

Fe(II)-initiated reduction of hexavalent chromium in heterogeneous iron oxide suspension

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(Received 25 April 2007 • accepted 5 October 2007)

Abstract—The characteristics of Fe(II)-initiated reduction of Cr(VI) in iron oxide suspensions were investigated by conducting a series of kinetic experiments. A modified Langmuir-Hinshelwood kinetic model was used to provide a better description of Cr(VI) reduction kinetics which were believed to be occurring on the limited reactive site of reductant. The concentration of magnetite concentration as well as Cr(VI) concentration, significantly affected the reaction kinetics of Cr(VI). The reduction kinetics were improved with increasing magnetite and Cr(VI) concentration. Almost 95% of Cr(VI) reduction was achieved within 10 min at the condition of 8 g/L of magnetite and 80 mg/L of initial Cr(VI), respectively. The solution pH also affected the reaction rate in the range of 5.5 and 8.0 where a lower pH produced a faster reaction rate. The addition of Fe(II) on soil and magnetite showed the capability of improving Cr(VI) reduction kinetics, and their reduction kinetics was also well described by using a Langmuir-Hinshelwood kinetic model. The experimental results obtained in this research clearly show the advantage of additional reductant for reducing Cr(VI), and they can provide basic knowledge for the development of remediation technology for the treatment of groundwater and soil contaminated with Cr(VI).

Key words: Chromium(VI), Modified Langmuir-Hinshelwood Kinetics, Magnetite, Reduction, Fe(II) Addition

INTRODUCTION

Chromium generally exists in four oxidation states (Cr(0), Cr(II), Cr(III), and Cr(IV)) in natural and engineered environments, but the trivalent and hexavalent forms are predominant. Most studies have focused on Cr(VI) because of its toxic, carcinogenic, and mutagenic characteristics [1]. In contrast to the harmful characteristics of Cr(VI), Cr(III) that is immobile and insoluble in subsurface environments has been known to be less toxic and even an essential nutrient for plants and animals [2]. Therefore, the redox chemistry reducing Cr(VI) to Cr(III) has been applied to the development of most remedial technologies to treat groundwater and soil contaminated with Cr(VI). Natural attenuation and in-situ redox manipulation are examples of the application of redox chemistry to remediate contaminated sites. Surface-bound natural organic matters (NOMs) and iron-bearing soil minerals such as magnetite, green rust, and zero-valent iron significantly affect the reduction of Cr(VI) [3-5].

As one of recent remedial alternatives to expedite natural attenuation, in-situ redox manipulation by injecting reducing agents such as Fe(II) and sulfide into monitoring wells has been studied. A significant reduction of organic compounds has been observed in in-situ redox manipulation system as shown in soil mineral suspensions with reductants [6]. It has been reported that heterogeneous surface reactions cause reductive degradations of organic compounds. Kinetic rate constants for reductive degradation are influenced by the density of reactive Fe(II) bound on the mineral surfaces. Williams and Scherer [7] showed that Fe(II) bound on the mineral surfaces results in enhanced reductive degradation of organic com-

pounds. In contrast, Cr(VI) can be stoichiometrically reduced in the aqueous Fe(II) solution without any solid surfaces (except under high pH conditions) forming reactive precipitates, e.g., $(Cr_xFe_{1-x})_x(OH)_{3x}$ [8]. Based on previous experimental results, the Cr(VI) reduction seems to be affected by both aqueous Fe(II) and reactive solids in soil mineral suspensions.

Research has been conducted to investigate the reaction kinetics for the reduction of Cr(VI) in soil mineral suspensions with and without Fe(II) addition. However, little research has been carried out to fully characterize the reduction of Cr(VI) at the reactive surfaces of soil minerals. This research has investigated the reaction mechanism for the reduction of Cr(VI) at reactive solid surfaces and identified the effect of important physicochemical parameters on the reaction kinetics of Cr(VI). The contribution of aqueous Fe(II) and Fe(II) adsorbed on iron-bearing soil minerals to the reduction of Cr(VI) has been also estimated. Synthesized magnetite and Fe(II) have been used as representative iron-bearing soil mineral and reducing agent, respectively. Nontronite and soil have been used for comparison.

