Reduction of Hexavalent Chromium by Soil Humic Substances

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

Abstract

Reduction of Hexavalent Chromium
By Soil Humic Substances

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The oxidation state of chromium plays an important role in determining the environmental fate of this important industrial metal. The toxic and more mobile hexavalent chromium can be transformed to the less hazardous and less mobile trivalent chromium by reduction with common soil components such as humic substances. The objective of this research is to elucidate the conditions under which Cr(VI) reduction is likely to occur in the environment.

The reduction of hexavalent chromium by soil humic substances (SHSs) was investigated in batch reactors where the concentrations of $Cr(VI)_0$, H^+, SHS, temperature and background electrolyte were independently varied. An empirical rate law developed for soil fulvic acid (SFA) treats the SFA as a continuum of reactive species describing the effects of varying solution parameters on the rate of Cr(VI) reduction by SHS. The rate law is of the general form

$$R=-kX_e^n[HCrO_4^-][SHS][H^+]^m$$

where X_e is the equivalent fraction of SHS that has been oxidized. The order with respect to X_e, n, is approximately -1.0, and m is between 0.25 and 0.5. The rate law is based on experiments where up to 5% of the SHS has been oxidized. The model can be successfully applied to soil humic acids, though will less accuracy than for SFA. Rates of Cr(VI) reduction were shown to be temperature dependant, with rates increasing significantly with increasing temperature. Arrhenius plots for Cr(VI) reduction yield activation entropies of 62±4 and 68±3 kJ mol^{-1} for soil humic acid and soil fulvic acid, respectively.

Experiments using various mono- and divalent cations reveal that rates of Cr(VI) reduction are not greatly affected by changes in background electrolyte. Changes in ionic strength in the range 0.05 to 0.5 M do not affect the Cr(VI) reduction rate. The addition of Cr(III) to the system slightly decreased the rate of Cr(VI) reduction by soil humic acid but did not have an effect on the rate of reduction by soil fulvic acid.

The presence of ferric iron greatly increases the rate of hexavalent chromium reduction, even when only a small amount of Fe(III) is added to the system. It appears that the Fe participates in a redox cycle, alternately reduced by the SHS, then oxidized by the chromium.

CHAPTER 1

Introduction

Background

The contamination of the environment by chromium has become recognized as a major problem in industrialized areas because of its widespread use and its potential health hazards. Chromium is a known carcinogen (Nieboer and Shaw, 1988; Ono, 1988; Waterhouse, 1975; Yassi and Nieboer, 1988), a teratogen (Abasi and Soni, 1984), and a mutagen (Bianchi et al., 1983; Beyersmann et al., 1984; Bonatti et al., 1976). Although there are reported occurrences of elevated levels of Cr from natural sources (Robertson, 1975; Ericksen, 1983), anthropogenic sources such as metal plating shops, tanneries, wood treatment plants and ore processing facilities are the primary concern. Examples of contaminated sites include very high levels (19000 mg/L) of hexavalent chromium in groundwater at a hard chrome plating facility in Corvallis Oregon (CH2M Hill, 1985), groundwater contamination due to improper waste disposal at an industrial plant in Long Island, New York (Perlmutter and Lieber, 1970), groundwater contamination from a wood treating facility in Dixiana, South Carolina (US EPA, 1987), and extensive soil and groundwater contamination from the use of chromium refinery wastes as construction fill in Jersey City, NJ (Burke et al., 1991). Decisions concerning the remediation of such Cr-contaminated sites requires knowledge of the chemical processes affecting chromium in the subsurface.

The mobility and toxicity of chromium are determined primarily by its oxidation state, which ranges from -2 to +6 (Cotton and Wilkinson, 1988). While the transient states Cr(V) and Cr(IV) are known to occur, the two states most environmentally stable are Cr(VI) and Cr(III). Hexavalent chromium occurs as the oxyanions $HCrO_4^-$ (bichromate), CrO_4^{2-} (chromate), and the dimer $Cr_2O_7^{2-}$ (dichromate), and is more hazardous and generally more mobile than the trivalent forms. The hexavalent species are not strongly sorbed to soils under neutral to alkaline conditions (Zachara et al. 1989) and thus are mobile under many environmental conditions. In contrast, trivalent chromium is normally relatively immobile in nature, precipitating as the hydroxide solid $Cr(OH)_3$ or the solid solution $Cr_XFe_{1-X}(OH)_3$ (Rai et al. 1987, Sass and Rai, 1987). Therefore, chemical processes that transform Cr(VI) to Cr(III) are of great interest to scientists and engineers making decisions about the remediation of Cr-contaminated sites.

Naturally occurring reductants that can reduce the more hazardous Cr(VI) to the less toxic and less mobile Cr(III) are abundant in most soils. These reductants include ions in solution, ferrous iron minerals, simple organic molecules, and humic substances. In most surface soils, organic compounds are expected to be the primary reductants of Cr(VI) (Bartlett and James, 1988). Organic compounds in soils include bio-organic molecules, that are recognizable products of plant and animal decomposition, and humic substances. The bio-organic compounds are readily degraded and thus are generally found only in the upper meter or so of soil. Humic substances are much more refractory and are present in virtually all soils as the major component of both dissolved and particulate organic matter.

The exact molecular properties of humic substances, such as molecular weight, chemical formula or structure, are dependent upon its origin and method of isolation. Soil humic substances are operationally defined by their acid-base solubility as fulvic acid (FA), humic acid (HA) or humin. Fulvic acid is soluble in both acidic and alkaline solutions. Humic acid is soluble in basic solutions but precipitates under acidic conditions. Humin is insoluble in either acid or basic solutions. The ratio of HA to FA in soils typically ranges from 0.3 to 2.5 (Stevenson, 1985). Typically, HA contains more carbon than FA (Table 1.1). Component functional group analysis shows both HA and FA contain different amounts of aromatic, carboxylic, aliphatic, ester, ether, and phenolic groups. Humic acids have higher molecular weights, fewer carboxyl groups and are more aromatic than fulvic acids (Stevenson, 1985). These properties are expected to contribute to the rates of Cr(VI) reduction by SHSs.

Table 1.1 Elemental Compositions of Soil Humic Substances. Values Reported as Weight Percent. After Steelink, 1985.

Element	Humic Acids	Fulvic Acids
Carbon	53.8-58.7%	40.7-50.6%
Hydrogen	3.2-6.2%	3.8-7.0%
Oxygen	32.8-38.3%	39.7-49.8%
Nitrogen	0.8-4.3%	0.9-3.3%
Sulfur	1.0-1.5%	0.1-3.6%

While the ability of soil humic substances (SHSs) to reduce Cr(VI) has long been known, the body of literature on Cr(VI)-SHS reactions under environmentally relevant conditions is thin. Bartlett and Kimble (1976) found no Cr(VI) reduction in organic-free soils wi2thout the addition of an external source of organic matter. The addition of fulvic acid to groundwater samples spiked with Cr(VI) showed significant reduction, particularly to acidified samples (Stollenwerk and Grove, 1985). EPR studies have demonstrated that humic acid in the pH range 4 to 9 (Goodgame et al., 1984) and fulvic acid in the pH range 3 to 12 (Boyko and Goodgame, 1986) both reduce Cr(VI) to Cr(III), accompanied by the production of a Cr(V) intermediate product. Water-soluble soil organic matter was found to reduce Cr(VI) in the acidic to neutral pH range (Bloomfield and Pruden, 1980; Bartlett and Kimble, 1976). These reports have established that SHSs reduce Cr(VI) occurs over a range of pH values and that reduction is more rapid at low pH.

The research described in the literature has established that pH is important in determining the rate of Cr(VI) reduction by SHSs. However, the literature appears to be lacking in kinetic data on Cr(VI) reduction reactions by SHSs. A report by Eckert et al. (1990) on the reduction of Cr(VI) at sub-µg/L levels by fulvic acid is the only research on the kinetics of Cr(VI) reduction by SHSs known to the author. Eckert et al. (1990) calculated a pseudo-first-order reaction rate constant of 5.28×10^{-5} $\sec^{-1}$ at 25°C and pH 2. Sub-µg/L levels of Cr(VI) are typical of clean natural waters, thus these reaction kinetics may not apply to rates at the higher Cr(VI) concentrations found at contaminated sites. The research reported here describes laboratory experiments conducted to elucidate factors affecting the rate of reduction of Cr(VI) by SHSs.

