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Effects of Phosphate, HEDTA, and Light Sources on Cr(VI) Retention by Goethite

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Iron hydrous hydro(oxide) has been regarded as an important sorbent for Cr(VI) in soil systems due to its wide distribution. However, many factors, such as phosphate (P), organic ligands, and light sources, could influence Cr(VI) retention by the soil components. The existence of inorganic or organic ligands not only competes with solution Cr(VI) for surface sites, but also results in releasing sorbed Cr(VI). Although organic matter can reduce Cr(VI) to less toxic Cr(III), the reduction rate is extremely slow. The objective of this study was to evaluate the influence of P on Cr(VI) sorption by goethite. The reduction of Cr(VI) by N-hydroxyethyl-ethylenediamine-triacetic acid (HEDTA) and goethite under different intensity of light was also investigated. Competitive sorption experiment indicated that P had lower inhibition of Cr(VI) sorption when the initial Cr(VI) concentration was higher than P. Goethite suspensions could catalyze Cr(VI) reduction under growth chamber light. Goethite accompanied with light could also accelerate Cr(VI) reduction by HEDTA. This phenomenon could be evidenced by the formation of Cr(III) and decreasing desorption of retained Cr(VI) by P.

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INTRODUCTION

Chromium is widely distributed in soil and is the 21st most abundant element in the Earth's crust (Nieboer and Jusys, 1988). It exists predominantly in two oxidation states, Cr(VI) and Cr(III). Chromium(VI) is an anion and is highly mobile in soil profile, particularly in an alkaline environment. Chromium(III), on the other hand, is a cation. It is only sparingly soluble in soils at $pH > 5.5$ (James and Bartlett, 1983) because of its high hydrolyzation and precipitation.

Chromium is of interest to scientists not only because of its extensive use in industry but also because of its toxicity in the biosphere. Chromium(VI) is toxic to both plants (Bishnoi *et al*., 1993) and animals (Costa, 1997). The risk of Cr(VI) to aquatic habitats, algae, and bacteria has also been reported by Holdway (1988) and Loutit *et al*. (1988). Although the disadvantageous effects of Cr(III) have been discussed by Nakamuro *et al*. (1978) and Snow and Xu (1989), recent studies focus on nutritional research. Chromium deficiencies have been recognized to be responsible for some devastating degenerative diseases, such as diabetes. These studies believed that Cr(III) organic complex located on the cell wall could help the cell to uptake sugar from the blood, thus maintaining a balanced sugar concentration in the blood.

Conversion of Cr(VI) to Cr(III) by reductants such as Fe(II), Fe(0), organic compounds, H_2O_2, and H_2S has been reported to be feasible (Deng and Stone, 1996; Fendorf and Li, 1996; Peterson *et al*., 1996; Blowes *et al*., 1997; Patterson and Fendorf, 1997; Peterson *et al*., 1997; Ozer *et al*., 1997). Because Cr(III) has lower toxicity and mobility than Cr(VI), the redox reaction greatly decreases the danger of Cr to the biosphere. In view of the extremely slow reduction rate (Wittbrodt and Palmer, 1995) and high cost, organic compounds are considerably less employed in industry for Cr(VI) reduction. However, in the consideration of the wide distributions of organic matter in the top soil, river, and estuary, enhancement of Cr(VI) reduction by organic compounds offers another efficient pathway for alleviating Cr contamination in soil and aquatic systems.

Goethite is the most common Fe hydrous oxides in the field. In the past, it was considered an excellent sorbent for the sorption of anions such as Cr(VI), PO_4^{3-} and SO_4^{2-}. In this study, the role of goethite as a surface-catalyzed mineral was investigated in the presence or absence of HEDTA. The competitive sorption of P and Cr(VI) and the influence of light sources on Cr(VI) reduction through the application of HEDTA and goethite suspensions were also evaluated. Phosphate(P) was also used as a desorbent to investigate whether adsorbed Cr(VI) could be reduced on the goethite surface.

MATERIALS AND METHODS

Synthesis of Goethite

Goethite was prepared by precipitating 1 *M* $Fe(NO_3)_3$ with 5 *M* NaOH and incubating the precipitate for 60 h at 70°C (Schwertmann and Cornell, 1991). The suspensions were then dialyzed until the electric conductivity of the outer dialysis membrane was < 25 µS^{-1}. The suspension was stored at 2°C for the subsequent experiments.

Effect of Phosphate Concentrations on Cr(VI) Retention by Goethite

In order to investigate the competitive sorption between P and Cr(VI), final concentrations of 13.3 µ*M* of Na_2HPO_4 solution were added with 133 µ*M* and 13.3 µ*M* of Cr(VI) to goethite suspensions (0.2 g L^{-1}) to achieve final molar ratios of Cr:P=1:10 and 1:1, respectively. The suspension pH was immediately adjusted from 2 to 11.5. The reaction was conducted for 55 h before the suspension was passed through a 0.2-µm pore-size membrane filter. The purpose of passing goethite suspensions through a 0.2-µm filter was to unify the procedure used in the ferrihydrite experiments (not included). Chromium(VI) concentration in solution was determined by *s*-diphenylcarbazide (DPC method; Eaton *et al*., 1995) using a GBC Inc. UV/VIS spectrometer (Model 911A). The effect of P concentrations on Cr(VI) retention by goethite were obtained by calculating the changes in Cr(VI) concentration.