MATERIALS AND METHODS

1. Chemicals, Soil Minerals, and Soil

Reagents or higher grade chemicals were used as received without further treatment. Cr(VI) ($K_2Cr_2O_7$, 99.5%, Kanto) and $FeSO_4 \cdot 7H_2O$ (99%, Sigma-Aldrich) were used as a target contaminant and a reductant, respectively. $FeCl_2 \cdot 4H_2O$ (99-102%, Wako) and $Fe(NO_3)_3 \cdot 9H_2O$ (99%, Yakuri) were used to synthesize magnetite. Biological buffers, N-(2-hydroxyethyl)-piperazine-N-2-ethanesulfonic acid (HEPES, 99.5%, Sigma), 2-(N-Morpholino)ethanesulfonic acid (MES, 99.5%, Sigma), and a mixture of Tris(hydroxymethyl)aminomethane

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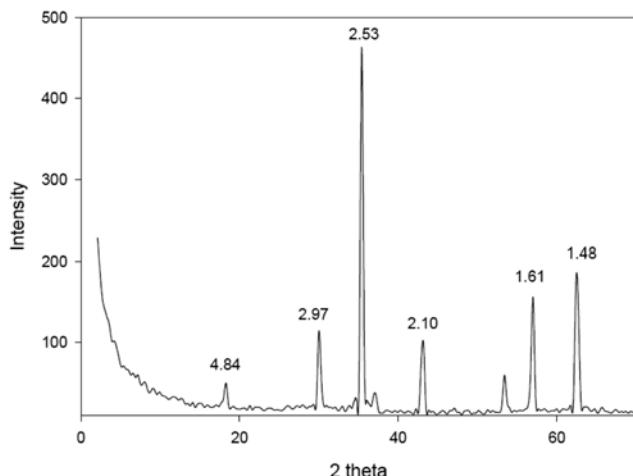


Fig. 1. X-ray diffraction of synthesized magnetite. The values represent the d-space values (Å).

(99.8%, Sigma-Aldrich) and Tris(hydroxymethyl)aminomethane hydrochloride (99%, Sigma) (TRIS buffer), were used to keep the constant pH of aqueous solutions and suspensions. The following chemicals were used for colorimetric analyses: 1,5-Diphenylcarbohydrazide (Kanto), 3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine-p,p'-disulfonic acid monosodium salt hydrate (97%, Aldrich), $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ (99.9%, Sigma-Aldrich), H_2SO_4 (95%, Junsei), HNO_3 (60%, Junsei), NaOH (96%, Junsei), Na_2SO_4 (99%, Junsei), ammonium acetate (97%, Yakuri), and hydroxylammonium chloride (97%, Junsei). All chemical reagents were prepared with deaerated deionized water by deoxygenating 18 $\text{M}\Omega\text{cm}$ deionized water with 99.9% nitrogen for two hours.

Magnetite was synthesized by modifying the method developed by Taylor et al. [9] and identified by XRD analysis. The result of XRD is shown in Fig. 1 with the obtained d-space values of the synthesized magnetite which are comparable to the results of magnetite in powder diffraction file. The magnetite was used for a day after the synthesis to preclude aging effect. The preparation and pretreatment of nontronite (Nontrone, France) and soil samples (Seoul, Korea) were conducted by following Lee and Batchelor's methods [10].

2. Experimental Procedures

Batch kinetic experiments were conducted in 20 mL amber glass vials with open-top cap and silicon septum lined with PTFE film. Magnetite (0.13 g), nontronite (2.5 g), and soil (2 g) were transferred to vials, and 2 mL of 1 M HEPES solution was added to adjust suspension pH to 7.2. The total volume of the suspension was 20 mL resulting in concentrations of 6.5, 125, and 100 g/L for magnetite, nontronite, and soil, respectively. An aliquot amount of Cr(VI) stock solution (0.4 mL, 1,000 mg/L) was spiked to the vials resulting in an initial Cr(VI) concentration of 20 mg/L.