This thesis incorporates the knowledge of Cr(VI) reduction reactions with simple organic compounds in the kinetic analysis. Many Cr(VI)-organic reactions at constant pH are first order with respect to both the organic and bichromate concentrations (Wiberg, 1965). Experimental evidence indicates that Cr(VI) reduction by alcohols (Lee and Stewart, 1967; Sengupta et al., 1986), thiols (Connett and Wetterhahn, 1986; Brauer and Wetterhahn, 1991), and phenolic compounds (Elovitz, 1993) occurs through formation of a chromate ester. The decomposition of the Cr(VI)-ester is the rate-limiting step in the reduction. A study of Cr(VI) reduction by substituted phenolic compounds (Elovitz, 1993) reveals that both substituent group composition and position can affect the rate of reduction by several orders of magnitude. Rates of Cr(VI) reduction vary by more than an order of magnitude for compounds containing the same reductive functional group (Stone et al., 1993). Humic substances contain a variety of reductive functional groups in many molecular configurations, leading to the possibility that Cr(VI) reduction by humics may behave similarly to a collection of these reactions.

Purpose and Relevance of Research

Decisions concerning the remediation of Cr-contaminated sites require the knowledge of chromium redox reactions that can occur in soils. More specifically, some researchers have suggested that subsurface environments have the ability to naturally reduce Cr(VI) and immobilize it in the soil as Cr(III) hydroxides. Such "natural attenuation" could decrease the potential risk exposure without the need for additional costly remediation measures. For example, active remediation efforts such as pump-and-treat are unlikely to achieve drinking water standards in any reasonable period of time. As chromium concentrations decrease, the decision must be made concerning concentrations of Cr(VI) that can be safely left in the ground. If the remaining haxavalent chromium can be reduced and immobilized in the soil, the pump-and-treat operation can be terminated. Likewise, if initial concentrations of Cr(VI) are only slightly above the maximum concentration level (MCL), a decision must be made whether an active remediation effort is required or if natural attenuation will achieve the desired level of environmental protection.

The feasibility of natural attenuation depends on the soil's reduction capacity and on rates of Cr(VI) reduction occurring at the site. While the reduction capacities of many soils are far greater than needed to reduce all of the hexavalent chromium contamination, the Cr(VI) persists in the soils for long periods of time. Thus, the limiting factor concerning natural attenuation is the rate of reduction. Although there are several reductants capable of reducing Cr(VI), SHSs are likely to be the most important ones in soils. This work addresses the need for kinetic data on Cr(VI)-SHSs redox reactions by building an empirical rate law based on experiments conducted under conditions that might be expected in soil environments. Information from this research can ultimately be used to develop more practical transport models that determine the potential for hexavalent chromium reduction in environmental systems. The results will contribute to better planning of expensive subsurface remediation measures and establishment of appropriate cleanup goals.

Outline of Thesis

The following chapters of this thesis describe the results of research on the redox interactions between Cr(VI) and soil humic substances. Chapters 2 through 4 are written as research papers to be submitted for publication, and as such the writing styles in these chapters reflect the format of the individual publication.

Chapter 2 focuses on the development of an empirical rate law for Cr(VI)/SFA reactions. Chapter 3 details the application of the Cr(VI)/SFA rate law to Cr(VI)/SHA reactions and discusses Cr(VI) reduction by various SHAs. The results identify the overall rates of reaction and describe variations in reduction rates due to variation in Cr(VI), SHS and H^+ concentrations. Experiments discussed in Chapters 2-4 were conducted with excess SHA over Cr(VI). Such concentrations would be typical of a site with a moderate level of Cr contamination and average SHS concentrations. Chapter 2 has been submitted to *Environmental Science and Technology*. Chapter 3 was written for submission to the *Journal of Soil Science*.

Chapter 4 characterizes the response of the reaction rates to variations in ionic strength, background electrolyte, temperature and the presence of redox-active elements in solution. A model for the redox cycling of Fe, alternatively acting as an electron acceptor from the SHA and electron donor to the Cr(VI), is presented. This chapter was written to be submitted to *Applied Geochemistry*.

The overall conclusions of this work are summarized in Chapter 5. The relevance of this work to environmental systems is discussed in terms of reaction timescales and the "natural attenuation" of chromium in soils and sediments.

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CHAPTER 2

Reduction of Cr(VI) in the Presence of Excess Soil Fulvic Acid

Abstract

The hazardous form of chromium (Cr(VI)) has been shown to be reduced to the less toxic form (Cr(III)) by naturally occurring organic compounds in soils such as fulvic acids. The rate of hexavalent chromium reduction by a soil fulvic acid (SFA) has been measured in aqueous solutions where concentrations of Cr(VI), H^+, and SFA were independently varied. The results clearly demonstrate that Cr(VI) can be reduced by SFA under a variety of conditions. Rates of reduction increase strongly with decreasing pH. Typical Cr(VI)-SFA reactions display a nonlinear reduction of Cr(VI) with time, that cannot adequately be modeled by either first-order or second-order rate equations. An empirical rate law that treats the SFA as a continuum of reactive

groups which reduce Cr(VI) at varying rates adequately describes the effects of solution parameters on the rates of Cr(VI) reduction. The rate law is

$$R=-k''[HCrO_4^-][SFA]_0[H^+]^m$$

where the rate coefficient (k'') varies with the equivalent fraction (X_e) of SFA reducing equivalents oxidized. The apparent rate coefficient can be written as kX_e^n, where k is 7.5×10^{-5} sec^{-1} and n is -1.12±0.04. The order (m) with respect to the proton concentration is 0.45±0.03. Rate experiments were conducted with an excess of SFA over Cr(VI) and the model is based on experiments where up to 5% of the SFA was oxidized.

Introduction

The extensive use of chromium in the metallurgic, leather tanning, electroplating, lumber, electricity generating and other industries has resulted in numerous sites where aqueous chromium has been released to the subsurface (1-5, 6). Chromium can be acutely toxic, carcinogenic, mutagenic and teratogenic (7-11). To evaluate potential risk of Cr exposure to public health and to develop effective remediation plans for contaminated sites, we must understand the processes governing the transport and fate of chromium in the environment. Since both the mobility and toxicity of Cr depend on its oxidation state, redox reactions involving Cr are extremely important in determining its fate in the environment and its risk to human health.

While chromium oxidation states range from -2 to +6 (12), the +3 and +6 states are most prevalent in the environment. The hexavalent form is more toxic and generally more mobile than trivalent chromium (13,14). The hexavalent chromium anions chromate (CrO_4^{2-}), bichromate ($HCrO_4^-$), and dichromate ($Cr_2O_7^{2-}$) are not strongly sorbed to many soils under alkaline to slightly acidic conditions (15), thus they can be very mobile in subsurface environment. In contrast, Cr(III) readily precipitates as $Cr(OH)_3$ or as the solid solution $Fe_xCr_{1-x}(OH)_3$ under alkaline to slightly acidic conditions (16,17). Cr(III) can also be chelated by organic molecules that are adsorbed to mineral surfaces (18,19).

Cr(VI) can be reduced to Cr(III) in soils by redox reactions with aqueous inorganic species, electron transfers at mineral surfaces, reaction with nonhumic organic substances such as carbohydrates and proteins, or reduction by soil humic substances (2). In a study of chromate reduction by various soils, Eary and Rai (20) concluded that Cr(VI) reduction by organic matter and Fe(II) were roughly equivalent with respect to total reduction capacity. Soil humic substances, which constitute the majority of the organic fraction in most soils, thus represent a significant reservoir of electron donors for Cr(VI) reduction. In this paper, we focus on fulvic acid, which constitutes roughly 25-75% of humic substances in soils (21). It is defined as the humic fraction that is soluble under all pH conditions (22).

While the reduction of Cr(VI) by soil organic matter has long been recognized, little is known about the reaction rates or processes likely to occur under environmental conditions. The relatively few investigations of redox reactions involving humic substances indicate that FA can reduce a variety of metal ions. Reduction reactions have been observed in the presence of fulvic acid for the Fe(III)/Fe(II), Hg(II)/Hg(0), I(0)/I(-1), I_3^-/I(-1), V(V)/V(IV), and Cr(VI)/Cr(III) redox couples (23-28, 28). Reported standard redox potentials of 0.7 V for an HA and 0.5 V for a FA suggest that FA is a better reducing agent than HA (23-26). Reduction of Cr(VI) by a reference surface water fulvic acid has been observed at the sub-µg/L levels of Cr(VI), typical of clean natural waters (29). Eckert et al. (29) calculated a pseudo-first-order reaction rate constant of 5.28×10^{-5} sec^{-1} at 25°C and pH 2. Rates of Cr(VI) reduction by FA at levels typically found at contaminant sites have not been addressed.

In this paper, we describe a series of laboratory experiments which quantify the rate of Cr(VI) reduction by a soil fulvic acid (SFA). The major goals of these experiments are to determine the variability of Cr(VI) reduction rates as a function of pH, Cr(VI) concentration, and SFA concentration and to develop an empirical rate law for Cr(VI)/SFA reactions.

