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# Oxidation of Cr(III) on birnessite surfaces: The effect of goethite and kaolinite

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## ABSTRACT

Oxidation of Cr(III) by manganese oxides may pose a potential threat to environments due to the formation of toxic Cr(VI) species. At present, it was still unclear whether the extent of Cr(III) oxidation and fate of Cr(VI) would be changed when manganese oxides co-exist with other minerals, the case commonly occurring in soils. This study investigated the influence of goethite and kaolinite on Cr(III) oxidation by birnessite under acidic pH condition (pH 3.5) and background electrolyte of 0.01 mol/L NaCl. Goethite was found not to affect Cr(III) oxidation, which was interpreted as the result of overwhelming adsorption of cationic Cr(III) onto the negatively-charged birnessite (point of zero charge (PZC) < 3.0) rather than the positively-charged goethite (PZC = 8.8). However, more Cr(VI) would be retained by the surface with the increase in addition of goethite because of its strong ability on adsorption of Cr(VI) at low pH. Moreover, either Cr(III) oxidation or distribution of the generated Cr(VI) between the solid and solution phases was not affected by kaolinite (PZC < 3.0), indicating its low affinity for Cr species. Reactions occurring in the present mixed systems were suggested, which could be partly representative of those in the soils and further indicates that the mobility and risk of Cr(VI) would be decreased if goethite was present.

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## Introduction

There has been a wide concern over the soil contamination by chromium, which mainly originated from the Cr-containing parent materials and improper disposal of waste from various Cr-processing industries (Choppala et al., 2013b). The total content of Cr in soil from the vicinity area at a ferroalloy plant has been reported to be elevated to 3500 mg/kg (Wang et al., 2011). Chromium exists in the environment predominantly as the form of Cr(III) and Cr(VI) species, which have contrasting toxicity and transport characteristics (Choppala et al., 2013a).

Cr(III) was generally believed to be less toxic to living organisms and mobile in soils than Cr(VI) (Rajapaksha et al., 2013). Recently, studies have reported that surface and groundwater could suffer from Cr(VI) contamination resulting from the oxidation of Cr(III) released from the dissolution of natural chromite (FeCr(III)<sub>2</sub>O<sub>4</sub>) by birnessite (Oze et al., 2009). Therefore, it is essential to investigate oxidation of Cr(III) on manganese mineral surfaces when evaluating the remediation strategy of Cr-contaminated soils through the pathway of Cr(V) reduction.

During the past decades, oxidation of Cr(III) by manganese oxide has been well documented (Fendorf, 1995). Generally,

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heterogeneous redox reaction of this type was expected to occur through a multiprocess mechanism, which included the formation of Cr(III)-MnO<sub>2</sub> surface complexes and subsequent electron transfer between Cr(III) and Mn(III/IV), followed by the release of the Cr(VI) to aqueous solution (Manceau and Charlet, 1992). Previous works have revealed that the reaction would be inhibited with the increase in pH due to the precipitation of aqueous Cr(III) (Feng et al., 2006b). Additionally, the extent of Cr(III) oxidation was also affected by Mn oxide diversity (Kim et al., 2002). Mn oxide with the lowest point of zero charge (PZC) has the highest capacity of oxidizing Cr(III) because positively charged Cr(III) species could be readily adsorbed onto negatively charged surfaces (Landrot et al., 2012).

Previous studies have provided valuable knowledge about interfacial chemistry of Cr(III) in Mn oxides/water suspensions. In soil environments, Mn oxides are not present alone, but always co-exist with Fe oxides and clay minerals. It is still unclear whether oxidation Cr(III) as well as the fate of Cr(VI) would be changed or not when these co-existing minerals are present. To gain insight into the geochemical knowledge of Cr(III), further work should be carried out in more complex systems. Indeed, recent works have indicated that mobility of As(III), another type of hazardous material in soils, could be largely reduced in the Fe–Mn binary systems when compared to that in single system (Deschamps et al., 2003; Ying et al., 2012; Zhang et al., 2012). Such combined effect was attributed to the transformation of As(III) to As(V) by Mn oxides and, subsequently, the oxidation product was more preferentially scavenged by Fe oxides.

