silvester and Manceau [23] observed weak dependence of the rate of Cr(III) oxidation by busserite on the solution pH.

The above inconsistency in the pH effect on the oxidation of Cr(III) by manganese oxides in literatures is not so surprising. It may result from different experimental conditions in different studies, such as the initial concentrations of Cr(III), the characteristics of the manganese oxides, and the medium conditions. However, it is the case that the chemical mechanisms of the pH effect on the Cr(III) oxidation by Mn oxide minerals are not fully understood. Is pH influencing Cr(III) oxidation by changing the surface properties of the manganese oxides or by altering the species of Cr(III) in solutions? Does the reaction between Cr(III) and manganese oxides reach an equilibrium? Is the pH effect controlled dynamically or thermodynamically? To answer these questions, more studies are needed.

In this work, three synthesized manganese oxide minerals, which are commonly distributed in soils and sediments, were taken as materials. The effects of pH on oxidation of Cr(III) by these manganese oxide minerals in a controlled system were investigated. The obtained results were extended to develop a theoretical explanation about the controlling effect of pH on Cr(III) oxidation using chemical equilibrium theory and chemical potential calculation.

2. Materials and methods

2.1. Manganese oxide minerals syntheses and characterization

Birnessite I was synthesized through reduction of potassium permanganate by hydrochloric acid [24]. A quantity of 250 mL of 5.5 M cool NaOH was added quickly to 200 mL 0.5 M

MnCl₂, and O₂ was bubbled through the mixture solution at 2 L/min for 5 h during vigorous stirring to prepared birnessite II [25,26]. Todorokite was synthesized at atmospheric pressure [27]. A quantity of 10 g of purified birnessite II in wet state was fully exchanged with 1 mol/L MgCl₂ for 12 h to obtain Mg-buserite. After centrifugation and washing, the Mg-buserite was transformed to todorokite by being dispersed in 300 mL water and heated to reflux under stirring for 24 h. The synthesized minerals were purified by electrical dialysis at a voltage of 150–220 V until the conductivity of the supernatant was below 2.0 $\mu\text{S}/\text{cm}$ and then freeze-dried.

X-ray diffraction (XRD) analysis was performed on a D/Max-3B diffractometer with monochromated FeK α radiation. The monochromated radiation had a tube voltage of 40 kV, a tube current of 20 mA, and a count time of 0.5 s per 0.02°. Transmission electron microscopy (TEM) analyses were carried out in Philips CM12. Samples were analyzed for elemental composition using Varian Vizta-MPX ICP-OES. The general molecular formula of the Mn oxide minerals were determined according to the method described by Kijima et al. [28].

PZC (point of zero charge) of the minerals was determined by a rapid potentiometric titration method similar to that used by Laverdier and Weaver [29]. Two parts of 0.5 g mineral sample were fully equilibrated with 10 mL of 0.02 and 2 mol/L KCl, respectively. The suspensions were titrated by adding 0.1–0.2 mL of either 0.01 mol/L HCl or 0.01 mol/L NaOH at 2-min intervals, after which the pH value was measured. The titration was carried out under intermittent bubbling of N₂ gas. The titrations on the blank solution of the same volume and salt concentration were also carried out without the sample. The adsorption amounts of H⁺ and OH[−] at a given pH were taken as the amount of the HCl or NaOH added minus the amount of acid or base required to bring a blank solution to the same pH. Using adsorption amounts of H⁺/OH[−] as y-axis and pH as x-axis, two RPT curves for 0.02 and 2 mol/L KCl media were drawn, their intersection point was PZC.

2.2. Chemicals

Distilled deionized water (DDW, 18 M Ω , from Labconco Water Pro Ps) after boiling for 1 h to remove the dissolved air was used throughout the experiment. All chemicals (HNO₃, NaOH, KNO₃, and Cr(NO₃)₃) were of reagent grade. All glassware and polyethylene centrifuge tubes were rinsed with 0.01 mol/L HNO₃ and DDW before use.

2.3. Oxidation of Cr(III)

Each manganese oxide mineral sample was mixed with DDW to prepare mineral suspension at mineral concentration of 20 mg/mL. The suspension was fully dispersed by ultrasonic treatment, shaken for 1 wk to hydrate the mineral, and then stored in the hydrated state and kept stirring before use.