Experimental Section

Materials. Soil fulvic acid (SFA) was obtained from the International Humic Substances Society (IHSS) collection of reference humic materials (ref. # 1R102F). NMR Spectra have been reported by other researchers (30). The elemental composition of the fulvic acid used is summarized in Table 2.1. Solutions were prepared with ultrapure (~18 mega-ohm) water from a Nanopure water purification system (Barnstead, Dubuque, IA). All chemicals were reagent grade. The glass reaction vessels were foil-wrapped to prevent photo-reactions.

Analytical and Experimental Methods. The maximum quantity of reducing equivalents per milligram of SFA was determined by a modified Walkley-Black method (31). A mixture of 0.4 mL of 1000 mg/L SFA and 0.2 mL of 20 mM Cr(VI) solution was added to 2.0 mL of conc. H_2SO_4 in a glass centrifuge tube. The reaction vessel was kept in a water bath at 90°C and Cr(VI) concentrations were monitored over time. The reactions were complete after approximately 60 min. The number of SFA reducing equivalents is calculated as three times the difference between initial and final Cr(VI) concentrations (mmol/L) divided by the concentration of SFA used (mg/L).

The reduction of Cr(VI) by SFA was determined by measuring the time-dependent concentration of Cr(VI) in reaction vessels (foil-wrapped scintillation vials). Experiments were performed in triplicate tests at room temperature (25±2°C). Reduction experiments were conducted with excess (20 to 400x) SFA as determined from the modified Walkley-Black tests. The background electrolyte was 0.1 M LiCl. Lithium ion was used as the background cation because it does not exhibit site-specific binding with humic acid (32).

Several experiments determined the effect of pH on the rate of Cr(VI) reduction by SFA. Aliquots (20 mL) of a stock solution containing 100 mg/L SFA were equilibrated for 24 h. at pH 1, 2, 3, 4, 5, 6 and 7 before being spiked with 0.02 mM Cr(VI). The pH was maintained within ±0.1 pH unit by additions of H_2SO_4 or LiOH. For pH ≤ 5 the change in pH during an experiment was <0.05 units. Cr(VI) concentrations were measured over time by mixing a 0.5 mL sample with 0.1 ml of diphenylcarbazide (DPC) and 2.0 mL of 0.1 N H_2SO_4 (33). This solution was then filtered through a 0.1µm polysulfonate filter. Ten minutes after the DPC addition, the absorbance at 540 nm was measured.

A similar set of rate experiments was conducted at a fixed pH of 2.0, an initial SFA concentration of 100 mg/L, and initial Cr(VI) concentrations of 0.01, 0.02, 0.05, 0.1 and 0.2 mM to determine reduction rates as a function of initial Cr(VI) concentration. A third set of batch experiments was performed at pH 2.0, an initial Cr(VI) concentration of 0.02 mM, and with initial SFA concentrations of 25, 50, 100, 150, 200, and 250 mg/L.

Additional experiments designed to test the applicability of the empirically derived rate law were conducted. The first involved spiking a 40 mL aliquot of 100 mg/L SHS solution at pH 2.0 with 0.1 mM Cr(VI) and monitoring Cr(VI) loss over time. When there was no detectable Cr(VI) remaining in solution (<1.0 µmol/L), another spike of Cr(VI) was added. The second type experiment was to monitor

Cr(VI) reduction rates in 40 mL solutions of 100 mg/L SHS spiked with 0.8 mM Cr(VI). These experiments allow us to determine reduction rates over a greater fraction of SHS and a greater Cr(VI) concentration than was used to establish the rate law.

An EPR spectroscopic study of Cr(VI)/SFA solutions was conducted in the g=2 region using a Varian E-109 EPR spectrometer with a flat quartz cell. A solution of 100 mg/L SFA adjusted to pH 2 with H_2SO_4 was spiked with 5.0 mM Cr(VI). EPR studies were made at X-band frequency (9.5 GHz) and monitored for approximately one hour after spiking with Cr.

Results

SFA Reducing Capacity. The modified Walkley-Black tests are a measure of the reducing capacity of the SFA. That is, it reveals the amount of Cr(VI) reducible by SFA under extremely acidic conditions. The concentration of reducing equivalents available in the IHSS reference SFA as determined by the modified Walkley-Black tests is 37.5±2.1 μmole Cr/mg SFA = 112.5±6.3 μeq/mg SFA. This value is used here as the initial concentration of SFA reducing equivalents, $[SFA]_0$. Using carbon concentrations in the SFA (Table 2.1) and the results from the Walkley-Black tests we calculate the number of reducing equivalents per carbon to be approximately 2.7.

In all of the rate experiments used to determine the form of the rate equation, less than 5% of the SFA reducing equivalents were oxidized. Thus, the rates of reduction determined in these tests represent the rates of reduction by the most reactive groups in the SFA. Rates are expected to decrease as a larger fraction of the SFA is oxidized, with only the more recalcitrant components remaining.

pH Effects. Reduction of Cr(VI) was observed at all pH values in the range 1 to 7. As expected, the rates of reduction are strongly pH dependent, the rate increasing with decreasing pH (Fig. 2.1). A typical Cr(VI)-SFA reaction is characterized by a nonlinear decline in [Cr(VI)] with the rate of reduction diminishing with time. Plots of log relative Cr(VI) concentration versus time display a linear trend after an initial rapid loss of Cr(VI) (Fig. 2.2). The rapid initial drop is likely due to functional groups that are much more reactive than the bulk of reduction sites in the fulvic acid. Other possible explanations for this initial decrease could be adsorption or complexation. Since fulvic acid is a dissolved constituent and Cr(VI) concentration did not increase in our blanks, adsorption can be ruled out. Complexation of fulvic acid with the chromate species cannot be dismissed as easily.

It is believed that chromate ester formation is a precursor to reduction of Cr(VI) (12). Elovitz (34) suggests that chromate-ester formation for phenols is rapid, reversible, and independent of pH. He found that chromate-phenol ester formation is essentially instantaneous in the pH range 2 to 5. Our results at early times are very pH dependent, and although the initial decrease in Cr(VI) concentration is rapid, it is not instantaneous. Additionally, the strong binding of Cr(VI) to DPC should complex the Cr(VI) which is weakly bound as chromate esters. This suggests that we are observing reduction of Cr(VI) rather than just chromate-ester formation. Our results show a strong pH dependance at early times, which is when complexation/ester formation would be expected to occur. Thus, it is likely that the observed rapid decrease is due to Cr(VI) reduction rather than complexation.

EPR Spectra. The EPR spectrum in the g=2 region for aqueous solutions of SFA and K_2CrO_7 has a Cr(V) band which matches that identified by Boyko and Goodgame (27, 27) in their Cr(VI)/SFA study (Fig. 2.3). In contrast to their study, we did not identify a Cr(III) band. We did observe a precipitate and suspect it to be similar to their Cr(III)-fulvic acid precipitate. In our study, the Cr(V) signal was present during the first scan (~7 min after Cr(VI) spiking), became broader during repeated scans and was still apparent though greatly diminished after 45 minutes. Similar observations were made by Boyko and Goodgame (27, 27).

Effect of Initial Cr(VI) Concentration. The relative rate of Cr(VI) reduction at pH 2 decreases with increasing initial Cr(VI) concentrations in the range $[Cr(VI)]_o$ = 0.01 mM to 0.2 mM (Fig. 2.4a). The shape of the plots of the log of relative concentration versus time in Fig. 2.4 is similar to those in Fig. 2.2 in that there is an initial rapid drop in Cr(VI) concentration which becomes linear at later times.

Effect of SFA Concentration. The rate of Cr(VI) reduction at pH 2 increases with increasing SFA concentration in the range $[SFA]_0$ = 25-250 mg/L. The reaction is characterized by a non-linear decline in Cr(VI) concentration with time. As is the case with both various pH and various initial Cr(VI) concentration, plots of log relative Cr(VI) concentration versus time appear linear after an initial rapid drop (Fig. 2.4b).

Effect of Evolving SHS Composition. The multiple spiking experiment and the higher initial Cr(VI) tests were conducted to determine how the rates of reduction change as a greater fraction of the SFA is oxidized. As the fraction of SFA oxidized becomes greater, one would expect that the more reactive components to be oxidized first, and only the more recalcitrant components remain. The multiple spiking experiment shows a decrease in Cr(VI) reduction rate with each successive addition of chromate (Fig. 2.5). The experiments with 0.8 mmol/L initial Cr(VI) show a nonlinear rapid loss of Cr(VI) at the beginning, followed by a much slower reduction of chromate (Fig. 2.6). This is similar to the behavior observed in experiments with much smaller concentrations of chromate.