Because birnessite is one of the most common forms of Mn minerals identified in soils (McKenzie, 1971), it has received wide attention when studying Cr(III) oxidation in the environments. According to Feng et al. (2006b), Cr(III) oxidation by birnessite was most favorable at low pH condition, indicating that Cr(III) oxidation could commonly occur in those highly weathered and acidic soils, such as red soil or latosol distributed in south China. To simulate conditions in the soil of this kind, goethite and kaolinite were selected to examine the influence of co-existing minerals on Cr(III) oxidation by birnessite since they are abundant in these soils, and then the results could be more representative of the case occurring in the natural environments. The presence of goethite or kaolinite possibly can exert influence on Cr(III) oxidation in two aspects. On the one hand, co-existing minerals might inhibit Cr(III) oxidation if they could compete with birnessite for adsorption of Cr(III) (Charlet and Manceau, 1992; Bhattacharyya and Gupta, 2008). On the other hand, the generated Cr(VI) could be adsorbed onto goethite or kaolinite surfaces, and then its mobility would be inhibited. Up to date, no such study was reported, and thus it is worthwhile to examine the Cr(III) oxidation in the binary solid systems of birnessite–goethite or kaolinite, which will improve our understanding of environmental risk posed by the oxidation of Cr(III) to Cr(VI).

The objective of this study was to reveal the influence of goethite or kaolinite on Cr(III) oxidation by birnessite as well as the related mechanisms. Because the reaction was highly pH-dependent and most effective at pH 3.0–3.5 (Feng et al., 2006b), pH condition used in the present experiments was controlled at 3.5. In addition, the formation and structure of soil birnessite–goethite or kaolinite associations were still unclear, and hence this study was carried out in binary mixed systems.

## 1. Materials and methods

### 1.1. Chemicals and oxides

Kaolinite was obtained from Fluka and other reagents were purchased from Fisher Scientific. All the solutions were made with the deionized water, with a conductivity less than 1.0  $\mu$ S/cm. The glassware used was soaked in 10% HNO<sub>3</sub> overnight and then thoroughly rinsed with double distilled water prior to being used. The Cr(III) solution was prepared daily from chromium chloride, a few hours before the experiments to avoid the polymerization.

Birnessite and goethite were synthesized according to the method of McKenzie (1971) and Atkinson et al. (1967), respectively. The obtained precipitate was dialyzed against the deionized water until the conductivity of the dialysis water was less than 1.0  $\mu$ S/cm, and freeze-dried. The mineralogy of synthesized oxides was confirmed with X-ray diffraction (XRD, Philips X'Pert X-Ray Diffractometer, Fig. 1). Each oxide sample was mixed with deionized water to prepare mineral suspension at mass concentration. After being ultrasonically dispersed, suspension was shaken for one week to hydrate the mineral, and then stored in the hydrated state and kept stirring before use.

### 1.2. Experimental procedures

A batch method was adopted to investigate the Cr(III) oxidation by birnessite, and concentrations of birnessite and background electrolyte were similar with those used in the previous studies. Initially, oxide suspension, diluted to the desired mineral concentration (4.0 g/L), was equilibrated at the pH 3.5  $\pm$  0.05 for two days. The oxidation reactions were performed in 50 mL centrifuge tubes, and were initiated by mixing 2.5 mL of 4 g/L birnessite suspension with 0.2 mL of 1.0 mol/L NaCl (pH 3.5) and different amounts of freshly prepared 4 mmol/L CrCl<sub>3</sub> at pH 3.5. The final volume of suspension was made to 20 mL by the addition of deionized water. Thus, the suspension contained 0.01 mol/L NaCl as background electrolyte and 0.5 g/L birnessite at the beginning of the reaction, with concentration of Cr(III) ranging from 0.25 to 4.0 mmol/L. After being shaken for 4 hr, tubes were centrifuged at 12,500 r/min for 15 min, and supernatant was passed through 0.22  $\mu$ m nylon filter, followed by determination of Cr(VI) concentration and pH of the samples.

