



Role of clay minerals on reduction of Cr(VI)

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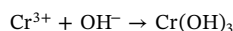
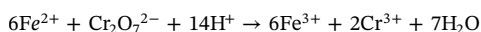
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ABSTRACT

Clay minerals could reduce Cr(VI) to Cr(III) in the soil, but the mechanisms and influential factors for the reduction reaction have not been clearly reported. In this study, it was hypothesized that the Fe(II) released from the clay minerals or adsorbed on the clay surface plays a crucial role in the reduction of Cr(VI). The Fe(II) released from clay minerals reduced Cr(VI) rapidly in the aqueous phase at the initial stage, and the amount of Fe(II) in the aqueous phase was directly proportional to the amount of Cr(VI) reduced. Cr(VI) was then reduced gradually by the Fe(II) adsorbed on the clay minerals. XPS analysis confirmed the change of Fe speciation on the surface of the clay minerals. Therefore, we concluded that the reduction in Cr(VI) by the clay minerals was due to the Fe in the clay minerals.

1. Introduction

Chromium (Cr) has several oxidation states from -2 to 6 , and the trivalent (Cr(III)) and hexavalent (Cr(VI)) states are primary oxidation states in nature. Cr(III) is an essential nutrient, has relatively low toxicity, and is less mobile than Cr(VI). Therefore, it is classified as a non-dangerous substance. However, Cr(VI) is 100 times more toxic than Cr(III) and is highly mobile because it exists as an oxy-anionic form (Ahmadi et al., 2016; Haroon et al., 2016). Additionally, Cr(VI) is a well-known carcinogen (Stearns et al., 1995). Cr can be discharged during the manufacture of dyes, leather smelting, and timber industries and can be deposited into the soil (Fendorf, 1995; Prasanthi et al., 2016). In the soil, Cr(VI) can be reduced to Cr(III) by soil organic matter (Banks et al., 2006; Wittbrodt and Palmer, 1995; Wittbrodt and Palmer, 1997) and Fe(II) minerals. However, the reduction rate is too slow in nature, and Cr(VI) should be reduced by other mechanisms or artificial treatment to minimize its harmful effects. Additionally, less toxic Cr(III) could be oxidized by Mn(IV), and reduction and oxidation can co-occur in nature. Cr(VI) in the aqueous phase can be treated by membrane filtration, ion exchange, reduction, extraction, or adsorption (Barrera-Diaz et al., 2012; Jeon et al., 2017; Owlad et al., 2009). The most feasible way is to reduce Cr(VI) to Cr(III), after which it can be precipitated as Cr(OH)₃. Reducing agents are required to change the oxidation state of Cr, and Fe(II) is the most common reducing agent for Cr(VI), and the reaction is as follows:



Mn(II) cannot be redox-coupled with Cr(VI) thermodynamically (Wu et al., 2015), but co-presence of organic acids including oxalate and citrate, can play roles as electron shuttles for redox-coupling (Kwak et al., 2017; Sarkar et al., 2013; Wrobel et al., 2015).

Iron-bearing minerals and clay minerals including pyrite, goethite, hematite, biotite, and montmorillonite can reduce Cr(VI), and Cr(VI) can be reduced by the Fe(II) released from the minerals (Eary and Rai, 1989; Kantar et al., 2015; Kim et al., 2007; Zouboulis et al., 1995). Several researchers have reported that the surface of the clay minerals could stimulate the reduction reaction (Buerge and Hug, 1997; Buerge and Hug, 1998; Buerge and Hug, 1999). Other researchers have investigated the roles of the clay minerals such as kaolinite, montmorillonite, and illite (Brookshaw et al., 2014; Deng et al., 2003; Liu et al., 2011; Vinuth et al., 2015) with respect to the reduction of Cr(VI) in the presence of organic acids. Even though clay minerals can reduce Cr(VI) in the presence or absence of organic acids and Mn(II) (Kwak et al., 2017), the mechanism is not clear. Therefore, we hypothesized that the Fe(II) released from the clay minerals and the Fe(II) adsorbed on the surface of the minerals might be key factors in the reduction of Cr(VI). In this study, we investigated the reduction of Cr(VI) by the Fe(II) released from the clay minerals and the Fe(II) adsorbed on the surface of the minerals and speculated on the relative contribution of Fe(II) to the reduction reaction.