The oxidation reactions were performed in 50-mL polyethylene centrifuge tubes by shaking at 25 $\pm$ 1 °C for 4 h. Preliminary kinetic studies indicated that the reactions were very quick at the initial 1 h, subsequently became slower, and

Fig. 1. Diagram of Cr(III) stability as a function of Cr(III) concentration and pH (modified from Rai et al., 1987 [20]). The plotted points represent solution conditions before reaction. The PZCs of birnessite I, birnessite II, and todorokite are labeled on the pH axis.

approached equilibrium after 4 h. Reactions were initiated by mixing a aliquot of mineral suspension (1 mL) with 0.24 mL of 0.5 mol/L KNO_3 , a known volume of freshly prepared 4 mmol/L $\text{Cr}(\text{NO}_3)_3$ at pH 2.0 and a certain volume of DDW. The reaction solutions was then immediately switched to a series of desired pH of 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, or 6.5 (± 0.1) by adjusting with 0.1 and 0.01 mol/L NaOH or HNO_3 . The final reaction solutions contained 0.01 mol/L KNO_3 and 1.67 g/L manganese oxide mineral. Our preliminary experiment indicated that the maximum amounts of Cr(III) oxidation for birnessite I, birnessite II, and todorokite were about 1790, 180, and 100 mmol/kg. Thus 3.33, 0.33, and 0.17 mmol/L of $\text{Cr}(\text{NO}_3)_3$ for the systems of birnessite I, birnessite II, and todorokite, respectively, were used so that Cr(III) in each system could not be exhausted after the reaction and the relation between the amount of Cr(III) oxidized by each mineral after reaction and pH in the system could be perceptible. If the added Cr(III) was all adsorbed by the three minerals before oxidation, the initial surface coverages of Cr(III) on birnessite I, birnessite II, and todorokite were 41.4, 5.53, and 1.04 $\mu\text{mol}/\text{m}^2$. The points labeled in Fig. 1 indicate the solution conditions employed in each of our experiments. The stability of Cr(III) in the aqueous phase was studied in detail by Rai et al. [20] and is described in Fig. 1. The PZCs of the minerals were also labeled on the pH axis. As could be seen, the experimental conditions for each mineral were across a range from Cr(III) undersaturation to oversaturation with respect to $\text{Cr}(\text{OH})_3(\text{s})$. The Cr(III) species distribution in the reaction solution and the surface charge amount and/or charge sign (changed from positive to negative) for each mineral in the solution were also different under these conditions.

After reaction, the tubes were centrifuged at 7800g for 10 min and the supernatants were collected. Cr(VI), total Cr, and Mn^{2+} concentrations in the supernatants were determined. Ten milliliters of 0.04 mol/L KH_2PO_4 was added to the residues to release the adsorbed Cr(VI) on their surfaces

[19], shaken at $25 \pm 1^\circ\text{C}$ for 1 h, and then centrifuged at 7800g for 10 min. The supernatants were also collected. Cr(VI) concentration in the supernatants was determined. Total Cr(VI) of the double treatments was regarded as the amount of Cr(III) oxidized. Each run was made in triplicate. Manganese and total chromium were determined by atomic adsorption spectroscopy, and Cr(VI) was determined using the diphenylcarbazide colorimetric methods [30].

3. Results and discussion

3.1. Characterization of Mn oxide minerals

Fig. 2 shows powder XRD patterns of the synthesized Mn oxide minerals. Birnessite I were poorly crystalline, being indicated by only four broad and weak peaks at 0.739, 0.366, 0.246, 0.142 nm in its XRD pattern (Fig. 2a) and its micromorphology (Fig. 3a). These peaks were characteristic of birnessite (JCPDS (Joint Committee of Powder Diffraction Standards) file card No. 23-1239, JCPDS 23-1239) and in good agreement with that reported in other study [31]. It consisted of so-called balls of needles as described in the literature [32]. The balls were actually randomly stacked thin plates from being observed in high multiples [33].