Application of Light

Two different intensities of light, laboratory light and growth chamber light, were used in the following experiments. The wavelength of laboratory light ranged from 400 to 700 nm, with a maximum intensity of 0.02 µmol/m^2s at 600 nm [measured by LiC or portable spectroradio meter (LI-1800)]. The wavelength range of growth chamber light was the same as that of laboratory light; however, the maximum intensity of growth chamber light was about 40 times higher than that of laboratory light. In the dark experiments, the reaction vessels were covered with Al foil.

Chromium(VI) Retention by Goethite

Light Sources and pH. To investigate the impact of light on Cr(VI) retention by goethite at different pH, experiments were designed by adding Cr(VI) to goethite suspensions. Suspension pH was adjusted from 3 to 11.5 and diluted to 30 mL to make final concentrations of 13.3 µ*M* Cr(VI) and 0.4 g L^{-1} goethite in a 50-mL vial. Vials were covered with Al foil for the dark experiments or were conducted under laboratory light or moved to the growth chamber to evaluate the effect of light on Cr(VI) retention by goethite. All the experiments were conducted for 20 h. Five milliliters of suspensions were withdrawn by a syringe and passed through a 0.2-µm pore-size membrane filter. Chromium(VI) in supernatant was colorimetrically determined by DPC method.

Following Cr(VI) retention, a final concentration of 0.3 m*M* P was added to each vial (the pH of P solution was preadjusted to the pH of added vial) to desorb Cr(VI) from goethite surfaces. Desorption was conducted in the dark for 20 h to prevent any light-catalyzed Cr(VI) reduction. After desorption experiment, release of Cr(VI) was extracted, filtered, and measured as described in the previous section.

Time and Light Sources. A total volume of 500 mL polyethylene container with 40 μ*M* Cr(VI), 0.2 g L^{-1} goethite suspension, and 0.01 *M* $NaNO_3$ was used in the study. The reaction was conducted at pH 4 for 24 h under laboratory light, growth chamber light, and in the dark with three replications for each treatment. Five milliliters of suspensions were extracted and filtered periodically. Chromium(VI) in the supernatant was determined by DPC method. After 24 h, NaH_2PO_4 (final concentration of 1 m*M*, pH 4) was added to the suspension. The desorption of Cr(VI) by P as a function of reaction time was then investigated.

Effect of HEDTA on Cr(VI) Retention by Goethite

pH and Light Sources. Final suspensions of 0.2 g L^{-1} goethite were obtained by diluting 0.6 g L^{-1} goethite suspensions to 30 mL to give a final concentration of 0.01 M $NaNO_3$, 13.3 μ*M* Cr(VI), and/or 13.3 μ*M* HEDTA. The pH was adjusted from 3 to 11.5 before each vial was quantified volumetrically to 30 mL. *N*-hydroxyethyl- ethylenediamine-triacetic acid (HEDTA) was purchased as commercial products without further purification. Chromium(VI) concentration was reconfirmed by measuring diluted solution in each vial (including all reactants except goethite).

The sample suspensions were conducted under laboratory light, growth chamber light, and in the dark for 55 h with constant pH adjusted. The retention of Cr(VI) was calculated by the difference between initial and final Cr(VI) concentrations. Total Cr was determined by atomic absorption spectroscopy (AAS, Perkin Elmer Model 3100), and Cr(III) was calculated from the difference between total Cr and Cr(VI). The release of Fe in solution due to organic ligand complexation was determined by colorimetric method at 510 nm (Loeppert and Inskeep, 1996).

pH and Reaction Time. To evaluate the effects of reaction time on Cr(VI) reduction by goethite, final concentrations of 0.2 m*M* HEDTA, 40 μ*M* Cr(VI), and 0.01 *M* $NaNO_3$ electrolyte solutions were added to 0.2 g L^{-1} goethite. The reactions were conducted with three replications in the dark, laboratory light, and growth chamber light at pH 4. Acceleration of 40 μ*M* Cr(VI) reduction by 0.2 m*M* HEDTA was also conducted under growth chamber light without goethite. The experiment was designed to distinguish the role of HEDTA and goethite on Cr(VI) reduction. The suspension or solution was extracted periodically, and Cr(VI) was determined by DPC method.

RESULTS AND DISCUSSION

Effect of P Concentration on Cr(VI) Retention by Goethite as a Function of pH

At low pH (pH < 6), P influenced strongly Cr(VI) sorption by goethite when P and Cr(VI) had the same concentrations; nonetheless, the effect was not significant when initial Cr(VI) concentration was increased to 10 times that of P concentration (i.e., Cr:P=10:1) (Figure 1). The inhibition of Cr(VI) sorption by P was not observed at higher pH (i.e., pH > 7).