To examine the influence of goethite or kaolinite on Cr(III) oxidation, different volumes of 2 g/L goethite or 10 g/L kaolinite suspensions, which have been hydrated at pH 3.5  $\pm$  0.05 for 2 days, were added to the pre-weighted tubes containing 2.5 mL of 4 g/L birnessite suspension, followed by the addition of deionized water (pH 3.5) to make the volume of the suspension to 15 mL. Subsequently, 5 mL of freshly prepared 2 mmol/L CrCl<sub>3</sub> (pH 3.5) using 0.04 mol/L NaCl as background electrolyte was added to the suspensions. After reaction for 4 hr, filtrate samples were obtained by using the same method as described above. Additionally, 20 mL of 0.01 mol/L KH<sub>2</sub>PO<sub>4</sub> was added to the residues which remained in tubes to release the Cr(VI) adsorbed on surfaces (Feng et al., 2006b), followed by shaking for 24 hr and centrifugation at 12,500 r/min for 15 min. The supernatant was also collected for the determination of Cr(VI) concentration.

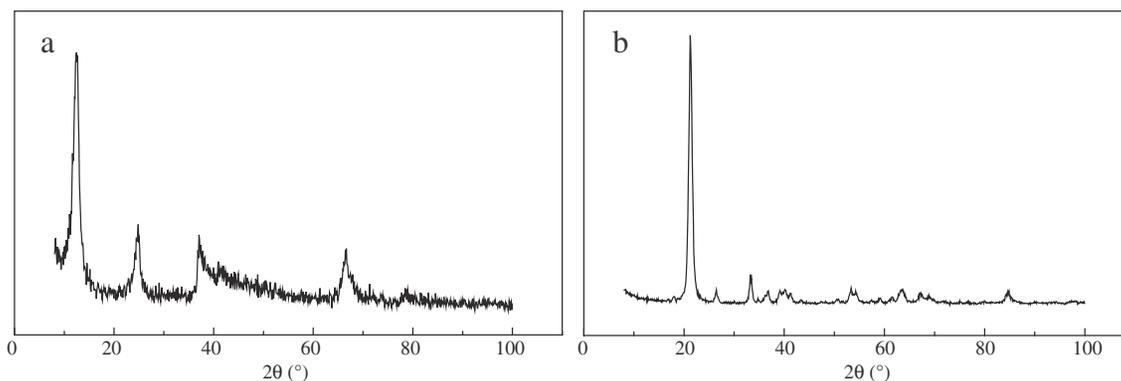


Fig. 1 – X-ray diffraction pattern of the synthesized birnessite (a) and goethite (b).

To further explore the effect exerted by goethite, Cr(III) was pre-equilibrated with goethite for 24 hr before the addition of birnessite. Five milliliters of freshly prepared 2 mmol/L  $\text{CrCl}_3$  (pH 3.5) with 0.04 mol/L NaCl as background electrolyte was added to tubes containing various amounts of 2 g/L goethite suspensions (1.25, 2.5, 5.0 or 10.0 mL). Then, the volume of the suspension was made to 15 mL by the addition of deionized water (pH 3.5). After 24 hr equilibration, 2.5 mL of 4 g/L birnessite suspension was added to tubes. According to the same procedure detailed previously, aqueous samples were collected for measuring the concentration of Cr(VI) in the supernatant as well as that adsorbed onto the surfaces.