Based on the results of the batch kinetic experiments, parametric studies were conducted to identify the effect of important geochemical parameters on the Cr(VI) reduction kinetics. Magnetite was chosen as a representative soil mineral. The effects of magnetite concentration, target compound concentration, and pH were separately investigated. Each parametric study had the following experimental conditions: (1) The concentration of magnetite was varied

from 5 to 8 g/L under the initial Cr(VI) concentration of 50 mg/L, (2) the concentration of Cr(VI) differed from 20 to 80 mg/L, and (3) the pH of magnetite suspensions was adjusted from 5.5 to 8.0 by using biological buffers (MES, HEPES, and TRIS, respectively). Based on the study by Alowitz and Scherer, the Cr(VI) reduction by iron metal was dependent on the type of biological buffer [11]. But we think that a biological buffer is better than an inorganic buffer such as phosphate buffer to maintain the pH in this study. Cr(VI) reduction might be less interfered by a biological buffer compared to an inorganic buffer since the chemicals in an inorganic buffer could react with iron and chromium. Sample preparation procedures generally followed that for the batch kinetic experiments described above.

To identify the effect of Fe(II) addition on the kinetics of Cr(VI) reduction, Fe(II) stock solution was added to magnetite suspensions before spiking Cr(VI) resulting in the desired ratios of ferrous iron to chromate in the range of 0.6 to 3.0. The concentrations of magnetite and Cr(VI) were 6.5 g/L and 80 mg/L, respectively. The pH of the mixed suspension was kept constant at 7.2 with a TRIS buffer. Batch kinetic experiments were also conducted to compare the effect of pH in magnetite suspensions with and without Fe(II) in the pH range of 5.5 to 8.0 under the same concentrations of magnetite and Cr(VI).

All vials were quickly and tightly capped, mounted on a tumbler, and then completely mixed at 7 rpm under room temperature ($20 \pm 0.5^\circ\text{C}$). After each reaction time, a desorbing agent (0.284 g of Na_2SO_4) was added into the vials to result in 0.1 M sulfate. The suspensions were vigorously mixed on an orbital shaker for 1 day to promote the desorption of Cr(VI) from soil mineral surfaces [12] and centrifuged at 2,000 g for five minutes. The supernatant from each vial was used for the measurement of Cr(VI) and iron concentrations in aqueous solution. All samples were prepared in duplicate. Control samples were prepared to check losses due to sorption on walls of vials and septum and volatilization. The control samples were prepared in the same way described above excluding the addition of soil minerals and soil.

3. Analytical Procedures

The concentrations of Cr(VI) and iron (Fe(II) and total iron) in the aqueous phase were measured by colorimetric analysis using a UV/VIS spectrophotometer (Spectronic® GENESYS™ 2, Thermo Electron Corporation). The Cr(VI) concentration was determined by using the diphenylcarbazide method at a wavelength of 540 nm [13]. The concentration of Fe(II) was directly measured by the ferrozine method at a wavelength of 562 nm [14], and the concentration of total iron was measured as a form of Fe(II) at the same wavelength after reducing Fe(III) to Fe(II) by adding a 10% hydroxylamine solution. The concentration of Fe(III) was calculated by subtracting the Fe(II) concentration from the total iron concentration.

X-ray diffraction analysis was performed with a RigaKu automated diffractometer using $\text{Cu K}\alpha$ radiation. Solids were separated by centrifugation at 2,960 g for 5 min and carefully dried in an anaerobic chamber. The samples were scanned between 2.1° to $70^\circ 2\theta$ with a scan speed of $1^\circ 2\theta\text{min}^{-1}$.