Phosphate was commonly used as a desorbent for desorption of sorbed Cr(VI) (Bartlett and Kimble, 1976) because these two anions probably occupied the same sorption sites. Competitive sorption experiment indicated stronger sorption ability for P on the goethite surface sites because of the great drop in the percentage of Cr(VI) sorption when the ratio of P to Cr(VI) was 1 to 1 (Figure 1). Although P inhibited Cr(VI) sorption, an increase in Cr(VI) sorption was still observed when solution pH was gradually decreased. This phenomenon indicated that even if P and Cr(VI) had very similar sorption sites, there were preferential sites for Cr(VI). The increase in Cr(VI) sorption probably resulted from the increase in positive

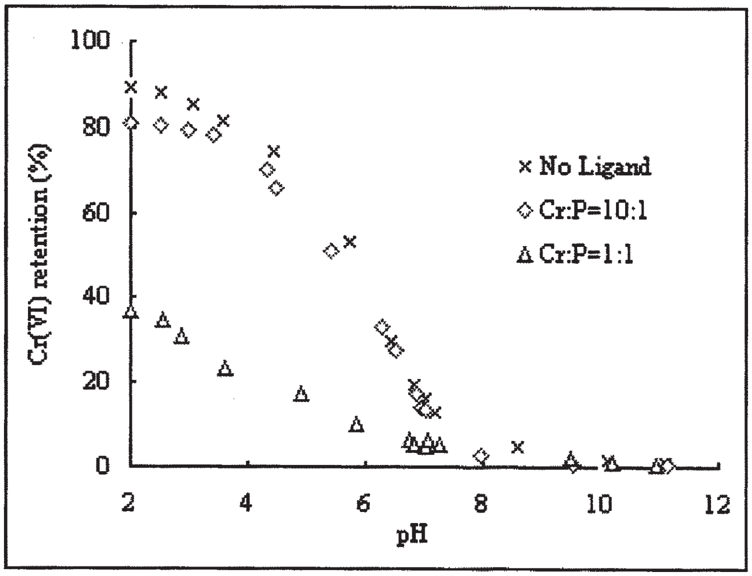


FIGURE 1

The retention of 13.3 μM of Cr(VI) by goethite (0.2g L⁻¹) as a function of pH. The competitive sorption of 133 (10:1) and 13.3 μM (1:1) of Cr(VI) with 13.3 μM P on 0.2 g L⁻¹ goethite was also shown.

charges due to protonation of goethite surface or from the dimer- or polymerization of Cr(VI) onto the goethite surface at low pH. Phosphate only slightly affected the sorption of high concentrations of Cr(VI). The reason for low inhibitive sorption of high concentrations of Cr(VI) by P is not clear and merits further study. The dimerization of chromate to dichromate had been reported by Baes and Mesmer (1976) in acidic solution at concentrations >10 m*M*. Some of the sorbed Cr(VI) was dimerized to dichromate under higher Cr(VI) concentration at low pH, which caused the enhancement of Cr(VI) sorption in the presence of P. However, the hypothesis of the occurrence of Cr(VI) surface dimer- or polymerization still needs to be confirmed further.

Chromium(VI) Sorption by goethite and Desorption by P

Effect of pH on Cr(VI) sorption. Chromium(VI) retention by 0.4 g L^{-1} goethite was affected greatly by pH. More than 90% of the added Cr(VI) was sorbed at pH < 4; however, less than 10% of the added Cr(VI) was retained at pH > 9 (Figure 2, solid circle curve). Surface protonation and the elevation of positive charges explained high Cr(VI) sorption at low pH. The development of negative charges that repulsed Cr(VI) from surface sites and the competition with OH^- for surface sites resulted in low Cr(VI) sorption at high pH. The results were similar to those reported by Tzou and Wang (1998) in their investigation of the sorption of Cr(VI) by soil samples. In the dark condition, Cr(VI) retention by goethite was slightly lower than Cr(VI) retention under growth chamber light (Compare Figure 2a with 2b, solid circle curve). Owing to the existence of greater surface sites of goethite, most of the added Cr(VI) was retained. Thus, the sorption results could not distinguish the difference in effect between dark and light conditions.

Effect of pH on Cr(VI) Desorption. Chromium(VI) desorption by P was also evaluated at different pH. Low pH contributed to higher Cr(VI) retention. However, less than 40% of the added Cr(VI) was still retained by goethite at pH < 5 when sorption experiment was conducted in the dark (Figure 2a, open circle curve). That is, more than 60% of the retained Cr(VI) was desorbed by P at pH < 5. In contrast, only 20 to 30% of the retained Cr(VI) was desorbed by P when sorption experiment was conducted under growth chamber light at pH < 5 (Figure 2b, the difference in values between solid and open circle curves at pH < 5). The results suggested that low pH favored Cr(VI) reduction in the presence of goethite under growth chamber light. Owing to favorable conversions of sorbed Cr(VI) to Cr(III) in the presence of goethite under growth chamber light at low pH, less sorbed Cr(VI) could be desorbed by P.