The XRD patterns of the todorokite and birnessite II (Figs. 2b and 2c) synthesized in this study matched well with JCPDS cards 13-164 and 23-1046, respectively. The characteristic peaks (Fig. 2b) for the synthesized todorokite at 0.968, 0.715, 0.48, 0.445, 0.322, 0.246, 0.239, 0.234, 0.222, 0.198, 0.175, and 0.142 nm were also shown in its XRD pattern. The diffraction peaks for birnessite II were at d spacings of 0.712, 0.358, 0.252, 0.244, 0.223, 0.216, 0.186, 0.182, 0.163, 0.148, 0.145, and 0.142 nm (Fig. 2c). The narrow and strong XRD reflections indicated that they are well crystallized, as could also be shown in their TEM images (Figs. 3b and 3c). The crystallites of the birnessite II mainly consisted of well-stacked hexagonal plates along the direction of the (001) plane, about 1 μm in

Fig. 2. Powder X-ray diffraction patterns of the synthesized Mn oxide minerals: (a) birnessite I; (b) todorokite; (c) birnessite II.

Fig. 3. TEM images of the synthesized manganese oxide minerals: (a) birnessite I; (b) birnessite II; (c) todorokite.

Table 1
The basic properties of the tested manganese oxide minerals

Sample	Structure	AOS of Mn ^a	Chemical composition ^b	Specific surface area ^c (m ² /g)	PZC ^d	Crystallinity
Birnessite I	Layer	3.96	K _{0.05} MnO _{2.01} (H ₂ O) _{0.65}	48.3	1.75	Weak
Birnessite II	Layer	3.89	Na _{0.25} MnO _{2.07} (H ₂ O) _{0.66}	35.8	3.20	Good
Todorokite	Tunnel	3.82	Mg _{0.17} MnO _{2.10} (H ₂ O) _{0.88}	98.5	3.70	Good

^a Average oxidation state of Mn was determined with the titration method [27].

^b Calculated from elemental composition determined by Varian Vista-MPX ICP-OES and AOS of Mn [25,26].

^c Determined by BET measurement with N₂ gas adsorption.

^d Zero point of charge was determined by rapid potentiometric titration [29].

size (Fig. 3b). The todorokite consisted of fibers extended from a platy trilling matrix (Fig. 3c), which was characteristic of todorokite [34]. Thus, the synthesized Mn oxide minerals were confirmed to be single crystalline phases by XRD and TEM. The basic properties of the tested manganese oxide minerals are listed in Table 1.

3.2. pH effects on the oxidation of Cr(III)

Our previous work indicates that most of the Cr(VI) adsorbed on the surface of manganese oxide minerals is easily desorbed by KH₂PO₄ solution [18,19]. After oxidation of Cr(III) by the manganese oxide minerals, the concentration of

Fig. 4. Concentrations of Cr(VI) produced in the equilibrium solutions (equ.) and in the desorption supernatants (des.) by KH_2PO_4 at different pH after oxidation by the manganese oxide minerals. Concentrations of Cr(III) added in the systems of (a) birnessite I, (b) birnessite II, and (c) todorokite are 3.33, 0.33, and 0.17 mmol/L, respectively.

Cr(VI) in the equilibrium solution and subsequent desorption supernatants by KH_2PO_4 solution was regarded as the amount of Cr(III) oxidized in the following. Cr(VI) in desorption supernatants represents the adsorption of Cr(VI). Fig. 4 shows Cr(VI) concentration distribution in the equilibrium and desorption solutions at different pHs (pH 2.5, 3.5, 4.5, 5.5, 6.5) after oxidation. Cr(VI) adsorption at different pHs has only a small proportion of the total Cr(VI) produced (from 1.9% for

Fig. 5. Amounts of Cr(III) oxidized by the manganese oxide minerals versus pH. Concentrations of Cr(III) added in the systems of (a) birnessite I, (b) birnessite II, and (c) todorokite are 3.33, 0.33, and 0.17 mmol/L, respectively.

birnessite at pH 2.5 to 29.6% for todorokite at pH 6.5), especially at low pH, indicating that Cr(VI) has a weak affinity for adsorption on the surface of manganese oxide minerals.