4. Data Treatment for the Reduction Kinetics of Cr(VI) by Magnetite

Reductive degradation of Cr(VI) by iron-bearing soil minerals and soil was monitored for one hour. Cr(VI) in the soil mineral and

soil suspensions showed rapid disappearance initially followed by slow disappearance or constant concentrations depending on the reductive capacity of soil minerals and soil. This indicates that the Cr(VI) reduction kinetics cannot be properly explained by a pseudo-first-order or zero-order rate law. A modified Langmuir-Hinshelwood kinetic model (Eq. (1)) was used to properly describe Cr(VI) reduction kinetics. This model could give a proper description of kinetic data since the reduction of Cr(VI) might occur on the finite reactive site of magnetite surface [10]. The kinetic model shown below can be obtained by combining a material balance equation in a batch reactor and a rate equation.

$$\frac{dC_{Cr(VI)}}{dt} = -\frac{(k/p_{Cr(VI)})\{C_{RC}^0 - p_{Cr(VI)}(C_{Cr(VI)}^0 - C_{Cr(VI)})\}C_{Cr(VI)}}{1/K + C_{Cr(VI)}} \quad (1)$$

where $C_{Cr(VI)}$ is the aqueous concentration of Cr(VI) at time t ; k is the rate constant for the decay of Cr(VI) at the reactive sites in time $^{-1}$; $p_{Cr(VI)}$ is the partitioning factor to explain the effect of partitioning of Cr(VI) among aqueous, gas, and solid (soil mineral+vial wall+septum liner) phases assuming instantaneous equilibrium among the three phases; C_{RC}^0 is the initial reductive capacity of magnetite for the Cr(VI) in concentration; $C_{Cr(VI)}^0$ is the aqueous concentration of Cr(VI) at time zero; and K is the sorption coefficient of Cr(VI) with units of inverse concentration.

RESULTS AND DISCUSSION

1. Reaction Kinetics for the Reduction of Cr(VI) by Iron-bearing Soil Minerals and Soil

Fig. 2 shows the reaction kinetics for the reduction of Cr(VI) by magnetite, nontronite, and soil. Cr(VI) was completely degraded in 10 minutes in the magnetite suspension, while more than 90% of the initial Cr(VI) was recovered in the soil and nontronite suspensions at the last sampling time. Magnetite having the smallest surface concentration ($284.7 \text{ m}^2/\text{L}$) shows the greatest kinetic rate constant (2.06 min^{-1}). Although nontronite and soil have approximately 46 and 8 times greater surface concentrations than magnetite, they have smaller rate constants (1.42 min^{-1} and 1.28 min^{-1} , respectively). This indicates the surface concentration is not a unique geochemi-

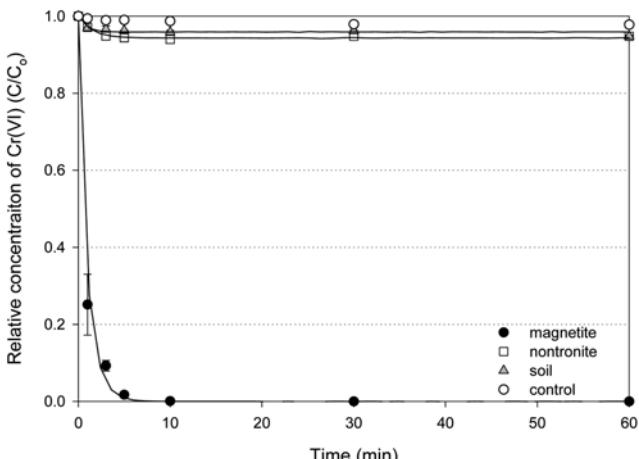


Fig. 2. Reduction of Cr(VI) by magnetite, nontronite, and soil at pH 7.2.

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cal factor significantly affecting the reduction of Cr(VI) in soil and soil mineral suspensions. On the other hand, the total iron content of magnetite including both Fe(II) (201 mg/g) and Fe(III) (512 mg/g) is approximately 140 and 7 times greater than that of soil and nontronite. Fe(II) content of soil was measured to be less than 1 mg/g, and most iron measured in nontronite was identified as Fe(III). Therefore, the iron content (especially, the surface Fe(II) concentration) could be the more significant factor explaining the great differences in the reduction kinetics of Cr(VI) in the solid suspensions. Peterson et al. showed similar experimental results [15]. Cr(VI) in groundwater was fully reduced to Cr(III) by the soil containing a high concentration of magnetite, but Cr(VI) was rarely reduced by the soil containing natural iron-bearing phyllosilicates [15]. The results obtained in this research and by Peterson et al. [15] confirm the assumption that the reaction kinetics for the reduction of Cr(VI) are significantly influenced by the content of Fe(II) on the surface of soil minerals and soil. The curves fitted by the Langmuir-Hinshelwood kinetic model at Fig. 2 seem to properly explain the reduction kinetics of Cr(VI) in soil mineral and soil suspensions.