Effects of Time and Light Sources on Cr(VI) Sorption. About 30% of the added Cr(VI) (40 μ*M*) was retained by 0.2 g L^{-1} goethite within several hours. Slightly

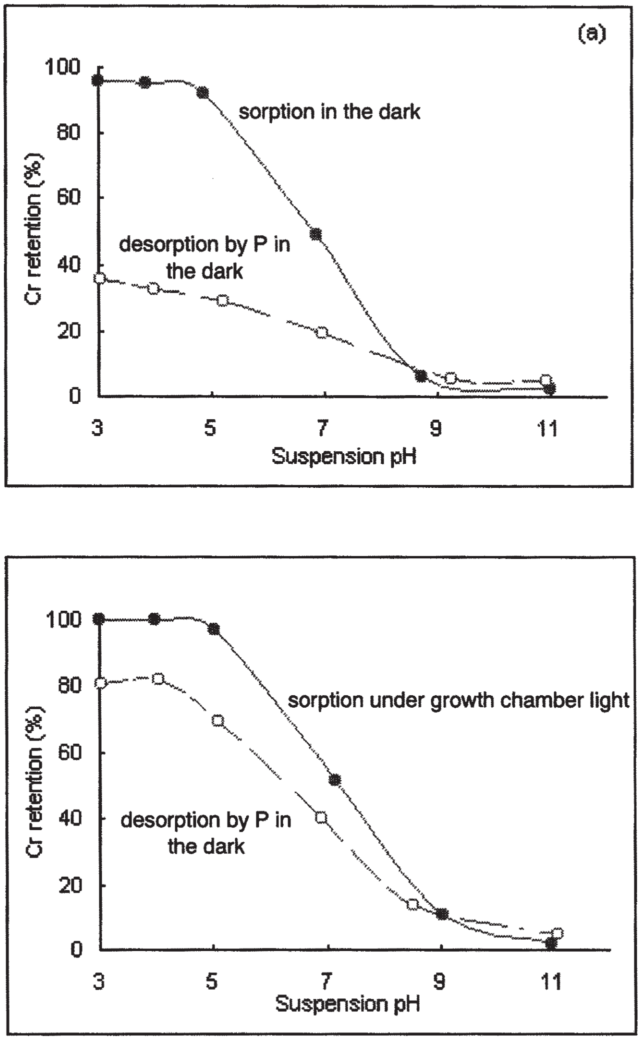


FIGURE 2

Retention of 13.3 μM Cr(VI) by 0.4 g L^{-1} goethite as a function of pH (a) in the dark and (b) under growth chamber light. Following Cr(VI) retention experiment, 0.3 mM NaH_2PO_4 was used for Cr(VI) desorption. The desorption experiment was conducted in the dark for 20 h.

increased Cr(VI) retention was observed through the reaction time when the experiment was conducted in the dark or under laboratory light (Figure 3, open circle curve).

Chromium(VI) retention by goethite reached the maximum rapidly in the dark and under laboratory light condition (Figure 3, open circle curve); however, the gradual increase in Cr(VI) retention by goethite was observed under growth chamber light (Figure 3, solid circle curve). As no organic compound was included in the system and light was the only variable, the increase in Cr(VI) retention by goethite obviously contributed to the addition of strong light energy (i.e., growth chamber light). Figure 4 illustrated the proposed scheme for Cr(VI) reduction in the presence of goethite suspension under growth chamber light. In the presence of Cr(VI) and energy (i.e., growth chamber light), the sorbed surface H_2O might be split offering electrons to Fe(III) site of goethite. When Fe(III) was reduced to Fe(II), the goethite surface structure became unstable, and the OH bond might be broken. Thus, Cr(VI) was allowed to penetrate and complexed with Fe(II) for subsequent electron transfer (Figure 4, pathway I). This was a redox procedure. During this procedure, Cr(VI) was reduced and O_2 was released. Owing to the low release of O_2 and possible adsorption of O_2 by goethite surface, the increase in dissolved O_2 by oxygen electrode could not be measured. The applications of spectroscopic technologies, such as X-ray fine structure spectroscopy (EXAFS), can inspect the local surface environment at atomic level. It gives clearer clues and explanations for the proposed mechanism in the future.

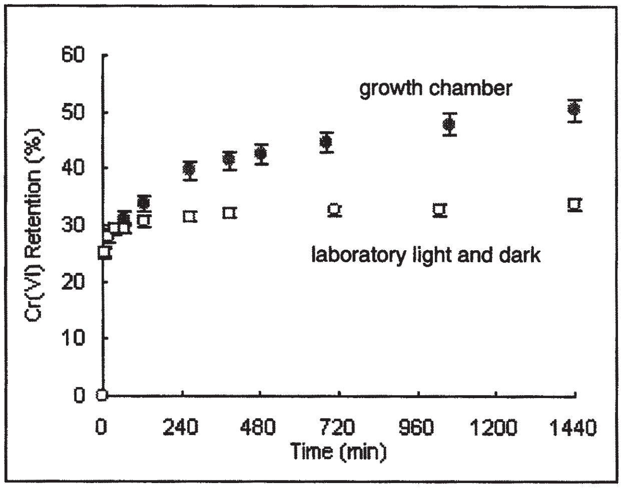


FIGURE 3

The kinetic retention of 40 μM Cr(VI) by 0.2 g L^{-1} goethite in the dark, under laboratory light, and growth chamber light at pH 4. Error bars represent mean and standard deviations of three samples each.