Discussion

Development of Rate Law. The key objective of this study is to develop a rate law for Cr(VI)/SFA reactions. Due to the poorly defined structure of fulvic acids, this rate law must ultimately be empirical rather than mechanistic. Nonetheless, we can incorporate the knowledge of the reactions for simple organic compounds into the development of a rate equation. We determined reaction order with respect to Cr(VI) by establishing pseudo-zeroth-order conditions with respect to SFA concentration (20-200 fold excess SFA) and $[H^+]$ (constant pH).

Plots of log (C/C_0) versus time (Figures 2.2, 2.4) exhibit an initial curved portion where [Cr(VI)] drops rapidly before becoming linear for the remainder of the experiment. This behavior suggests that after some initial fraction of the SFA has been oxidized, the reaction is first-order with respect to Cr(VI). When plotted on a second-order type plot of $[(1/C)-(1/C_0)]$ versus time, the data do not plot on a straight line but instead display a continually increasing slope (Fig. 2.7), indicating that the reaction is not second-order.

An alternative to a purely first-order or second-order reaction is a multi-component model. For example, discrete multi-component models have been used to describe the degradation of natural organic matter (35-37). These models assume that organic matter is composed of a finite number of components, each with a different reactivity. A similar approach can be used to describe the reduction of Cr(VI) by soil humic substances.

In developing a general rate law for the reduction of Cr(VI) by soil fulvic acid, we rely on studies of simple organic compounds as models. Studies of the reduction of Cr(VI) by alcohols (38-41) and phenolic compounds (34) indicate that the first step in the reduction is the formation of the chromate ester

$$HCrO_4^- + ArOH \underset{k_r}{\overset{k_f}{\rightleftharpoons}} [HCrO_4^- \bullet ArOH] \tag{1}$$

Chromate ester formation is believed to be fast and reversible. Elovitz (34) found essentially instantaneous chromate-phenol ester formation in the pH range 2-5. The electron transfer occurs during the irreversible decomposition of the ester. The decomposition

$$[HCrO_4^- \bullet ArOH] \xrightarrow{k_d} products \tag{2}$$

is the rate limiting step. The chromate ester formation is thought to be less dependent on pH than is the redox step (34). At constant pH, the rate of reduction of Cr(VI), R, should follow

$$R = -k_d[HCrO_4^- \cdot ArOH] = -k_d K_e[HCrO_4^-][ArOH] \tag{3}$$

where K_e is the equilibrium constant for the chromate-ester formation (= k_f/k_r). Setting (k_dK_e) equal to k''' yields

$$R = \frac{d[Cr(VI)]}{dt} = -k'''[HCrO_4^-][ArOH] \tag{4}$$

Many Cr(VI)-organic reactions at constant pH follow a rate law similar to Eq. 4 (42). The reaction is first order with respect to both the organic and bichromate concentrations. We expect the reduction of Cr(VI) by any single functional group in SFA to follow a similar rate law. If these reactions occur in parallel, then the overall rate of Cr(VI) reduction by SFA is simply the sum of these individual reactions

$$R=\left(-\sum_{i=1}^{n}k_i'''[SFA_i]\right)[HCrO_4^-] \tag{5}$$

where k_i''' are the rate coefficients and $[SFA_i]$ are the concentrations of reducing equivalents for each of the reactive functional groups. Eq. 5 can be written in terms of the fraction of reducing equivalents in the functional group i ($f_i = [SFA_i]/[SFA]$), where [SFA] denotes the total concentration of reducing equivalents

$$R=\left(-\sum_{i=1}^{n}k_i'''f_i\right)[SFA][HCrO_4^-] \tag{6}$$

If we define an overall rate coefficient, k'', by

$$\sum_{i=1}^{n}k_i'''f_i=k'' \tag{7}$$

we obtain a rate law similar to Eq. 4, except that the rate coefficient, k'', depends on the fraction of reducing equivalents of the amount of SFA oxidized. The experiments described here were conducted with excess SFA to minimize changes in equivalent fraction of the functional groups.

Our data can be fit to a discrete model with two components, a fast reacting component of finite quantity and a slower reacting component present in excess quantity relative to the oxidant. Such a multi-component system is illustrated in Figure 2.8 where SFA_1 and SFA_2 are the rapid and slower reactive components, respectively, in the SFA. A rate law for the model just described is given by Eq. (6) with n=2. However, Middleburg (43) points out that such a model, which relies on graphical analysis to extract the number of types of reactive functional groups, results in the identification of only two or three types regardless of the actual number involved. This is evident from a comparison of rate coefficients determined from the linear segments of the first-order plots in Figure 2.4a. Plots of the observed rate coefficient (k'') for SFA_2 versus $[Cr(VI)]_0$ (Fig. 2.9) show that the first-order rate coefficient is not the same for all experiments. This implies that k changes as the fraction of SFA oxidized changes. If it were truly a simple two-component system, the rate coefficient would remain constant as the fraction of SFA oxidized changes.

Another multi-component model is the continuum version, which considers an infinite number of reactive groups such that the rate coefficient k is a continuously varying parameter (44-48). The overall rate coefficient, k'', is a function of the distribution of reactive groups in the organic matter. In theory, a continuum model for fulvic acids makes more sense than a discrete multi-component model. Fulvic acids contain a variety of substituent groups in numerous configurations on the molecules, the reactivities of which are likely to vary widely depending on their local environment. Thus, it is unlikely that the reactivity of the SFA as a whole could be neatly divided into a small number of discrete components.

We apply a continuum model to our data with the apparent first-order rate coefficient varying as a function of the reducing equivalent fraction (X_e) of the SFA which has been oxidized. The distribution of reactivities of the SFA are empirically derived from our experiments. For a fixed pH, we assume the reactions follow a rate law of the form

$$R=-k''[Cr(VI)][SFA] \tag{8}$$

where k'' is the observed first-order rate coefficient during the reaction. Since we define our concentrations of SFA in terms of reducing equivalents, we can calculate the fraction of SFA oxidized from the amount of Cr(VI) reduced during the experiments.

Rate expressions for Cr(VI)/organic reactions are often expressed in terms of

$[HCrO_4^-]$, because bichromate is believed to be the reactive species (34,42). We can recalculate our apparent rate coefficient in terms of bichromate using the relationship

$$\frac{[HCrO_4^-]}{[Cr(VI)]_{tot}} = \frac{\{H^+\}}{K_{Cr}(\gamma_1/\gamma_2)+\{H^+\}} \tag{9}$$

where K_{Cr} is the acid dissociation constant for $HCrO_4^-$ and γ_1 and γ_2 are the activity coefficients calculated using the Davies equation for bichromate and chromate, respectively. We combine Eq. 8 and Eq. 9 with the equality $[SFA] = [SFA]_0\,(1-X_e)$ to yield a rate law in terms of bichromate

$$R=-k''[HCrO_4^-][SFA]_0(1-X_e) \tag{10}$$

where k'' is the observed rate coefficient divided by the right-hand term in Equation 9.

Plots of log k'' versus log X_e for experiments at a constant pH and with the fraction of SFA oxidized varying (Fig. 2.10a & b) display linear relationships. The observed rate coefficient at a given X_e was calculated for our data using a central difference approximation of the first derivative between sampling intervals. The total fraction oxidized was varied using several $[Cr(VI)]_0$ or $[SFA]_0$. A plot of log k'' versus log X_e (Fig. 10a) for the various $[Cr(VI)]_0$ experiments displays a linear relationship with a mean slope of -1.26±0.05 (df = 49). A similar plot for the various $[SFA]_0$ experiments (Fig. 10b) also displays parallel linear relationships for each independent test. These curves have a mean slope of -0.88±0.05 (df =81)(Table 2.2). There is good agreement between the experiments with differing $[Cr(VI)]_0$ and those with various $[SFA]_0$. The exponent for X_e, n, can be calculated from the slope of the line, and a new rate coefficient (k') from the y-intercept of the line (Table 2.2). A t-test indicates that observed slopes are not significantly different from -1.0 at the 90% confidence level. The rate equation for chromate reduction by SFA at a given pH is then

$$R=-k'X_e^n[HCrO_4^-][SFA]_0(1-X_e) \tag{11}$$

The variation of the rate coefficient, k', as a function of H^+ was investigated by a comparison of the experiments at various pH's. A plot of log k'' versus log X_e (Fig. 2.11) yields an array of subparallel lines with slopes of n and intercepts of log k' (Table 2.2). As is the case for the previously discussed experiments, the exponent of X_e for these experiments (n) is close to -1. A plot of log k' versus log $[H^+]$ (Fig. 12a) displays a roughly linear trend with a slope equal to the reaction order (m) for $[H^+]$ (0.35±0.13) and an intercept of log k. The considerable variance in the calculated coefficients is the result of employing a finite difference approximation to the derivative using the raw data curves. To overcome this numerical limitation, we used the integrated form of Eq. 11 to calculate the rate coefficients, k', with the raw data. The term $(1-X_e)$ was left out of the integration since it is roughly equal to one (0.995) for the experiments at various pH values. This method allowed us to obtain more precise results because the data is smoothed by the regression process. The reaction order with respect to $[H^+]$ is the slope the plot of log k' versus log $[H^+]$ (Fig. 2.12b). When we apply this criteria to our data, the calculated reaction order for $[H^+]$ is 0.45±0.03. We now can include $[H^+]$ in the rate law to yield

$$R=-kX_e^n[HCrO_4^-][SFA]_0(1-X_e)[H^+]^m \tag{12}$$

where log k = -4.12±0.15 s^{-1}. The non-integer value for the order with respect to $[H^+]$ is not surprising considering the empirical nature in which it was derived. It suggests that the parallel reactions involve different numbers of electron transfers. Elovitz (34) found that the rate dependence of Cr(VI) reduction by phenols was governed by three parallel redox pathways involving zero, one and two protons. Oxidation products of that study indicate that both one- and two-electron transfers occur.