2. Effect of Physicochemical Parameters on the Reduction Kinetics of Cr(VI)

Fig. 3 shows the effect of magnetite concentration on the reduction of Cr(VI) in the magnetite suspension. The removal of Cr(VI) increased 5 times as the content of magnetite increased by 1.6 times. This is due to the limited active site and different activity of sites. Almost 95% of Cr(VI) was removed in 0.5 hour from the suspension of different magnetite concentrations, and part of the remaining Cr(VI) was slowly degraded. The result is consistent with previous results [4]. The early rapid removal of Cr(VI) followed by its gradual decrease has been reported to be mainly due to the accumulation of Cr(III) monolayer and subsequent exhaustion of available Fe(II) at the soil mineral surfaces. This assumption was also supported in this study by that the content of Fe(II) in the magnetite concentration of 6.5 g/L was 14 times higher than the stoichiometric amount required for the full Cr(VI) reduction, but 30% of Cr(VI) was still recovered in the aqueous phase. This means that part of Fe(II) measured in the magnetite exists as structural Fe(II), which cannot be easily used for fast kinetic reactions, or that the Cr(III)

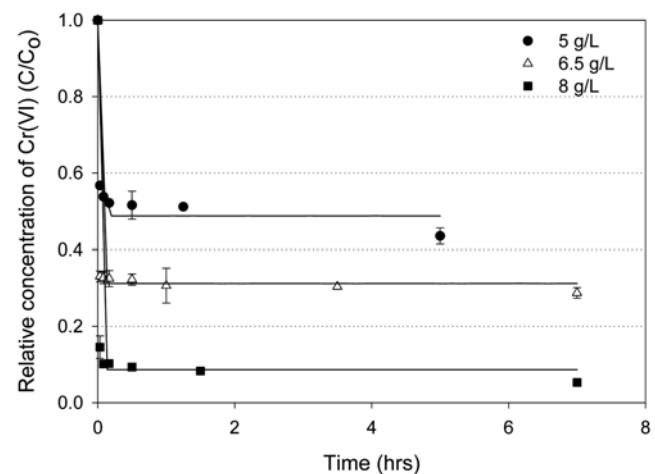


Fig. 3. Effect of magnetite dosage on the reaction kinetics of Cr(VI) at pH 7.2.

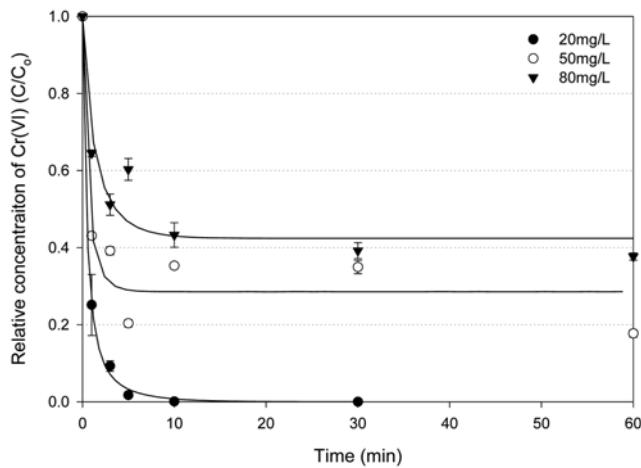


Fig. 4. Effect of initial Cr(VI) concentration on the reaction kinetics of Cr(VI) at pH 7.2.

layer formed hampers additional reactions. These processes can cause a significant deviation from the well-fitted pseudo first-order kinetics for the reduction of Cr(VI) in the soil mineral suspensions.