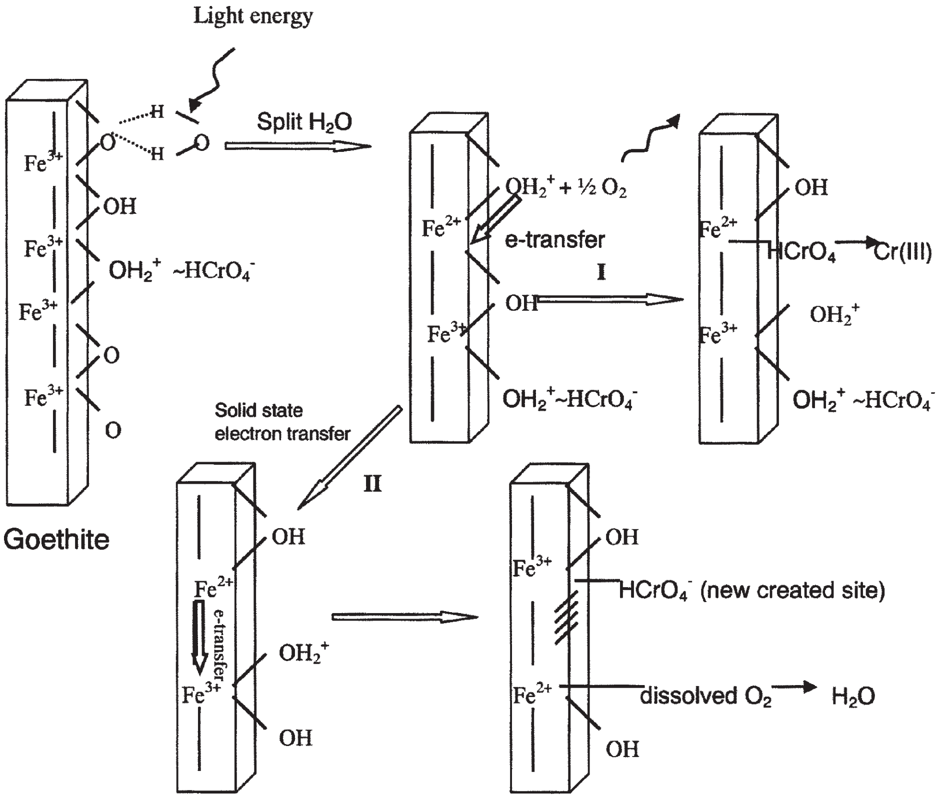


FIGURE 4

The two possible pathways for increasing Cr(VI) retention: (I) reduction of Cr(VI) under growth chamber light-catalyzed goethite H_2O split; (II) creation of new sorption sites due to bond breakage.

Another possible mechanism was through solid state electron transfer, which allowed electron transfer from Fe(II) to Fe(III) (Figure 4, pathway II). In this pathway, one new sorbed site was created and made available for Cr(VI) adsorption. Because the solid state electron transfer and bond breakage proceeded very slowly, this might account for the slow Cr(VI) retention through reaction time under growth chamber light.

Effects of Time and Light Sources on Cr(VI) Desorption. Following Cr(VI) retention by goethite under growth chamber light and in the dark (Figure 3), the subsequent desorption of retained Cr(VI) was examined by adding P (Figure 5). The initial desorption of retained Cr(VI) was rapid when P was added, but it decreased gradually through the desorption time. After 24 h, about 33% and 27% of Cr(VI) were desorbed by P under growth chamber light and in the dark conditions, respectively (Figure 5, curve a and curve b, respectively). Although

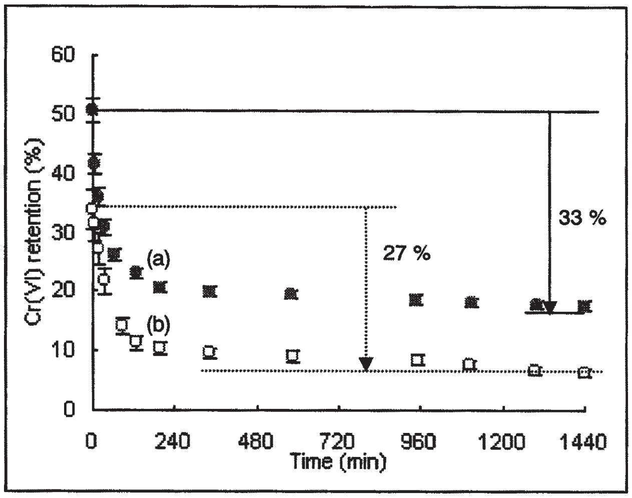


FIGURE 5

Following Cr(VI) retention at Figure 3, a final concentration of 0.1 *M* NaH_2PO_4 (pH 4) was added to desorb retained Cr(VI) for 24 h in the dark. Curves (a) and (b) indicate that Cr(VI) retention experiment was conducted under growth chamber light and in the dark, respectively. Error bars represent mean and standard deviations of three samples each.