If one- or two-electron transfers occur, the intermediate oxidation states, Cr(V) and Cr(IV) can form. However, these intermediate products are believed to be transient species that are short-lived (27, 27). The results of our EPR study demonstrate that Cr(V) is indeed present as an intermediate product in the reduction of Cr(VI) to Cr(III) by SFA. It has been reported that the DPC analysis measures not only Cr(VI) but also about 60% of the Cr(V) (49). Thus, our empirical interpretation can more generally be described as the reduction of DPC-measurable chromium to Cr(III).

Extension of Rate Law. The multiple spiking and the 0.8 mM $[Cr(VI)]_0$ experiments were designed to determine if the rate law previously described is applicable as the fraction of SHS oxidized becomes larger. The data from the multiple spiking experiments can be modeled extremely well using the optimal rate constant determined from the integrated form of the rate law (Fig. 2.5). The model begins to deviate from the observed data during the third spiking event. In contrast, using the rate constant calculated in earlier experiments, the model accurately predicts the third spiking event while predicting longer times for the first two events. The higher Cr(VI) experiment can be modelled extremely well using the optimal rate coefficient (r^2 = 0.995) (Fig. 2.6). The model using the previously computed rate coefficient slightly underpredicts reaction times. A plot of the log of the apparent rate coefficient versus the log of the fraction of SFA oxidized show a linear relationship (Fig. 2.13), with a slope of -1.01±0.18, indicating that the assumption of a value of -1.0 for the exponent on X_e is probably a valid one.

Conclusions

Soil fulvic acid effectively reduces Cr(VI) in aqueous solution in the pH range

1-7, with the Cr(VI) reduction rate increasing with decreasing pH, increasing $[SFA]_0$ and increasing $[Cr(VI)]_0$. The rate of reduction is non-linear and cannot be adequately described by either a first- or a second-order rate law.

A multi-component model that describes the interaction of a complex macromolecule such as fulvic acid with a reactive species such as chromium can describe the reaction with functional groups that react at different rates. While only a small fraction of the SFA is oxidized during our experiments, it is likely that numerous parallel reactions with functional groups of widely varying reactivities are involved. A reactive continuum model which sufficiently describes the Cr(VI)-SFA redox reactions was developed. In this model, the rate coefficient is a continuously varying parameter, the value of which is determined by the fraction of SFA reducing equivalents that have been oxidized. The rate model is valid in the pH range 1-7, Cr(VI) concentrations from 0.02 to 0.8 mM and SFA concentrations from 25-250 mg/L. Our results clearly show that the reactivity of even a small fraction of the SFA varies over several orders of magnitude.

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Table 2.1. Elemental Analysis of IHSS Reference Fulvic Acid (IHSS # 1R102F)

Sample	C	H	O	N	S	P	Ash
USGS[1]	50.08	3.98	42.26	2.66	0.62	0.05	0.79
OGI[2]	47.58	4.05	n.a.	4.27	n.a.	n.a.	n.a.

1. Values reported by IHSS as weight percent on an ash-free moisture-free basis.

2. Values determined by OGI on Carlos Erba Instruments NA 1500 Series 2 N/C/S Analyzer. Means of duplicate samples. n.a. = not analyzed.

Table 2.2. Calculated rate coefficients (k') and reaction order (n) with respect to X_e for each set of triplicate experiments conducted.

$[Cr]_{init}$	$[SFA]_0$	pH	log k'	n	r^2
0.01	100	2	-4.81±0.08	-1.25±0.10	0.997
0.02	100	2	-5.02±0.14	-1.02±0.09	0.992
0.05	100	2	-5.28±0.34	-0.82±0.14	0.95
0.1	100	2	-5.45±0.45	-0.91±0.16	0.91
0.2	100	2	-5.70±0.13	-0.97±0.11	0.996
0.02	25	2	-5.06±0.11	-0.80±0.07	0.97
0.02	50	2	-5.16±0.21	-0.91±0.09	0.98
0.02	100	2	-4.81±0.08	-1.13±0.11	0.997
0.02	150	2	-5.28±0.05	-1.08±0.17	0.999
0.02	200	2	-5.18±0.15	-1.26±0.15	0.993
0.02	250	2	-5.06±0.19	-0.79±0.18	0.99
0.02	100	1	-4.57±0.08	-1.16±0.22	0.998
0.02	100	2	-5.02±0.13	-0.80±0.05	0.997
0.02	100	3	-5.78±0.20	-0.94±0.10	0.99
0.02	100	4	-6.03±0.63	-0.35±0.10	0.93
0.02	100	5	-6.52±0.54	-0.62±0.16	0.93
0.02	100	6	-6.59±0.29	-0.44±0.06	0.95
0.02	100	7	-7.48±0.40	-0.77±1.07	0.96

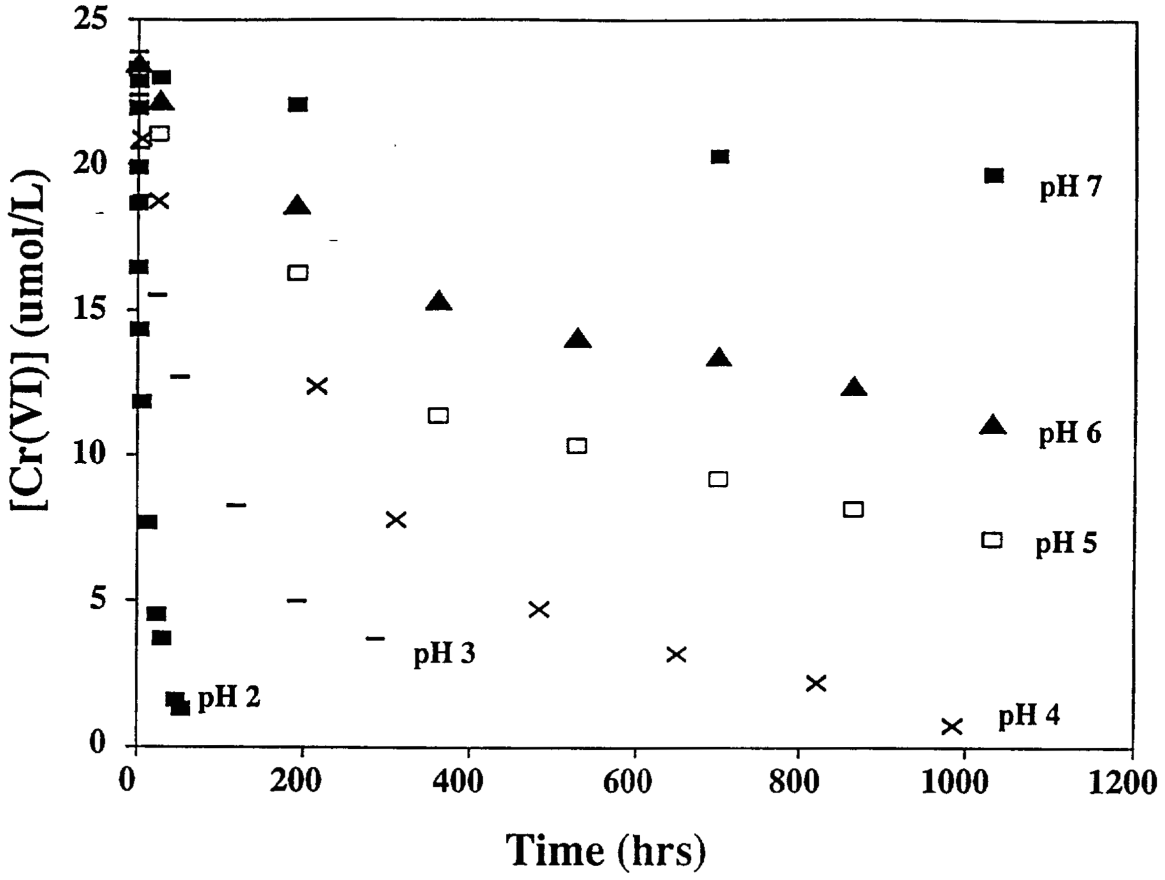


Figure 2.1. Reduction of Cr(VI) by soil fulvic acid. Plot of Cr(VI) concentrations as a function of time for batch experiments at various pH. Points represent means of triplicate experiments for each pH. $[Cr(VI)]_0$ = 0.02 mM, $[SFA]_0$ = 100 mg/L.