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2. Materials and methods

All chemicals used in this study were reagent grade. $K_2Cr_2O_7$ and ferrous sulfate were utilized for the sources of Cr(VI) and Fe(II), respectively. A phthalate buffer solution with a pH of 3 was prepared using $C_8H_8KO_4$ and HCl to prevent the precipitation of Fe(III). All bottles and beakers used in the experiments were washed with 5% HCl and covered with aluminum foil to prevent photo-reduction or photo-oxidation. A diphenyl carbazide solution (0.25 g of 1,5-diphenylcarbazine dissolved in 50 ml acetone) was stored in a brown bottle in cold storage. Montmorillonite, kaolinite, vermiculite and illite were purchased from Sigma-Aldrich and Yong Koong-illite(Korea).

Inorganic acids have been used to remove Fe(II) from the surface of clay minerals (Amonette et al., 2000); therefore, 0.5 M HCl was selected for this study to remove Fe(II) on the surface of the clay minerals. A solid-liquid ratio of 1:10 was shaken at 200 rpm for 2 h and centrifuged at 6000 rpm for 10 min to separate the solids. Kaolinite contains little adsorbed Fe(II), but montmorillonite and vermiculite contain relatively large amounts of adsorbed Fe, up to 1700 mg/kg. The supernatant was discarded, and the solid was washed using deionized water to eliminate the remaining acid, i.e., HCl, from the clay minerals. Additionally, clay minerals were heated at 440 °C for 24 h to remove organic matter (reference). The amounts of organic matter in kaolinite, montmorillonite, vermiculite and illite were 10%, 15%, 5% and 2%, respectively. The properties of the clay minerals are summarized in Table 1.

The amount of Fe(II) released from the mineral surface was evaluated in the control experiment without Cr(VI). A clay mineral mass of 0.09 g was mixed with a 30 ml reaction mixture in a 50 ml conical tube. The initial concentration of Cr(VI) was 200 μM in the phthalate buffer solution with a pH of 3.0. For comparison, the control experiment was performed without Cr(VI) in the same condition. Additionally, the same amount of Fe(II) that was released from the montmorillonite was added to confirm the reaction role of the Fe(II) released. Kinetic tests were performed to evaluate the reduction kinetics of Cr(VI) in a 1.0 L beaker, and the clay mineral to liquid ratio and Cr(VI) concentration were the same as in the other tests. At designed time intervals, samples were collected and filtered by a 0.45 μm syringe filter to measure the concentrations of Cr(VI) and Fe(II).

Cr(VI) and Fe(II) were analyzed by the diphenyl carbazide and ferrozine methods, respectively, using a UV-VIS spectrophotometer (USEPA, 1992; Viollier et al., 2000). The specific surface area of the clay minerals was analyzed by the methylene blue method (Yukselen-Aksoy and Kaya, 2008), and total Cr and Fe were determined by inductively coupled plasma with optical emission spectrometry (ICP-OES, 720-ES, Agilent, USA). The oxidation state of the adsorbed Fe on the clay mineral surface was confirmed using X-ray photoelectron spectroscopy (XPS, MultiLab 2000, Thermo, USA) (Selvaraj et al., 2016).

Table 1
Characteristics of clay minerals used in this study.

Clay mineral	CEC (meq/ 100 g)	SSA* (m ² /g)	Organic matter (wt%)	Adsorbed Fe(II) (mg/kg)	Adsorbed Fe(III) (mg/kg)
Kaolinite	7.4	17.7	1.0	18.9	14.8
Montmorillonite	58.1	80.6	1.5	1724.9	10,237.6
Illite	14.2	13.0	0.2	475.5	1024.4
Vermiculite	55.4	23.4	0.5	1708.1	622.4
**W.Montmorillonite				147.2	630.6

*Soil surface area.