Kinetics studies were also conducted to examine the Cr(III) oxidation in the absence and presence of goethite. A certain volume of birnessite with and without goethite was added to a 200 mL beaker, followed by the addition of water and  $\text{CrCl}_3$  solution using NaCl as the supporting electrolyte to a total volume of 120 mL. Initially, the pH of the suspension was 3.5, with 0.5 g/L birnessite, 0 or 2.0 g/L goethite, 0.5 mmol/L Cr(III) and 0.01 mol/L NaCl. By the use of the magnetic stir bar, the suspension was fully stirred. At different time intervals: 5 min, 10 min, 15 min, 30 min, 60 min (1 hr), 120 min (2 hr), 180 min (3 hr) and 360 min (6 hr), 5 mL aliquots were taken from the beaker and filtered through a 0.22  $\mu\text{m}$  nylon filter. The concentrations of aqueous Cr(III) and Cr(VI) in the filtrate solution were measured.

Adsorption of Cr(III) onto goethite and kaolinite as a function of pH was initiated by mixing 10 mL 2.0 g/L goethite or 10.0 g/L kaolinite suspension with 10 mL 1.0 mmol/L Cr(III) solution containing 0.02 mol/L NaCl in the 50 mL centrifugation tubes. After adjusting the suspension pH within the range of 3.0 to 7.5 by the addition of 0.1 mol/L HCl or NaOH, the tubes were agitated for 4 hr, followed by centrifugation at 12,500 r/min for 15 min. Then, the supernatant was passed through 0.22  $\mu\text{m}$  nylon filter, and filtrate sample was collected for determination of pH and Cr concentration.

The  $\zeta$ -potential of mineral particles was measured by a ZetaPals (Brookhaven Instruments Corporation, Holtsville, NY, USA). Twenty milliliters of 50 mg/L mineral suspension with 0.01 mol/L NaCl as supporting electrolyte was placed in a 40 mL glass vial, followed by the addition of appropriate amounts of 0.1 mol/L HCl or NaOH to adjust the pH ranging from 3.0 to 11. After 72 hr shaking, during which the

suspension pH needed to be readjusted, a sample of several milliliters was taken to measure  $\zeta$ -potential.

### 1.3. Analysis methods

Concentration of total Cr in solutions was determined with ICP-OES (iCAP 6500, Thermo Fisher Scientific, Waltham, MA, USA). Concentration of Cr(VI) was measured by using the method of Bartlett and James (1979). Concentration of Cr(III) was calculated from the difference between the total Cr and Cr(VI) concentration. All experiments were replicated three times, and the results were presented as the mean values  $\pm$  standard deviations.

## 2. Results and discussion

### 2.1. Effect of goethite on Cr(III) oxidation

Birnessite had a high capacity for oxidizing Cr(III), reaching to 4.08 mmol/g under the present reaction conditions (Fig. 2). This result was close to that obtained by Kim et al. (2002), but was lower than that reported by Landrot et al. (2012), who conducted

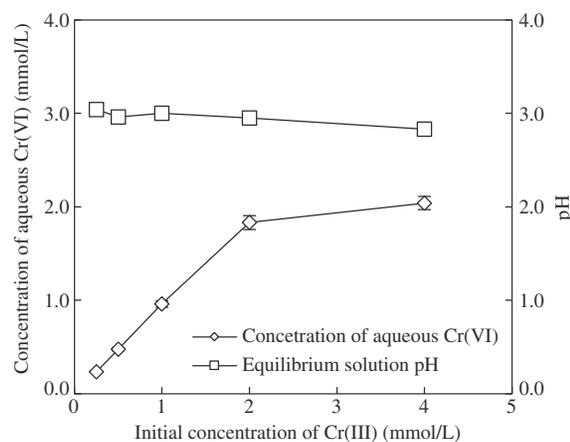
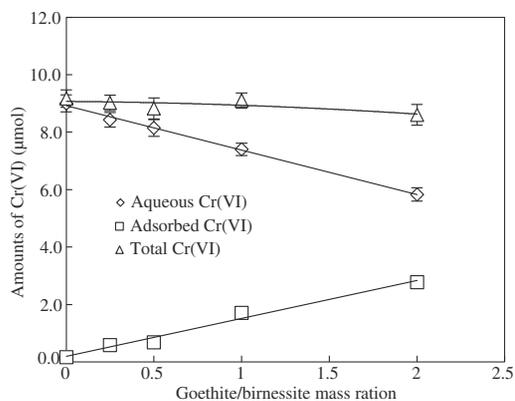