The effect of Cr(VI) concentration on the reaction kinetics is shown in Fig. 4. Cr(VI) at $C_{Cr(VI)}^0=20$ mg/L was completely reduced in 10 minutes and well fitted by the first-order rate law with respect to Cr(VI) concentration ($R^2=0.94$). As the initial concentration of Cr(VI) increased, different reduction patterns were observed. Although a similar rapid reduction of Cr(VI) at early sampling times was found at the initial Cr(VI) concentration of 50 and 80 mg/L, the reduction kinetics of Cr(VI) under these higher concentrations was not well fitted by the first-order kinetics but properly fitted by the modified Langmuir-Hinshelwood kinetic model. This implies that the reaction kinetics for the reduction of Cr(VI) is not simply dependent on the Cr(VI) concentration but dependent on both concentrations of Cr(VI) and reactive surfaces on magnetite.

The pH of magnetite suspensions significantly affected the reduction kinetics of Cr(VI) as shown in Fig. 5. The reduction rates of Cr(VI) increased with the decrease of pH (from 8 to 5.5), which is similar to the experimental result observed in the reduction of aque-

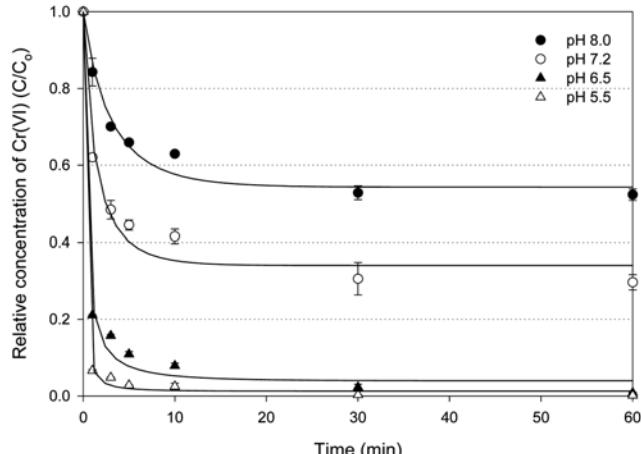
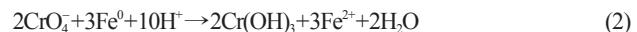


Fig. 5. Effect of pH on the reaction kinetics of Cr(VI).

ous transition metal species on the surfaces of Fe(II)-bearing oxides [3]. The Cr(VI) injected was fully removed under pH 6.5, but 30 and 52% of Cr(VI) were recovered at pH 7.2 and 8.0, respectively. The initial rapid drop of Cr(VI) concentration was mainly caused by fast Cr(VI) adsorption to magnetite, followed by the slow decrease of Cr(VI) mainly due to Cr(VI) reduction [16]. The rapid adsorption is mainly related with the zero point charge (zpc) of magnetite surface. The zpc of magnetite has been reported in the pH range of 6.4 to 6.85 [17]. If the pH of suspensions is lower or higher than the zpc of magnetite, the magnetite surfaces can be charged positively or negatively. Cr(VI) ($Cr_2O_7^{2-}$) may experience different electrostatic forces from the magnetite surfaces depending on the pH, i.e., attraction under the zpc and repulsion above the zpc. Cr(VI) adsorption, the first step for the reduction of Cr(VI) at the surfaces, at pH 7.2 and 8.0 could be interrupted by electrostatic repulsion. Thus, the pH is an important factor that controls the reaction kinetics of Cr(VI). In addition, the reduction of Cr(VI) can consume the H^+ from solution based on the following equation [11]. Therefore, the reduction of Cr(VI) could be favorable at the lower pH condition and was comparable with the results of this study.