The effects of pH in the reaction systems on the oxidation of Cr(III) were similar for three manganese oxide minerals (Fig. 5). When pH was very low (<3), the amount of Cr(III) oxidized by three manganese oxide minerals increased with increase of pH. The oxidized amounts for birnessite I and todorokite reached a maximum at pH 3.0 and peaked at pH 3.0–3.5 after a slight increase from pH 2.0 for birnessite II. Then with continual increase of pH (>5) The amount of Cr(III) oxidized by the three manganese oxide minerals sharply decreased. Un-

til pH was higher than 5.0 or 5.5, variation of oxidized amounts with pH got slower abruptly (for todorokite) or became nearly imperceptible (for birnessite I and birnessite II). The results are in approximate agreement with the previous reports in the literature that Cr(III) oxidation was largest at pH 4.5–6.0 [21] and changed little in rate and extent from pH 5.5 to 7.0 [10].

Chen et al. [21] attributed pH effects before and after the maximum oxidation of Cr(III) to the two opposing processes and effects. At lower pH, a small amount of negative surface charge or positive surface charge on the surface of manganese oxide minerals inhibited sorption and subsequent oxidation of Cr(III) on the mineral surface; i.e., increase of pH led to more negative surface charge, and thus increased sorption and oxidation of Cr(III). At higher pH, complexation and precipitation of Cr(III) with OH^- occurred and the reactions promoted as pH increased; interaction and reaction between Cr(III) and the minerals were thus restrained.

The concentrations of Cr(III) in systems of birnessite I, birnessite II, and todorokite before reaction were 3.33, 0.33, and 0.17 mmol/L, respectively. According to the stability relation (Fig. 1) of Cr(III) species in aqueous solution [20], $\text{Cr}(\text{OH})_3$ precipitation would appear at pH 4.13, 4.63, and 4.79 (pH 4–5), respectively, at above initial Cr(III) concentrations without regard to adsorption and oxidation. It is difficult to know the exact adsorption properties of Cr(III) on the surface of manganese oxide minerals because adsorbed Cr(III) dynamically undergoes oxidation and whether the adsorbed Cr is Cr(III) or Cr(VI) is difficult to distinguish in situ. As mentioned above, the produced Cr(VI) had a small adsorption capacity on the surface of manganese oxide minerals and was easily desorbed by KH_2PO_4 . Besides the Cr in the equilibrium solution and desorption solution by KH_2PO_4 , the residual Cr on the surfaces of manganese oxide minerals can be approximately attributed to Cr(III) adsorption (including $\text{Cr}(\text{OH})_3$ precipitation). Fig. 6 shows such Cr(III) adsorption and Cr(VI) adsorption at different pHs (pH 2.5, 3.5, 4.5, 5.5, 6.5) after oxidation. Excluding nondetection of Cr(III) adsorption for birnessite II at pH 2.5, manganese oxide minerals adsorbed much more Cr(III) than Cr(VI). The Cr(III) adsorption increased sharply with increased pH. In contrast, the concentrations of Cr(III) in the equilibrium solutions at different pH after oxidation were very low (Table 2). The concentrations of Cr(III) in the desorption supernatants by KH_2PO_4 were lower than those in the equilibrium solutions at different pH, and most of them could not be detected. Taking oxidation and adsorption of part of Cr(III) during the reaction into consideration (Fig. 6), $\text{Cr}(\text{OH})_3$ precipitation should appear at pH 5.0–5.5 in the solution and surface of the minerals under the experimental conditions. Part of the surface

sites would be blocked by the precipitation. Therefore, when pH was above 5.5, extent of oxidation of Cr(III) was mainly controlled by dissolution of $\text{Cr}(\text{OH})_3$ precipitation and exposure of surface sites, and was less influenced by pH. If only the

Fig. 6. Adsorption of Cr(VI) and Cr(III) by manganese oxide minerals at different pH after oxidation. Concentrations of Cr(III) added in the systems of (a) birnessite I, (b) birnessite II, and (c) todorokite are 3.33, 0.33, and 0.17 mmol/L, respectively.