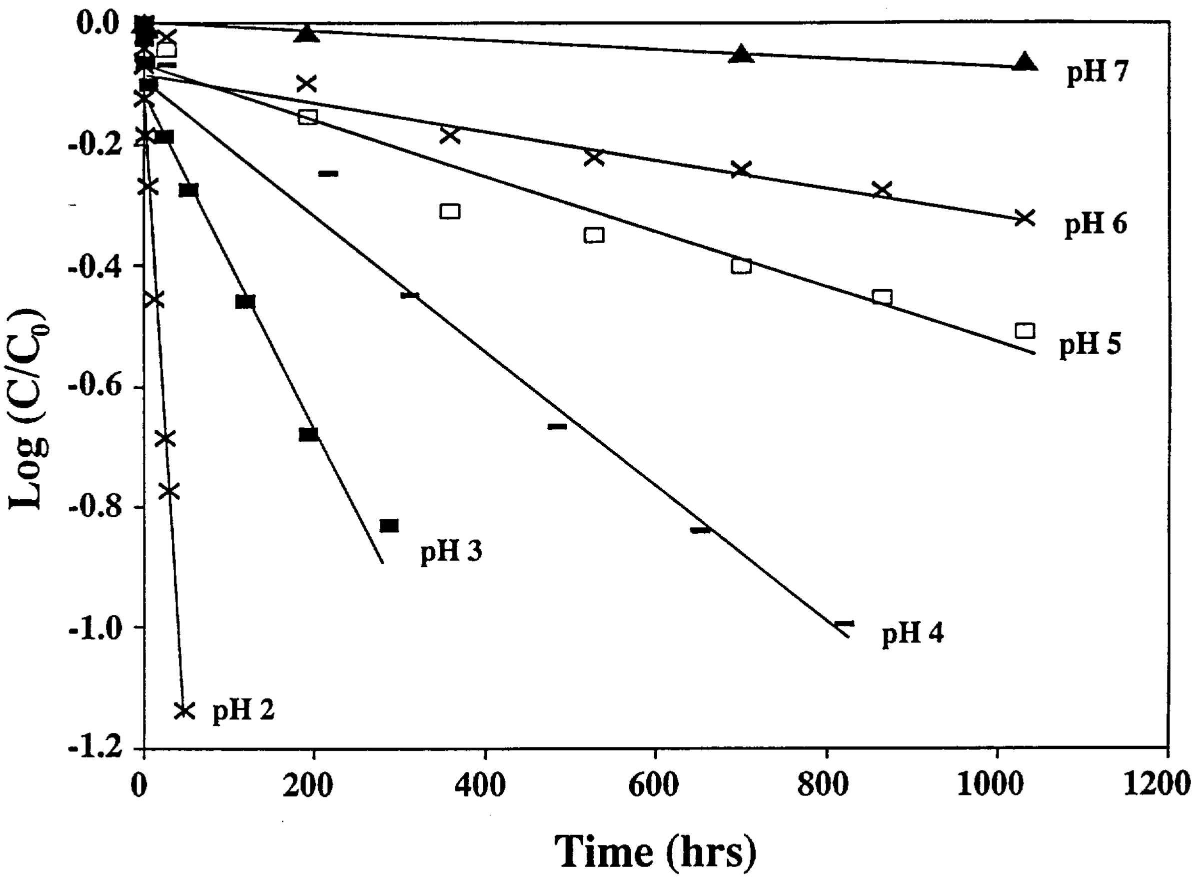


Figure 2.2. Typical first-order plot of log relative Cr(VI) concentration versus time for experiments at various pH.

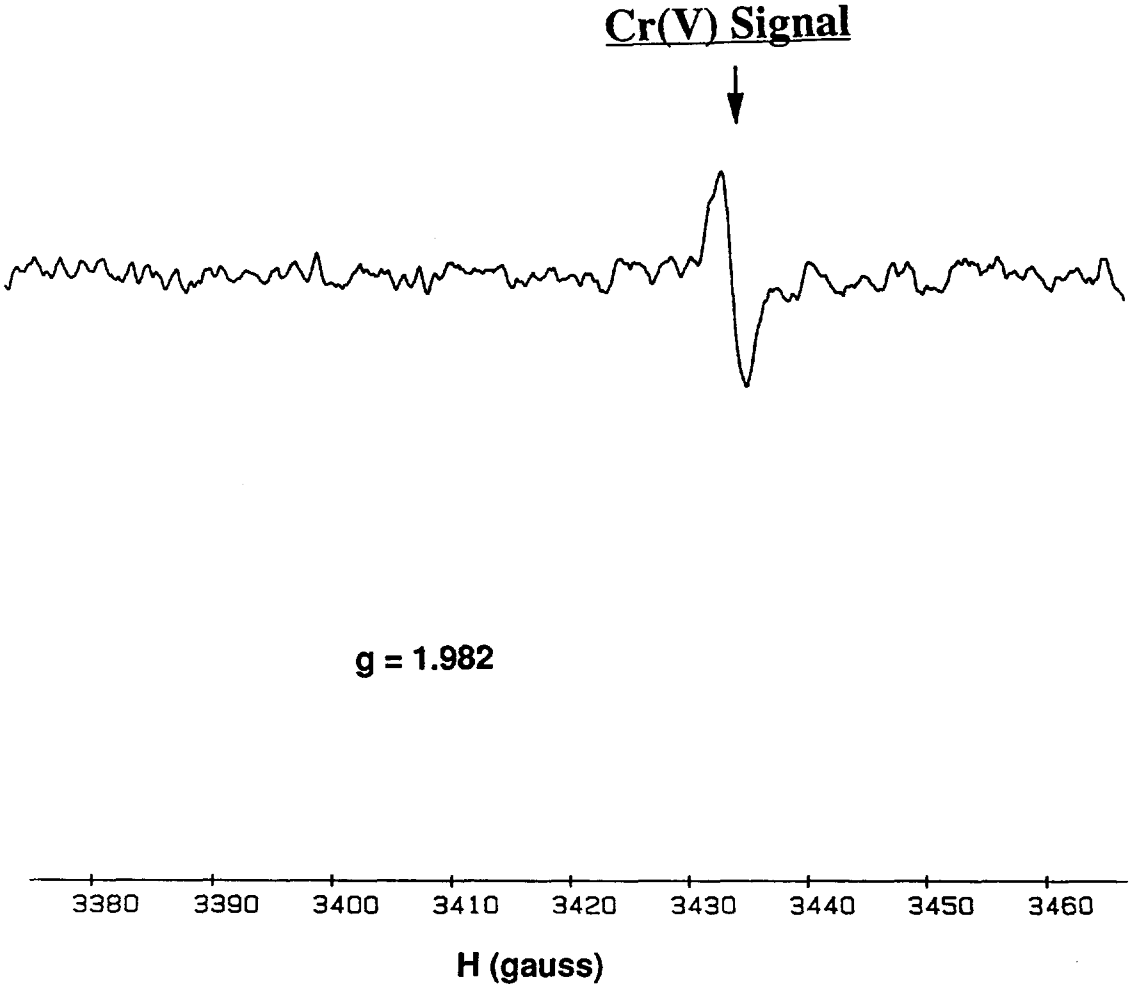


Figure 2.3. EPR spectrum of a solution of 100 mg/L SFA and 5.0 mM Cr(VI) at pH 2.0.