Fig. 2 – Oxidation of Cr(III) by birnessite as a function of initial concentration. Experimental conditions: 0.5 g/L birnessite, 0.01 mol/L NaCl, initial pH 3.50. Data are the means of three replicates  $\pm$  SD.

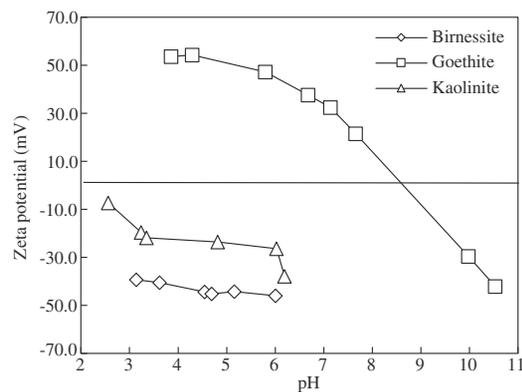
their study under more acidic pH condition. Regardless of the amounts of Cr(III) added, a decrease in the suspension pH from 3.5 to  $3.0 \pm 0.05$  was observed at the end of the reaction, indicating the generation of  $H^+$  during the Cr(III) oxidation. Although the mechanism was still unclear, an overall reaction has been proposed:  $1.5 MnO_2 + Cr^{+3} + H_2O = HCrO_4^- + 1.5 Mn^{2+} + H^+$  (Banerjee and Nesbitt, 1999), which could tentatively account for the decrease in suspension pH.

With the increase in the addition of goethite, the amounts of aqueous Cr(VI) gradually decreased (Fig. 3). For example,  $9.0 \mu\text{mol}$  of aqueous Cr(VI) could be detected at the end of Cr(III) oxidation by birnessite in the absence of goethite, while which decreased to  $5.83 \mu\text{mol}$  when the initial goethite/birnessite mass ratio was 2.0. On the contrary, the amounts of adsorbed Cr(VI) were increased as the increase in amounts of goethite added (Fig. 3). Because  $0.01 \text{ mol/L } KH_2PO_4$  has been proved to be able to release all adsorbed Cr(VI) (Feng et al., 2006b), the sum of amounts of aqueous and adsorbed Cr(VI) represented the total Cr(VI) produced during oxidation of Cr(III) by birnessite, which could be used to assess whether or not the extent of Cr(III) oxidation was changed in the presence of goethite. According to Fig. 3, it could be concluded that Cr(III) oxidation was unaffected in the presence of goethite since there was no significant difference in the amounts of total Cr(VI) ( $p < 0.05$ , t test).

The result above could be attributed to the contrasting surface characteristics of the two oxides. From the  $\zeta$ -potential results (Fig. 4), birnessite surfaces were negatively charged and goethite surfaces were dominated by positive charges under the examined pH condition, which were consistent with the fact that the PZC of birnessite could be as low as  $2.3 \pm 0.1$  (Huang and Hardie, 2011), and goethite generally has a PZC of about 9.0 (Cornell and Schwertmann, 2003). At pH 3.5, adsorption of Cr(III) onto goethite was almost negligible because of electrostatic repulsion (Fig. 5). Bradl (2004) concluded that low pH was unfavorable for adsorption of heavy metal cations onto soils or their constituents. Therefore, goethite could not compete with birnessite for binding Cr(III) because cationic species would be more preferentially adsorbed onto negatively charged surfaces. As a consequence, Cr(III) oxidization reaction would not be