higher desorption of Cr(VI) was observed when sorption experiment was conducted under growth chamber light, there was still 17% of Cr(VI) retained by goethite (Figure 5, curve a). However, only 6% of Cr(VI) was retained by goethite after being desorbed by P in the dark (Figure 5, curve b). That is, the increases of 11% (i.e., 17% to- 6%) Cr(VI) reduction and 6% (i.e., 33% to 27%) Cr(VI) sorption were observed. The results gave more evidence supporting the proposed pathways I and II shown in Figure 4. As mentioned in the previous section, laboratory light could not catalyze Cr(VI) reduction by goethite. The presence of growth chamber light must have provided enough energy to overcome the energy barrier for electron transfer between Cr(VI) and the reducing agent (i.e., H_2O, Tzou, 2001), resulting in an increase in Cr(VI) reduction and adsorption.

A phenomenon was also found by comparing Figure 3 [Cr(VI) retention] with Figure 5 [Cr(VI) desorption]. An increase in Cr(VI) retention difference was observed (Figure 3, difference between the two curves). More than 40% of the difference was seen at the reaction time of 120 h (data not shown). In the same period, a constant 11% Cr(VI) retention difference was observed (Figure 5, difference in values between solid and open circles at 24 h). From sorption and desorption studies, the continuous increase in Cr(VI) retention under growth chamber light has two implications. (1) New adsorption sites as described in pathway II, Figure 4 explained the continuous increase in Cr(VI) retention. Phosphate(P) could also access the new sites and desorb retained Cr(VI); (2) Cr(VI) would not be reduced continuously. That is, only some goethite sites were able to reduce adsorbed Cr(VI) as described in pathway I, Figure 4.

Effects of HEDTA on Cr(VI) Retention by Goethite

pH and Light Sources. The effect of pH, light, and HEDTA on Cr(VI) retention by goethite was shown in Figure 6. Chromium(VI) retention by goethite in the presence of HEDTA was higher under growth chamber light, followed by laboratory light at lower pH (Figure 6, curve a and curve b, respectively). However, HEDTA free system had the lowest Cr(VI) retention (Figure 6, curve c). Chromium(VI) retention curve was overlapped between HEDTA-free and dark experiment (with HEDTA) (Figure 6, curve d). HEDTA did not show significant influence on Cr(VI) retention. In other words, the adsorption sites on goethite surfaces were different between two anions — HEDTA and Cr(VI). Thus, HEDTA would not inhibit Cr(VI) retention by goethite.

Under light conditions, Cr(VI) retention by goethite was greatly increased at pH < 8 in the presence of HEDTA (Figure 6, curve a and curve b). Compared with that in the dark and HEDTA-free conditions (Figure 7a, solid diamond and open triangle curves, respectively) the increase in aqueous Cr(III) at low pH could further prove that HEDTA serves as a reductive agent under laboratory light (Figure 7a, open square circle curve). The enhancement of Cr(VI) retention when

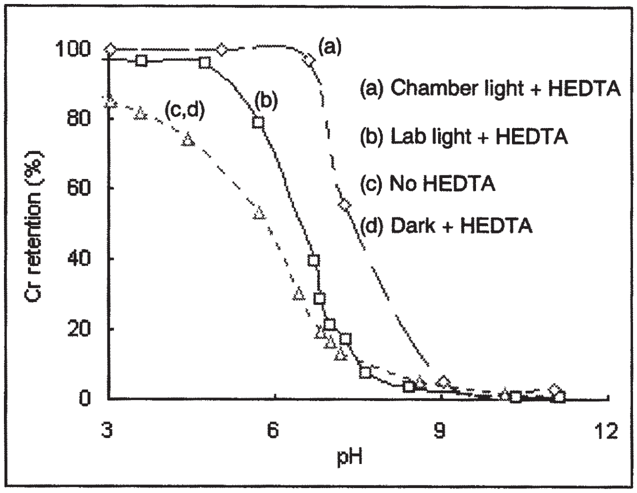
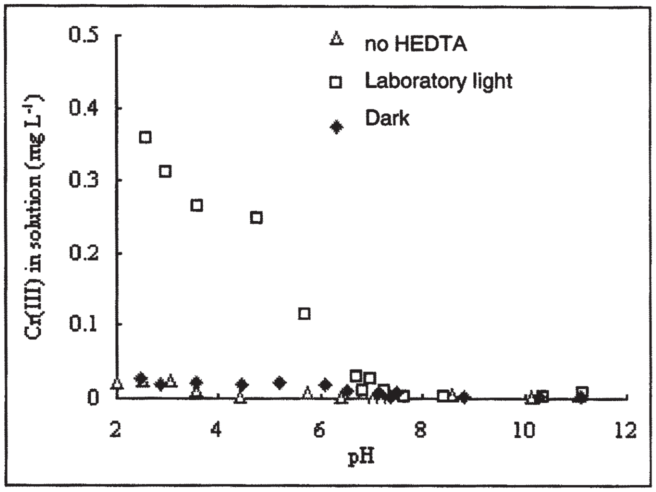


FIGURE 6

Retention of 13.3 μM Cr(VI) by 0.2 g L^{-1} goethite in the presence and absence of 13.3 μM HEDTA under laboratory and growth chamber light. L: Laboratory light; G: Growth Chamber light.