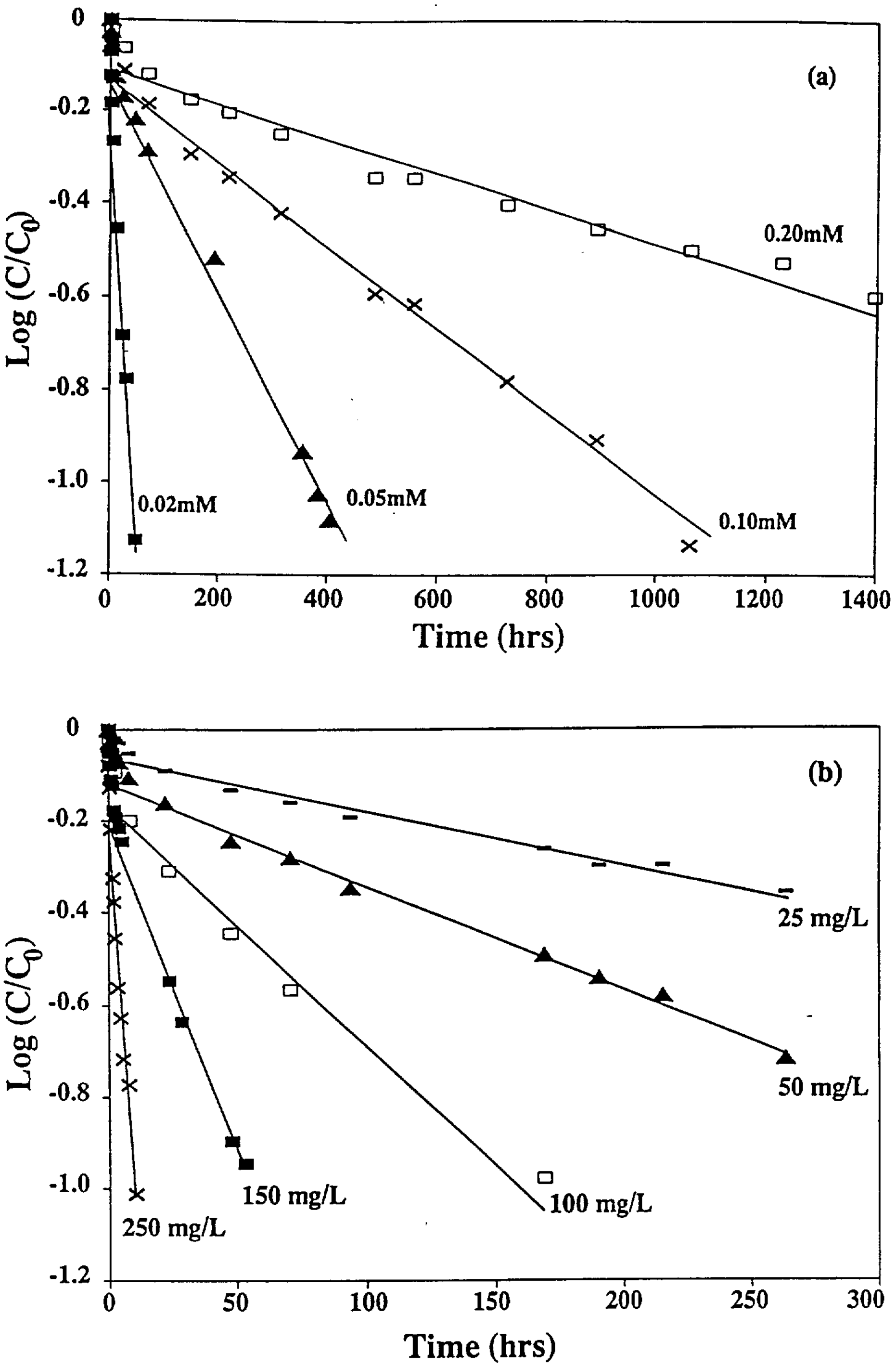


Figure 2.4. Pseudo-first-order plots of log relative Cr(VI) concentration versus time for experiments a) with various $[Cr(VI)]_0$ and b) at various $[SFA]_0$. Reactions were performed at pH = 2 and I = 0.1 M.

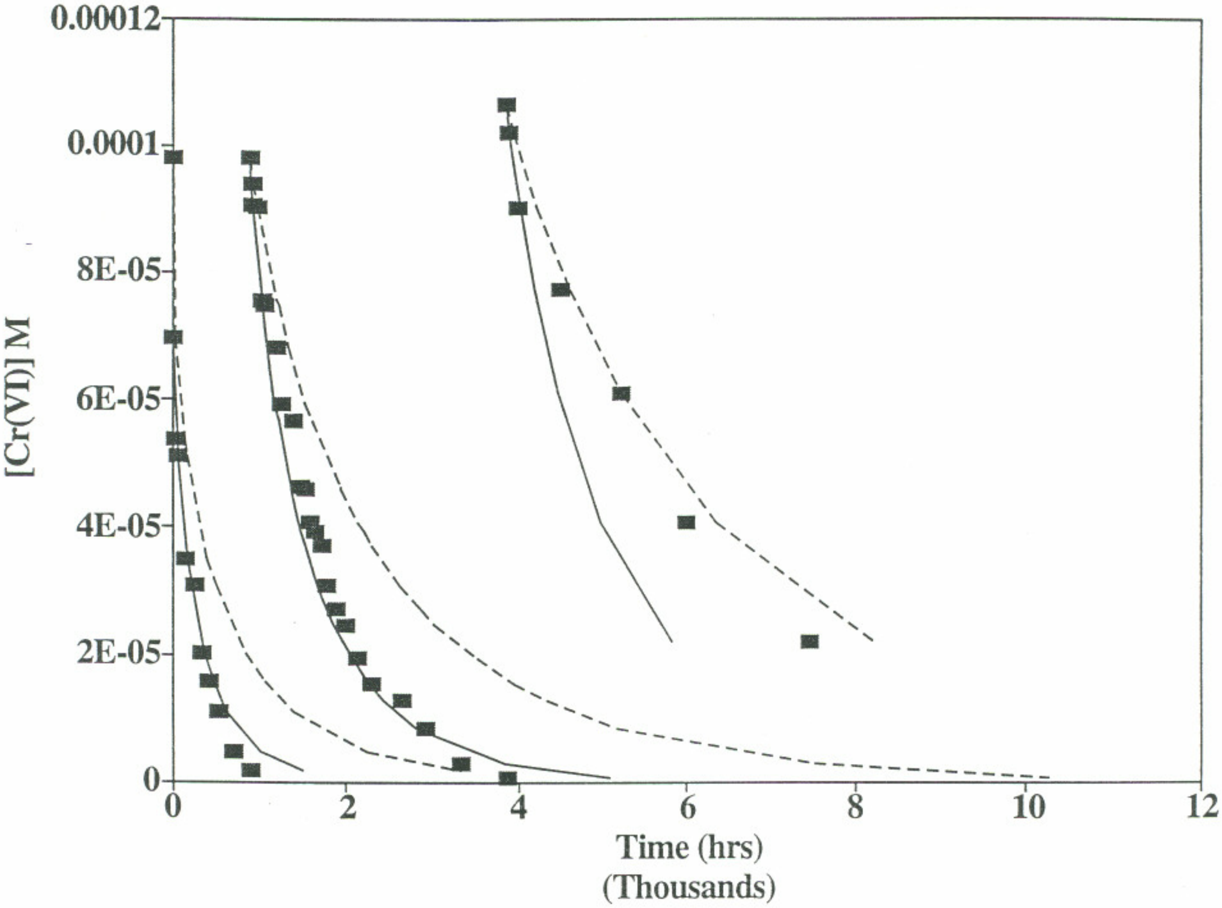


Figure 2.5. Reduction of Cr(VI) by soil fulvic acid for the multiple spiking experiment. $[Cr(VI)]_0$ = 0.1 mmol/L for each spike, pH = 2.0, $[SHS]_0$ = 100 mg/L. Solid line = optimized rate constant, dashed line = previously calculated rate constant.