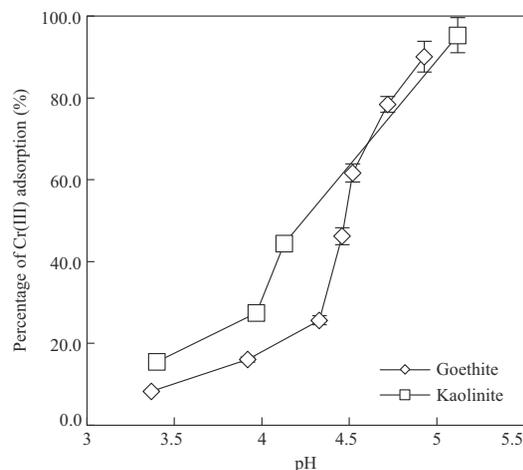
**Fig. 3 – Oxidation of 0.5 mmol/L Cr(III) by birnessite in the presence of goethite. Experimental conditions: 0.5 g/L birnessite, 0.01 mol/L NaCl of supporting electrolyte, initial pH 3.50. Data are the means of three replicates  $\pm$  SD.**



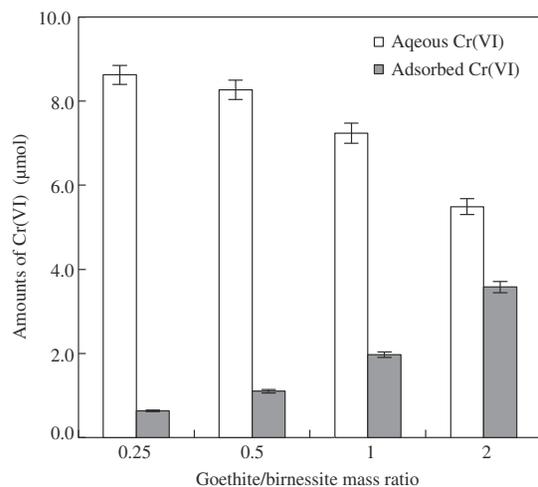
**Fig. 4 – The zeta potential of goethite, kaolinite and birnessite. Experimental conditions: solid concentration of 50 mg/L, 0.01 mol/L NaCl of supporting electrolyte.**

changed in the presence of goethite. Although Charlet and Manceau (1992) have confirmed the formation of inner-sphere complexes between Cr(III) and goethite surfaces, the pH condition they adopted was much higher than that used in the present study.

Results obtained from the experiments, in which goethite has been equilibrated with Cr(III) for 24 hr prior to addition of birnessite, also confirmed that oxidation of Cr(III) by birnessite would not be affected by goethite at low pH. As shown in Fig. 6, the amounts of total Cr(VI) still remained unchanged, and more Cr(VI) would be present as the form of adsorbed species. Additionally, such finding was further verified by kinetic study of Cr(III) oxidation in the goethite–birnessite binary systems. From Fig. 7, aqueous Cr(VI) concentration in the systems with addition of goethite was evidently lower than that in the absence of goethite. Meanwhile, kinetic results have also shown that the concentration of Cr(III) decreased quickly and reached to nearly zero ( $0.04 \text{ mmol/L}$ ) at  $t = 30 \text{ min}$ , demonstrating that the positively-charged Cr(III) was readily adsorbed onto the negatively-charged surfaces through electrostatic attraction (Sparks, 2011). Therefore, our results suggested that goethite



**Fig. 5 – Adsorption of 0.5 mmol/L Cr(III) by 2.0 g/L goethite and 5.0 g/L kaolinite in the presence of 0.01 mol/L NaCl. Data are the means of three replicates  $\pm$  SD.**