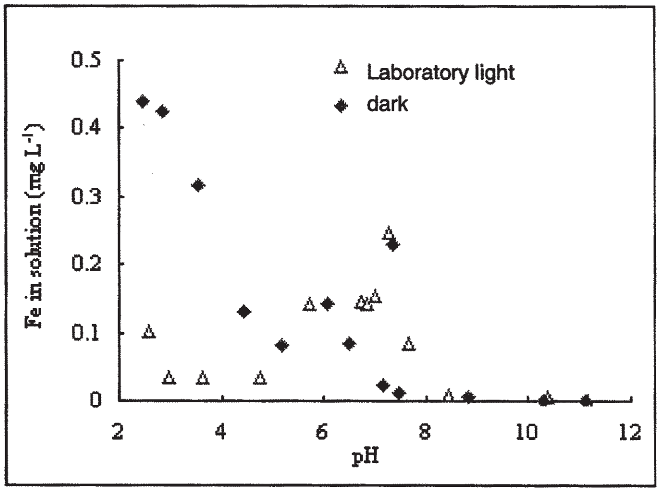


FIGURE 7

Calculated (a) formation of Cr(III) and (b) release of Fe(III) when 13.3 μM Cr(VI) reacted with 0.2 L^{-1} goethite in the presence of 13.3 μM HEDTA. The reaction was conducted in the dark and under laboratory light.

stronger growth chamber light was used instead of laboratory light combined two reactions: (1) goethite-catalyzed Cr(VI) reduction under growth chamber light, and (2) growth chamber light providing more energy to overcome an energy barrier to support greater Cr(VI) reduction.

According to the preliminary experiment, the reduction of Cr(VI) by HEDTA in a homogeneous system at pH > 2.5 under laboratory light was ignored. Also, goethite did not show any evidence of reduction of Cr(VI) as described in the previous section. Thus, the enhancement of Cr(VI) reduction in the study indicated that goethite could probably catalyze Cr(VI) reduction by HEDTA. Two possible mechanisms explained the observations. (1) Owing to the structural characteristics of goethite, the electron transfer from organic compound to Cr(VI) through the goethite structure (solid phase electron transfer) was accessible but less possible, unless a partial broken surface site or short-range disorder structures existed in goethite, which favored electron transfer. (2) Another proposed mechanism was the decrease in electron repulse between the organic compound and Cr(VI) due to the complexation of Fe(III) from goethite surface site by these organic ligands. This mechanism could be supported by the release of Fe(III) at lower pH (Figure 7b, open triangle curve).

A schematic diagram for goethite-catalyzed Cr(VI) reduction by HEDTA is described in Figure 8. The electron transfer from HEDTA through solution to Cr(VI) is impossible because electron has never existed in solution (Marcus, 1965). In order to carry out the redox reaction, these two reactants [(HEDTA and Cr(VI)) have to complex each other before the electron transfer becomes feasible. At pH > 2.5, both reactants are anions (H_4EDTA: $pK_1=2$, $pK_2=2.67$, $pK_3=6.16$, $pK_4=10.26$; H_2CrO_4: $pK_1=-0.6$, $pK_2=6.4$). Therefore, the combination of HEDTA and Cr(VI) for subsequent electron transfer is less possible. However, HEDTA could complex directly with Fe(III) on goethite surface and release Fe(III) as a Fe(III)-HEDTA. Subsequently, the metal-organic complex associated with Cr(VI), and electron transfer from metal-organic complex to Cr(VI) occurred under illumination. The

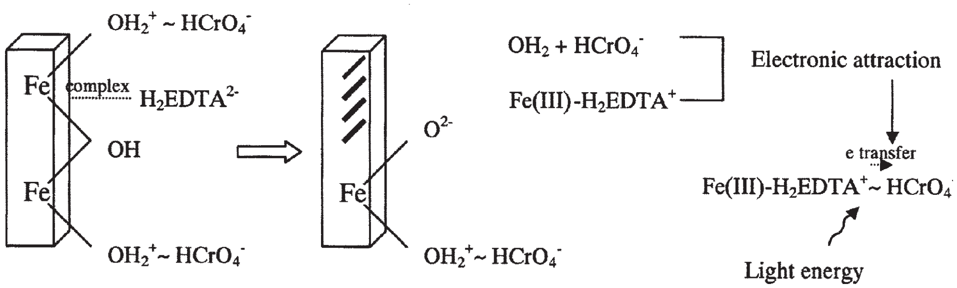


FIGURE 8

The proposal reduction of Cr(VI) by HEDTA as catalyzed by goethite.

acceleration of Cr(VI) reduction by organic compounds was also observed in a homogeneous system containing 0.02 m*M* Fe(III) (Tzou, 2001). Thus, the hypothesis for the role of Fe(III) in enhancing the electron transfer between Cr(VI) and organic ligands is further supported.