3. Reduction of Cr(VI) in the Suspensions of Soil Minerals and Soil with Fe(II)

Fig. 6 shows the reduction kinetics of Cr(VI) in nontronite, soil, and magnetite with Fe(II) ($Fe(II)/Cr(VI)=1.0$). The reduction kinetics of Cr(VI) in the aqueous Fe(II) solution and in the magnetite suspension are also shown as controls for comparison. The relative concentrations of Cr(VI) dropped at first sampling time and slowly approached 0.7 during the reaction time. The reduction patterns of Cr(VI) in nontronite and soil with Fe(II) are very similar; however, more Cr(VI) was removed by soil than by nontronite. This may be due to the high content of organic matter (0.76%) in soil sample whose influence on the reduction kinetics has been reported [18]. In contrast to the reductive dechlorination of chlorinated organic compounds, more Cr(VI) was removed in the aqueous Fe(II) solu-

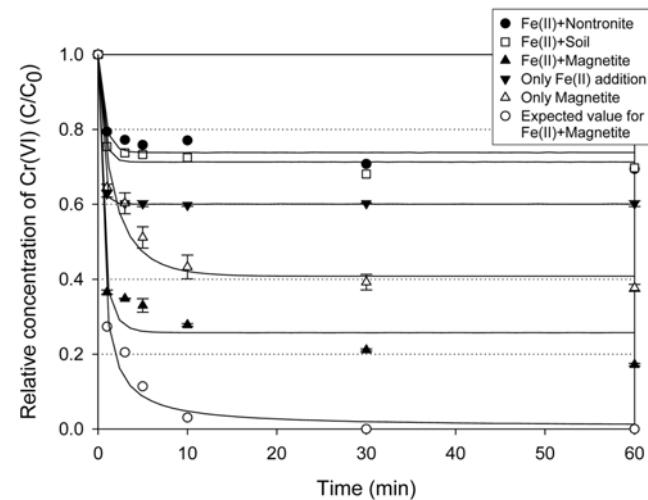


Fig. 6. Reduction of Cr(VI) in solid suspensions with and without Fe(II) and aqueous Fe(II) solution (pH 7.2, $Fe(II)/Cr(VI)=1.0$).

tion than in the soil and nontronite suspensions with Fe(II) addition. Chlorinated organic compounds have been known to be reductively degraded at the reactive surface sites, but no significant degradation has been reported in homogeneous reductant solutions such as Fe(II) solution. This result indicates that the reactive Fe(II) adsorbed on the soil and nontronite surfaces in heterogeneous systems does not effectively reduce Cr(VI) as much as aqueous Fe(II) does in the homogeneous system.

The reactivity of magnetite suspension was enhanced by the addition of Fe(II). More Cr(VI) was reduced in the magnetite suspension with Fe(II) (C/C_0 at 60 min=0.2) than in homogeneous Fe(II) solution (0.6) and in the magnetite suspension without Fe(II) (0.4), respectively. This indicates that the reductive capacity of magnetite was enhanced by forming the reactive surface sites (i.e., surface complexes/precipitates) and/or by regenerating the oxidized surface sites by the addition of Fe(II). However, the amount of Cr(VI) removed in magnetite suspension with Fe(II) is far less than that estimated under an assumption that the removal of Cr(VI) in the suspension with Fe(II) is the summation of each removal from aqueous Fe(II) solution and magnetite suspension under the same experimental conditions. Fig. 6 shows the estimated Cr(VI) removal completed in 30 min. A part of adsorbed Fe(II) may be oxidized to Fe(III) at the surfaces forming non-reactive complexes and/or precipitates. No measurement has been conducted to identify these non-reactive chemical species on the surfaces in this study.

Fig. 7 shows the effect of pH on the reduction of Cr(VI) in the magnetite suspension with Fe(II) in the range of suspension pH 5.5 to 8.0. A similar effect shown in magnetite suspension (Fig. 5) was also observed in the magnetite suspensions with Fe(II). The reduction rates of Cr(VI) increased with the decrease of suspension pH in both suspensions with and without Fe(II). The magnetite suspension with Fe(II) at pH 5.5 has the greatest reduction rate constant showing the full reduction of Cr(VI) in one hour, followed by those at pH 6.5>pH 7.2>pH 8.0>pH 7.2 without Fe(II). Because of the zpc of magnetite, the surfaces of magnetite at pH 5.5, pH 6.5, and >pH 7.2 are charged with negative ($-O^-$), neutral ($-OH$), and positive ($-OH_2^+$) surface species, respectively. This significantly affects the behavior of Cr(VI) and Fe(II) in the magnetite suspension. Gre-