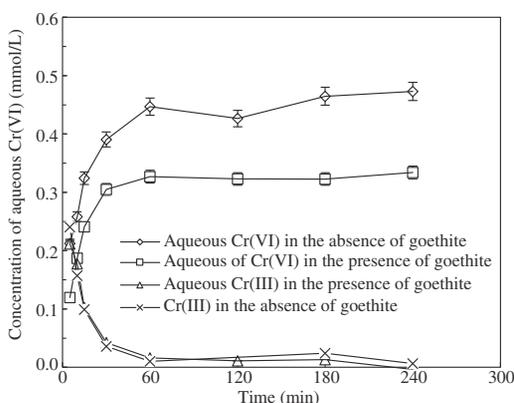


**Fig. 6 – Oxidation of 0.5 mmol/L Cr(III) with addition of goethite prior to birnessite. Experimental conditions: 0.5 g/L birnessite, 0.01 mol/L NaCl of supporting electrolyte, initial pH 3.50. Data are the means of three replicates.**

could serve as a sink for Cr(VI) generated during the Cr(III) oxidation by birnessite and then decrease its environmental impacts. Fandeur et al. (2009) also observed re-adsorption of Cr(VI) onto surrounding Fe-oxyhydroxides after oxidation by Mn oxides, which could largely lower the mobility of Cr(VI) in the natural systems. When studying the oxidation of As(III) by Mn oxides, Feng et al. (2006a) concluded that goethite could promote As(III) oxidation through adsorption of As(V) produced and then the concentration of aqueous As(V) was decreased.

## 2.2. Effect of kaolinite on Cr(III) oxidation

Similar to goethite, kaolinite did not affect the oxidation of Cr(III) by birnessite because total amounts of aqueous and adsorbed Cr(VI) remained unchanged regardless of the addition of kaolinite (Fig. 8). For example, no significant difference ( $p < 0.05$ ,  $t$  test) was found in the total quantities of aqueous

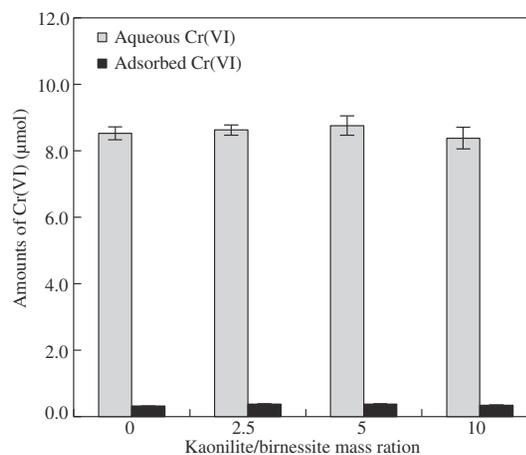


**Fig. 7 – Kinetics of 0.5 mmol/L Cr(III) oxidation by birnessite with or without addition of goethite. Experimental conditions: 0.5 g/L birnessite, 2.0 g/L goethite, 0.01 mol/L NaCl of supporting electrolyte, initial pH 3.50. Data are the means of three replicates  $\pm$  SD.**

and adsorbed Cr(VI) generated in the systems with and without the addition of 5 g/L kaolinite, which were 8.72 and 8.83  $\mu\text{mol}$ , respectively. However, reactions involved in oxidation of Cr(III) by birnessite in the presence of kaolinite were not exactly the same as those in the presence of goethite, which included an ion exchange process between adsorbed Cr(III) on kaolinite and ions present in solution.