Table 2

Concentrations of Cr(III) in mmol/L in the equilibrium solutions at different pH after oxidation by the manganese oxide minerals

Sample	pH 2.5	pH 3.5	pH 4.5	pH 5.5	pH 6.5
Birnessite I	0.091 ± 0.000	0.026 ± 0.010	0.119 ± 0.043	0.008 ± 0.012	0.011 ± 0.008
Birnessite II	0.069 ± 0.001	0.071 ± 0.008	0.0655 ± 0.004	0.059 ± 0.011	0.005 ± 0.007
Todorokite	0.001 ± 0.001	ND ^a	0.002 ± 0.001	ND ^a	0.004 ± 0.001

Note. Concentrations of Cr(III) added in the systems of birnessite I, birnessite II and todorokite are 3.33, 0.33, and 0.17 mmol/L, respectively.

^a ND—could not be detected.

mentioned opposing processes were accounted, the maximum oxidation of Cr(III) would occur at pH 5.0–5.5 or pH 4.0–5.0 (disregarding oxidation and adsorption of part of Cr(III)). However, in our experiments, the oxidation of Cr(III) peaked at pH 3.0–3.5. Besides the effect of pH-dependent surface charge of the minerals, or adsorption properties of Cr(III), other mechanisms should account for that.

3.3. Explanations of pH effects

Reactions between the manganese oxide minerals and Cr(III) were assumed to reach (or tend to reach) an equilibrium thermodynamically; thus reaction extent and oxidation amount of Cr(III) were determined to standard redox potential difference of the reaction (or equilibrium constant) and concentrations of initial reactants and products, i.e., potential difference of oxidation half-reaction and reduction half-reaction in the initial stage of the reaction. It was specifically referred to the potential difference of oxidation pairs $\text{MnO}_2/\text{Mn}^{2+}$ and reduction pairs $\text{HCrO}_4^-/\text{CrOH}^{2+}$ (denoted as ΔE). Greater ΔE meant that the reaction would occur to a larger extent till equilibrium and greater oxidation amount of Cr(III) would be obtained. Through changing species of Cr(III) and their distribution, pH in the system influenced concentrations and states of reactants and products, thereby altering ΔE and influencing oxidation extent of Cr(III). H_2CrO_4 is a kind of moderately strong acid; its disassociation constants, $\text{p}K_{\text{a}1}$ and $\text{p}K_{\text{a}2}$, are 0.95 and 6.51, respectively [35]. Therefore, under the experimental acid conditions, the oxidation product Cr(VI) mainly existed as HCrO_4^- ; however, species of Cr(III) were greatly influenced by pH. The reaction between manganese oxide and Cr(III) could be simply denoted as follows:

or

The above reactions took place in one system, concentrations of $\text{Cr}(\text{OH})_2^+$ and CrOH^{2+} were subjected to equilibrium of their transformation reaction. Thus either of the reactions could be chosen for potential calculation. The oxidation and reduction half-reactions for the above reaction (2) were given as

The corresponding potential could be expressed as:

$$E_{3\text{MnO}_2+12\text{H}^+/3\text{Mn}^{2+}} = E_{3\text{MnO}_2+12\text{H}^+/3\text{Mn}^{2+}}^0 + 0.059/6 \log([\text{H}^+]^{12}/[\text{Mn}^{2+}]^3),$$

$$E_{2\text{HCrO}_4^-+12\text{H}^+/2\text{CrOH}^{2+}} = E_{2\text{HCrO}_4^-+12\text{H}^+/2\text{CrOH}^{2+}}^0 + 0.059/6 \log([\text{HCrO}_4^-]^2[\text{H}^+]^{12}/[\text{CrOH}^{2+}]^2).$$

So we obtained an expression for ΔE :

$$\Delta E = E_{3\text{MnO}_2+12\text{H}^+/3\text{Mn}^{2+}}^0 - E_{2\text{HCrO}_4^-+12\text{H}^+/2\text{CrOH}^{2+}}^0 + 0.059/6 \log([\text{CrOH}^{2+}]^2/([\text{Mn}^{2+}]^3[\text{HCrO}_4^-]^2)). \quad (3)$$

Although Cr is widely used in industry and its potential toxicity has raised much attention, most thermodynamic data (e.g., equilibrium constant) reported in the literature for hydrolysis and polymerization of Cr(III) in solutions are still approximate values [20,36]. It would put great difficulty to quantitative description of Cr(III) species in solutions. Based on the chemical equilibrium theory and newly reported hydrolysis constants of Cr(III), analysis of Cr(III) species was preformed.