Time and Growth Chamber Light Sources. In the dark condition, no elevation of Cr(VI) retention by goethite over the reaction time indicated that adsorption reaction was the only factor affecting aqueous Cr(VI) concentrations (Figure 9, curve c). The acceleration of Cr(VI) retention in the presence of goethite and HEDTA under growth chamber light (Figure 9, curve a) further confirmed the importance of light in the redox reaction. Although growth chamber light enhanced Cr(VI) reduction by both HEDTA (Figure 9, curve d) and goethite (Figure 9, curve b), the summations of Cr(VI) reduction by individual HEDTA and goethite could not explain completely the rapid Cr(VI) retention in the presence of HEDTA and goethite. That is, curve (a) was greater than curve (b) plus curve (d) in Figure 9. Thus, goethite not only serves as a catalyst for Cr(VI) reduction, but also accelerates Cr(VI) reduction by HEDTA under growth chamber light.

CONCLUSION

Phosphate is a good desorbent for the desorption of Cr(VI) from surface sites. Phosphate (P) competed strongly with Cr(VI) on the surface sites of goethite when

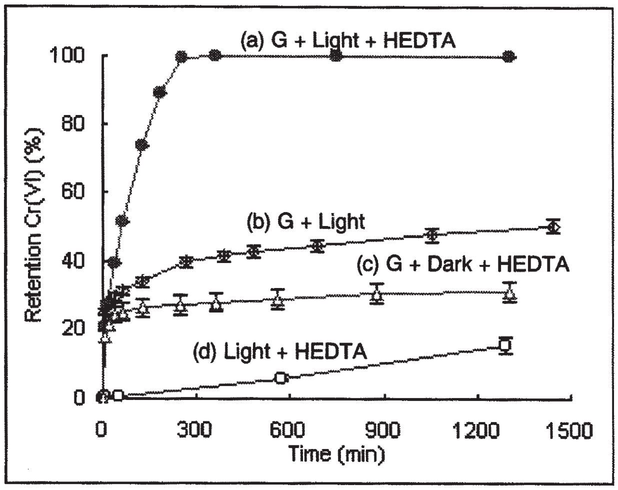


FIGURE 9

The kinetic retention of 40 μM Cr(VI) by 0.2 g L^{-1} goethite under laboratory light, growth chamber light, and in the dark in the presence of 0.2 mM HEDTA. FG: No goethite in suspensions. Error bars represent mean and standard deviations of three samples each.

P and Cr(VI) had the same initial concentrations. Nevertheless, the inhibition of Cr(VI) sorption by P was low when initial Cr(VI) concentration was 10 times larger than that of P. According to the results, the expectation of Cr(VI) sorption by goethite would be underestimated in the presence of low P concentration at low pH.

The sorption of Cr(VI) by goethite is rapid and affected greatly by suspension pH. Goethite serves as an adsorbent only when the reactions are conducted in the dark or under laboratory light. Under growth chamber light, goethite catalyzes Cr(VI) reduction, particularly at lower pH. Through desorption experiments, incomplete and low desorption of sorbed Cr(VI) by P further evidences Cr(VI) reduction. Although the enhancement of Cr(VI) reduction by goethite is observed in the study, the mechanism of Cr(VI) reduction by goethite under growth chamber light merits further study.

Organic compound usually serves as a reducing agent or a competitive ligand for Cr(VI). In this study, HEDTA ligand did not inhibit Cr(VI) retention by goethite in the dark condition. In a homogeneous system, Cr(VI) could be reduced by HEDTA only under growth chamber light at low pH. However, the acceleration of Cr(VI) reduction by HEDTA could occur even under laboratory light in the presence of goethite. Goethite-catalyzed Cr(VI) reduction by HEDTA resulted from the formation of Fe(III)-HEDTA complexes decreased the electronic repulse between HEDTA and Cr(VI).

Chromium(VI) reduction is affected greatly by pH, HEDTA, activated surface sites of goethite, and light sources. Suspension pH is extremely important because rapid Cr(VI) reduction occurs only at low pH, even under growth chamber light in the presence of electron-rich organic sources. The reduction of Cr(VI) by organic ligand is limited in subsoil because light can penetrate only several millimeters of surface soils. Nevertheless, the possibilities of remediating the bulk soils involving soil-washing or soil-flushing technologies are expected according to this work. By exposing the Cr(VI)-containing extracts to sunlight with organic compounds addition, Cr(VI) should be reduced rapidly within acceptable period; thus, the final goal of the remediation of Cr(VI)-contaminated soil can be reached.

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