gory et al. have reported that Fe(II) adsorbed on magnetite rapidly increases as the suspension pH increases from 6 to 8 [6]. While 30% of initial Fe(II) was adsorbed on the surfaces of magnetite at pH 6, 90% of the initial Fe(II) was adsorbed at pH 6.5 in this study. Fe(II) was not detected in the aqueous solution at pH 7.2 and 8. The higher reactivity of magnetite suspension with Fe(II) observed at lower pH (pH 5.5 and 6.5) is due to the significant reduction of Cr(VI) by Fe(II) in aqueous solution and Fe(II) adsorbed on magnetite surfaces, suggesting that the Cr(VI) reduction by aqueous Fe(II) and adsorbed Fe(II) is more reactive than that by Fe(II) adsorbed on magnetite surfaces alone.

CONCLUSIONS

The reduction of Cr(VI) in soil mineral suspensions was investigated. The concentration of reactive Fe(II) on the magnetite surfaces was a very important factor that significantly affected the reduction kinetics of Cr(VI). Unless the Cr(VI) concentration is much lower than the surface-bound reactive Fe(II), the slow reduction of Cr(VI) followed the rapid initial sorption of Cr(VI) onto the magnetite surfaces. Because of these characteristics of surface reduction, the reaction kinetics of Cr(VI) cannot be properly described by the zero-order or pseudo-first-order rate law, but well described by the modified Langmuir-Hinshelwood kinetic model.

The addition of Fe(II) to the magnetite suspensions enhanced the Cr(VI) reduction, which indicates that the reduction can be controlled and accelerated by the simple treatment. Most Fe(II) added into the magnetite suspension was adsorbed on the soil mineral surface and the Cr(VI) reduction rate increased at constant pH 7.2. However, the extent of Cr(VI) reduction in the magnetite suspension with Fe(II) did not reach the estimated value which was a simple summation of the reduced Cr(VI) in the magnetite suspension and that in the Fe(II) solution. An identical result was observed in the soil and the nontronite suspensions. These results showed that the soluble Fe(II) added cannot stoichiometrically convert the surface Fe(III) to Fe(II) and that electrons may transfer to the bulk suspension. The Fe(II)-initiated reduction of Cr(VI) was also significantly affected by suspension pH. The reduction rate of Cr(VI) decreased as the pH of magnetite suspension increased (above the zpc of magnetite). The results can be applied to the development of remediation technology and used for the optimal operation of in-situ redox manipulation and natural attenuation to treat groundwater and soil contaminated with Cr(VI).

ACKNOWLEDGMENTS

This research was supported by the grants from the Korean Ministry of Environment (Eco-Technopia 21). The contents do not necessarily reflect the views and policies of the sponsor nor does the mention of trade names or commercial products constitute endorsement or recommendation for use.

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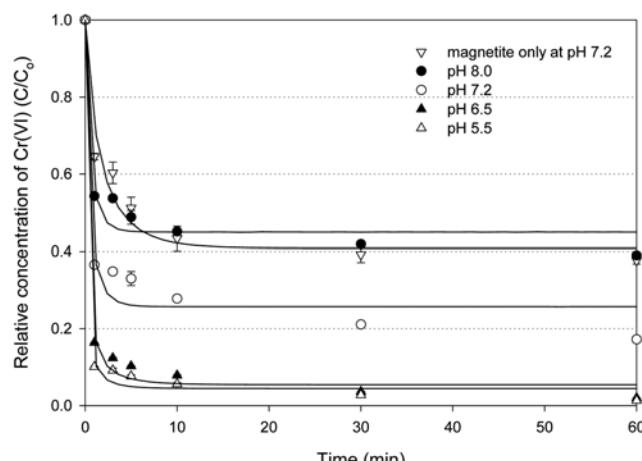


Fig. 7. Effect of pH on the reaction kinetics of Cr(VI) by magnetite with Fe(II).

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