For simplicity, the effect of ion strength on species of Cr(III) was overlooked. The polymerization of Cr(III) at room temperature can be ignored due to the slow kinetics of the formation of polymeric species [20]. With the increase of pH, hydrolysis of Cr(III) can be stronger and the first-order, second-order, third-order, and fourth-order hydrolysis becomes the dominant reaction in sequence, and the corresponding main species of Cr(III) are CrOH^{2+} , $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_3$, and $\text{Cr}(\text{OH})_4^-$, respectively. The products of third-order hydrolysis reactions of Cr(III) can be precipitation state $\text{Cr}(\text{OH})_3(\text{s})$ or dissolving state $\text{Cr}(\text{OH})_3^0(\text{aq})$, and the equilibrium constant for the former reaction is 10^6 times greater than that of the latter. Therefore, the concentration of dissolving state $\text{Cr}(\text{OH})_3^0(\text{aq})$ was also ignored in comparison with $\text{Cr}(\text{OH})_3(\text{s})$. Only when pH is higher than 11.5, fourth-order hydrolysis of Cr(III) can occur [20], and thus it was not appreciable for the analysis of Cr(III) species under our experimental acid conditions. Accordingly, species of Cr(III) in the experimental systems was composed of Cr^{3+} , CrOH^{2+} , $\text{Cr}(\text{OH})_2^+$, and $\text{Cr}(\text{OH})_3(\text{s})$. The equilibrium constants of first-order to third-order hydrolysis of Cr(III) ($\text{Cr}^{3+} + \text{H}_2\text{O} = \text{CrOH}^{2+} + \text{H}^+$, $\text{CrOH}^{2+} + \text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + \text{H}^+$, $\text{Cr}(\text{OH})_2^+ + \text{H}_2\text{O} = \text{Cr}(\text{OH})_3(\text{s}) + \text{H}^+$), denoted as K_1 , K_2 , K_3 , are $10^{-3.3}$, $10^{-5.5}$, and $10^{-0.8}$, respectively [36]. So the concentration of CrOH^{2+} can be given as

$$[\text{CrOH}^{2+}] = [\text{Cr(III)}]K_1[\text{H}^+]^2/([\text{H}^+]^3 + K_1[\text{H}^+]^2 + K_1K_2[\text{H}^+] + K_1K_2K_3), \quad (4)$$

where $[\text{Cr(III)}]$ is the initial concentration of added Cr(III). Substituting $[\text{CrOH}^{2+}]$ in Eq. (3) from Eq. (4), ΔE can be expressed as

$$\Delta E = E_{3\text{MnO}_2+12\text{H}^+/3\text{Mn}^{2+}}^0 - E_{2\text{HCrO}_4^-+12\text{H}^+/2\text{CrOH}^{2+}}^0 + 0.059/6 \log([\text{Cr(III)}]K_1[\text{H}^+]^2/([\text{H}^+]^3 + K_1[\text{H}^+]^2 + K_1K_2[\text{H}^+] + K_1K_2K_3))^2/([\text{Mn}^{2+}]^3[\text{HCrO}_4^-]^2)).$$

After transforming we obtain

$$\Delta E = E_{3\text{MnO}_2+12\text{H}^+/3\text{Mn}^{2+}}^0 - E_{2\text{HCrO}_4^-+12\text{H}^+/2\text{CrOH}^{2+}}^0 + 0.059/6 \log K_1^2[\text{Cr(III)}]^2/([\text{Mn}^{2+}]^3[\text{HCrO}_4^-]^2) + 0.059/6 \log([\text{H}^+]^2/([\text{H}^+]^3 + K_1[\text{H}^+]^2 + K_1K_2[\text{H}^+] + K_1K_2K_3))^2,$$

Fig. 7. Theoretic plot of $\Delta E'$ versus pH ($\Delta E' = \Delta E - K(\text{constant})$, ΔE is the potential difference between oxidation half reaction and reduction half reaction at the beginning of oxidation of Cr(III) by the manganese oxide minerals).