**Acid washable Fe(II) was removed from the surface of montmorillonite.

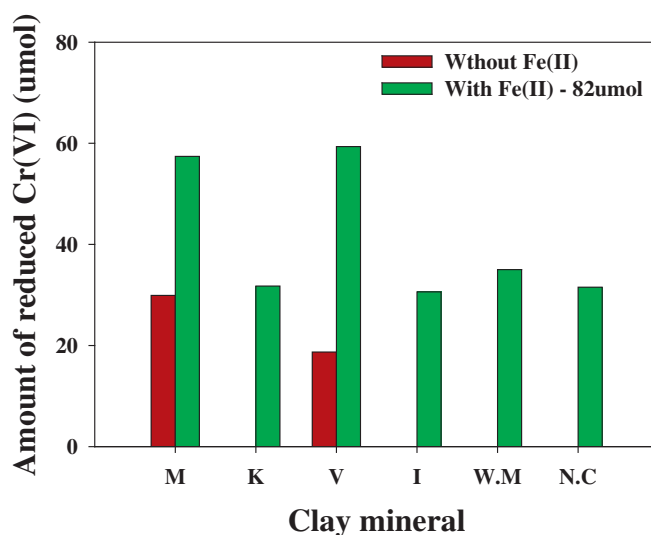


Fig. 1. Cr(VI) and Fe in the solution. Initial Cr(VI) was 200 μM, clay mineral was 3 g/L, shaking time was 90 min, and Fe(II) at 82 μmole was added. M: Montmorillonite, K: Kaolinite, I: Illite, V: Vermiculite, W.M: Washed Montmorillonite, and N.C.: No Clay.

3. Results and discussion

3.1. Influence of clay minerals on Cr(VI) reduction

The reduction of Cr(VI) by kaolinite(K), montmorillonite(M), illite (I), vermiculite(V), and washed montmorillonite(WM) is shown in Fig. 1. The pH of all the tests was maintained at 3 ± 0.15 by a phthalate buffer. The amount of Fe(II) released from clay minerals was measured in the absence of Cr(VI). Fe(II) was not released from kaolinite, illite, or washed montmorillonite, and only a small portion of Fe (III) was released. Therefore, the minerals could not reduce the Cr(VI); 25.1 and 1.7 mmol Fe(II)/kg of clay minerals was released from the montmorillonite and vermiculite, respectively, in the absence of Cr(VI). However, Fe(II) was not observed in the solution with Cr(VI) because the Fe(II) released from the clay minerals was used to reduce Cr(VI) spontaneously. Therefore, montmorillonite and vermiculite reduced 9.1 and 2.2 mmol Cr(VI)/kg of clay minerals, respectively. The amounts of dissolved or released Fe is highly dependent on the redox chemistry and pH of the system (Rinklebe et al., 2016). However, pH buffer solution was used in this study, pH effects could be same for all experimental sets, and the amounts of dissolved Fe(II) could reduce limited amounts of Cr(VI). The additional input of Fe(II) to the solution with kaolinite, illite, and washed montmorillonite reduced Cr(VI). Moreover, simple mixing of Fe(II) and Cr(VI) reduced the Cr(VI) without any clay mineral, which is a well-known reduction reaction for Cr(VI) in nature (Buerge and Hug, 1997). This result indicates that Cr(VI) reduction is highly dependent on the Fe(II) released from the clay minerals.

Reduction of Cr(VI) by Fe(II) might follow the reaction: $3Fe(II) + Cr(VI) \rightarrow 3Fe(III) + Cr(III)$, and the reaction shows that more than 3 times of Fe(II) are required to reduce Cr(VI). However, Fe(II) released from montmorillonite and vermiculite was not balanced stoichiometrically with the amount of reduced Cr(VI). In montmorillonite, the amount of Cr(VI) reduced was linearly proportional to the Fe(II) released into the solution (Fig. 2(a)). The Fe(II) released from montmorillonite was similar to the theoretical amount needed to reduce Cr(VI), even though slightly more Cr(VI) was reduced compared to the Fe(II) observed in solution. However, in vermiculite, the amount of Fe(II) released into solution was much less than the Fe(II) required to reduce

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