The  $\zeta$ -potential data indicated that kaolinite surfaces were dominated with negative charge under the present pH condition (Fig. 4), and about fifteen percent of the initially added Cr(III) was adsorbed onto the kaolinite surfaces at pH 3.40 (Fig. 5). Then, it could be expected that part of Cr(III) introduced to the binary systems would be adsorbed by kaolinite other than birnessite. Since Cr(III) adsorption onto birnessite was regarded as the prerequisite step for the occurrence of the surfaces-mediated redox reaction (Manceau and Charlet, 1992), it was reasonable for us to conclude that the Cr(III) adsorbed on kaolinite would be released to solution again and then oxidized by birnessite. Such statement was evidenced by the total oxidation of the initially added 0.5 mmol/L Cr(III) to Cr(VI) (Fig. 8). Otherwise, kaolinite would be found to have influence on the Cr(III) oxidation, while which was not the observed fact. As demonstrated by Turan et al. (2007), adsorption of Cr(III) by kaolinite was highly dependent on ionic strength due to the weak interaction, indicating that the adsorbed Cr(III) was ready to be released to solution through ion exchange process. In the present systems, 0.01 mol/L  $\text{Na}^+$  was used as the supporting electrolyte and, especially, the  $\text{H}^+$  generated during Cr(III) oxidation was believed to be able to effectively release the adsorbed Cr(III) from kaolinite surfaces.

Furthermore, distribution of Cr(VI) between solid and aqueous phases was also not changed with the addition of kaolinite (Fig. 8), which was inconsistent with that observed in the presence of goethite (Fig. 3). Evidently, it was the result of electrostatic repulsion between anionic Cr(VI) and negatively-charged kaolinite surfaces. Meanwhile, the competition between  $\text{Cl}^-$  and Cr(VI) for binding sites also contributed to the insignificant adsorption of Cr(VI). Fritzen et al. (2006) showed that adsorption of Cr(VI) on clay mineral surfaces could only be



**Fig. 8 – Oxidation of 0.5 mmol/L Cr(III) by birnessite in the presence of kaolinite. Experimental conditions: 0.5 g/L birnessite, 0.01 mol/L NaCl of supporting electrolyte, initial pH 3.50. Data are the means of three replicates  $\pm$  SD.**

observed at pH below PZC, and the mechanism was dominated by electrostatic attraction with the formation of outer-sphere complexes. According to Quirk (1960), kaolinite could adsorb appreciable amounts of chloride ions under acidic pH condition, and then the non-specific adsorption of Cr(VI) would be suppressed when its concentration was far less than that of chloride ions.

### 2.3. Mechanisms and environmental implications

According to the results described above, several mechanisms were proposed for better understanding the effect of goethite and kaolinite on the Cr(III) oxidation by birnessite. In the goethite–birnessite binary systems, Cr(III) oxidation under acidic pH condition was not affected by positively charged goethite due to electrostatic repulsion, but the generated Cr(VI) species were readily adsorbed by goethite. Although the negatively charged kaolinite was capable of retaining Cr(III) species, the adsorbed Cr(III) could be released to solution again through H<sup>+</sup> and Na<sup>+</sup> exchange process so that Cr(III) oxidation still remained unchanged even in the presence of kaolinite. Additionally, Cr(VI) species mainly existed in aqueous solution, which was different from the case where goethite was present. Therefore, the present study evidently indicated that environmental hazard arising from Cr(III) oxidation in the highly weathered tropical soils should not be overestimated since the abundant Fe oxides could largely decrease the migration of Cr(VI) through adsorption processes.

### 3. Conclusions

This study demonstrated that oxidation of Cr(III) to Cr(VI) by birnessite under low pH conditions (*e.g.*, pH 3.5) was not affected in the presence of goethite or kaolinite, which was attributed to the overwhelming adsorption of Cr(III) to the negatively-charged birnessite surfaces. However, Cr(VI) would be preferentially retained onto the surfaces with the addition of goethite, owing to its high affinity for Cr(VI) at low pH. By contrast, kaolinite has also been found to have no influence on partition of Cr(VI) between solid and aqueous phases. The mixed systems here would represent those commonly found in natural conditions, and results above suggested that environmental threat posed by the oxidation of Cr(III) to Cr(VI) could be eliminated in soils with high content of goethite, such as oxisol.

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