where $E^0_{3\text{MnO}_2+12\text{H}^+/3\text{Mn}^{2+}} - E^0_{2\text{HCrO}_4^-+12\text{H}^+/2\text{CrOH}^{2+}}$ is constant. In the initial stage of the reaction, $[\text{Mn}^{2+}]$ and $[\text{HCrO}_4^-]$ are very small, and can be regarded as constant. Thus, it can be assumed that

$$K(\text{constant}) = E^0_{3\text{MnO}_2+12\text{H}^+/3\text{Mn}^{2+}} - E^0_{2\text{HCrO}_4^-+12\text{H}^+/2\text{CrOH}^{2+}} + 0.059/6 \log K_1^2 [\text{Cr(III)}]^2 / ([\text{Mn}^{2+}]^3 [\text{HCrO}_4^-]^2);$$

thus, we obtain

$$\Delta E = K + \Delta E'.$$

In the equation,

$$\begin{aligned} \Delta E' &= 0.059/6 \log ([\text{H}^+]^2 / ([\text{H}^+]^3 + K_1 [\text{H}^+]^2 \\ &\quad + K_1 K_2 [\text{H}^+] + K_1 K_2 K_3))^2 \\ &= 0.0197 \log [\text{H}^+]^2 / ([\text{H}^+]^3 + K_1 [\text{H}^+]^2 \\ &\quad + K_1 K_2 [\text{H}^+] + K_1 K_2 K_3). \end{aligned}$$

Replacing $[\text{H}^+]$ by $10^{-\text{pH}}$, and substituting K_1 , K_2 and K_3 with their values, the expression of $\Delta E'$ we obtain is

$$\Delta E' = -0.0197 \log (10^{2\text{pH}-9.6} + 10^{\text{pH}-8.8} + 10^{-\text{pH}} + 10^{-3.3}).$$

A plot of $\Delta E'$ versus pH is showed in Fig. 7.

As can be seen in Fig. 7, $\Delta E'$ was maximized at pH 3.1. According to the above discussion, ΔE and oxidation amount also should have the maximum value at the same pH. In our study, oxidation amounts of Cr(III) for three manganese oxide minerals peaked at pH 3.0–3.5. The experimental results agree fairly with the theoretical assumption that reactions between the manganese oxide minerals and Cr(III) should reach (or tend to reach) a thermodynamic equilibrium and are controlled by the redox potential in the systems. However, whether surface negative charge increased with pH ($\text{pH} > \text{PZC}$) or the surface was charged from positively to negatively ($\text{pH} = \text{PZC}$), the oxidation extent of Cr(III) was less influenced by the surface charge.

Heavy metal cations such as Cr(III) adsorbed on the surface of manganese oxide minerals primarily in the form of specific adsorption [19,32,37]. Specific adsorption is chemical adsorption and surface charge has little direct effect on it [38]. This may possibly account for the smaller influence of surface charge on the oxidation extent of Cr(III).

4. Conclusion

Three synthesized Mn oxide minerals, birnessite I, birnessite II, and todorokite, could actively oxidize Cr(III) to Cr(VI), and varied greatly in their ability to oxidize. pH in the reaction systems significantly affected the oxidation of Cr(III) by three manganese oxide minerals in the similar way. The amount of Cr(III) oxidized first increased with increase of pH from pH 2.0, and then peaked in pH 3.0–3.5. While pH continually increased from 3.0 to 3.5, the amount of Cr(VI) production sharply decreased. Until pH was higher than 5.0–5.5, the Cr(VI) production changed not remarkable or kept stable. When pH was lower than 5.0, the reaction between Cr(III) with each of three tested manganese minerals was (or tended to be) a thermodynamic equilibrium reaction, and the reaction degree was controlled by the redox potential in the experimental systems. The pH greatly influenced the reaction mainly by changing the concentration of H^+ and the species of Cr(III) and their distribution in the solution and on the surfaces. However, the pH-dependent surface-variable charge had little effect on the oxidation extent of Cr(III). While pH was greater than 5.0, Cr(OH)_3 precipitate was produced in the system and amount of Cr(III) oxidized depended primarily on the dissolution equilibrium of the produced Cr(OH)_3 and exposure of surface sites.

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