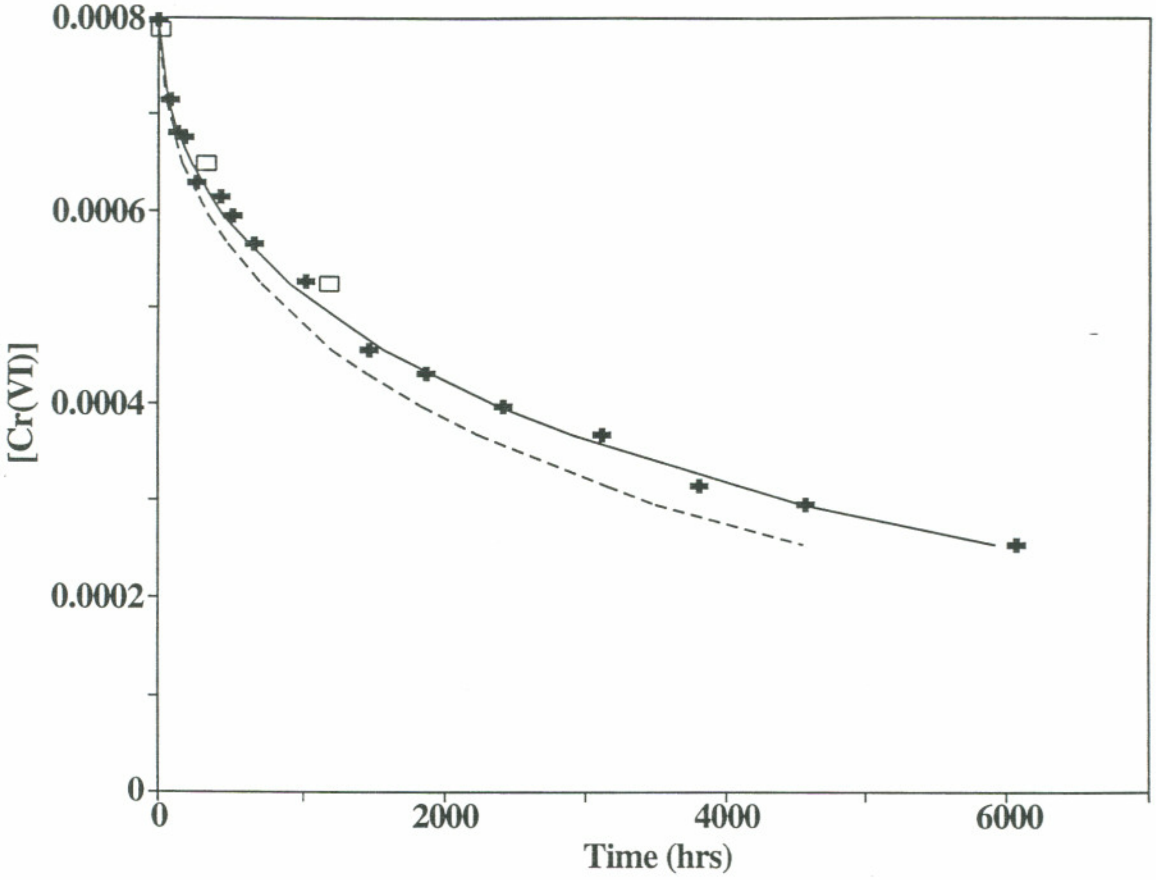


Figure 2.6. Plot of Cr(VI) concentration versus time for experiment with high initial Cr(VI). pH = 2.0, $[Cr(VI)]_0$ = 0.8 mM, $[SHS]_0$ = 100 mg/L. Solid line = optimized rate constant, dashed line = previously calculated rate constant.

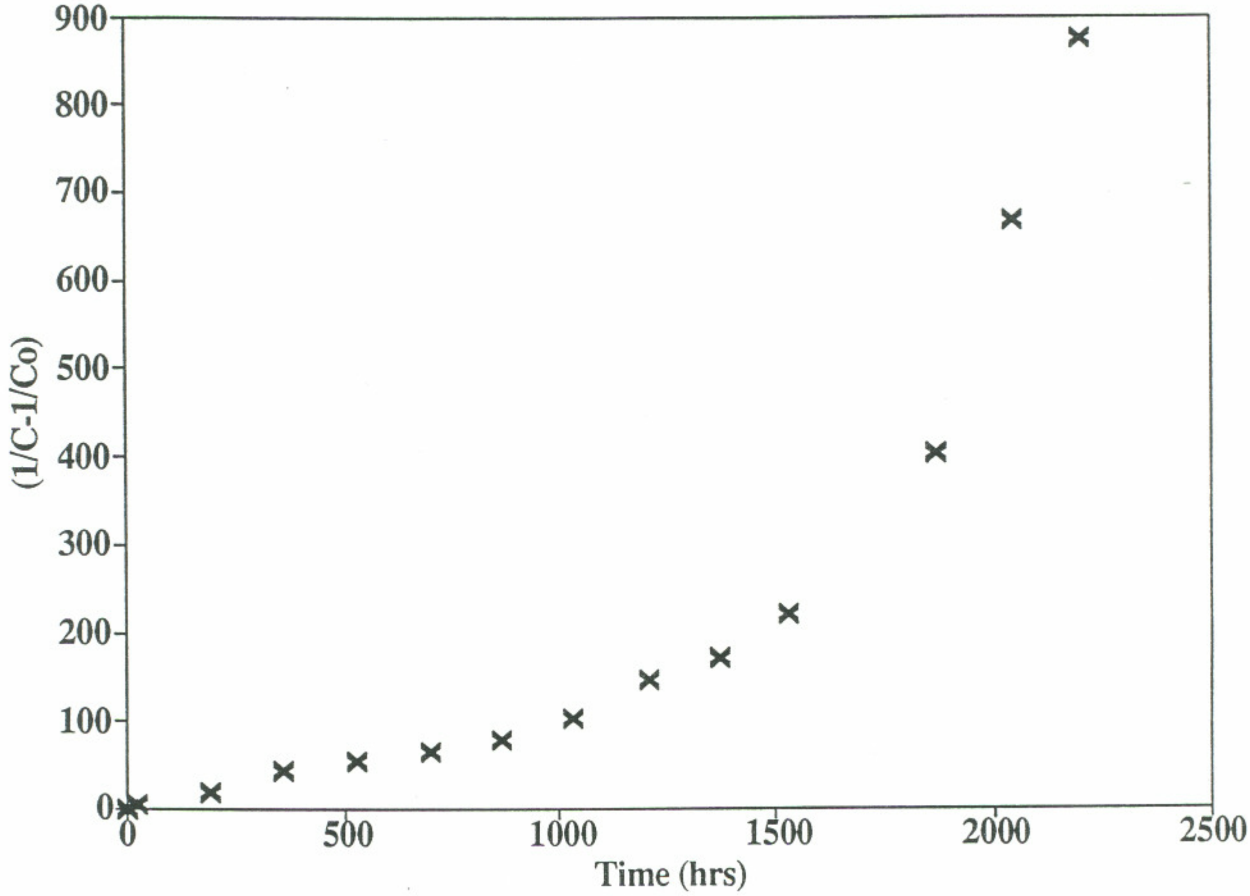


Figure 2.7. Second-order plot of (1/C)-(1/C_0) versus time at pH 5.0. $[SFA]_0$ = 100 mg/L, $[Cr(VI)]_0$ = 0.02 mM, *I* = 0.1 M.

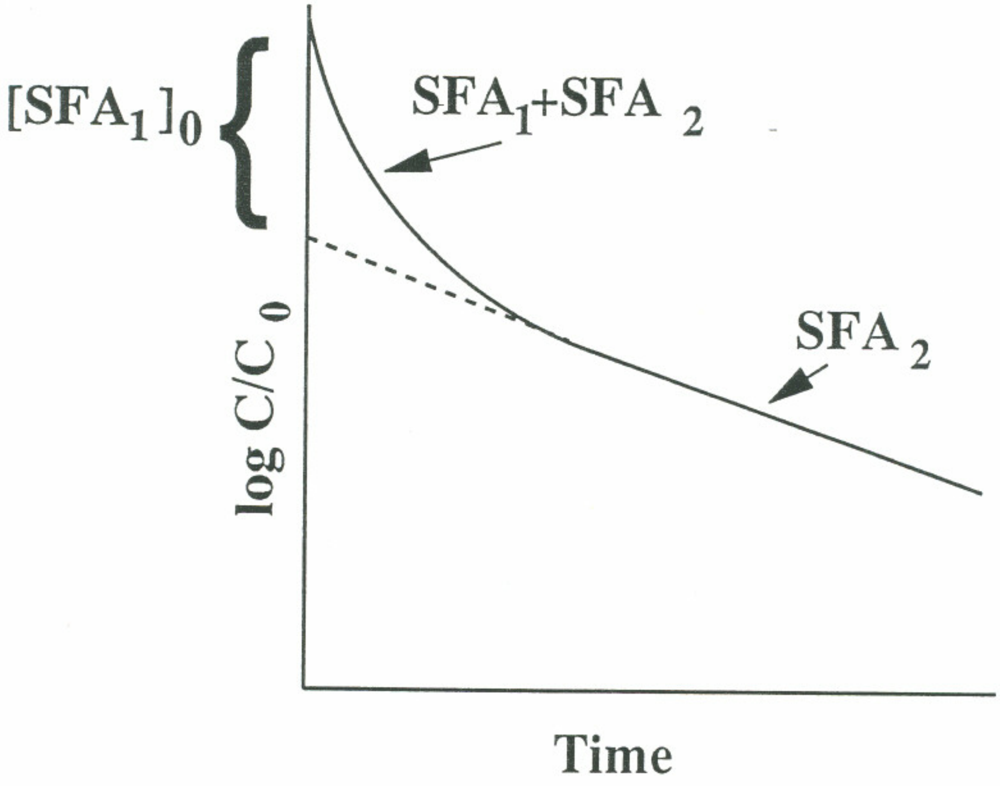


Figure 2.8. Illustration of first-order plot for a two-component system where the fast-reacting components of a finite quantity. The concentration $[SFA]_0$ is obtained from the residual between the observed [Cr(VI)] and linear extrapolation of log C/C_0 for SFA_2 to the y-intercept.

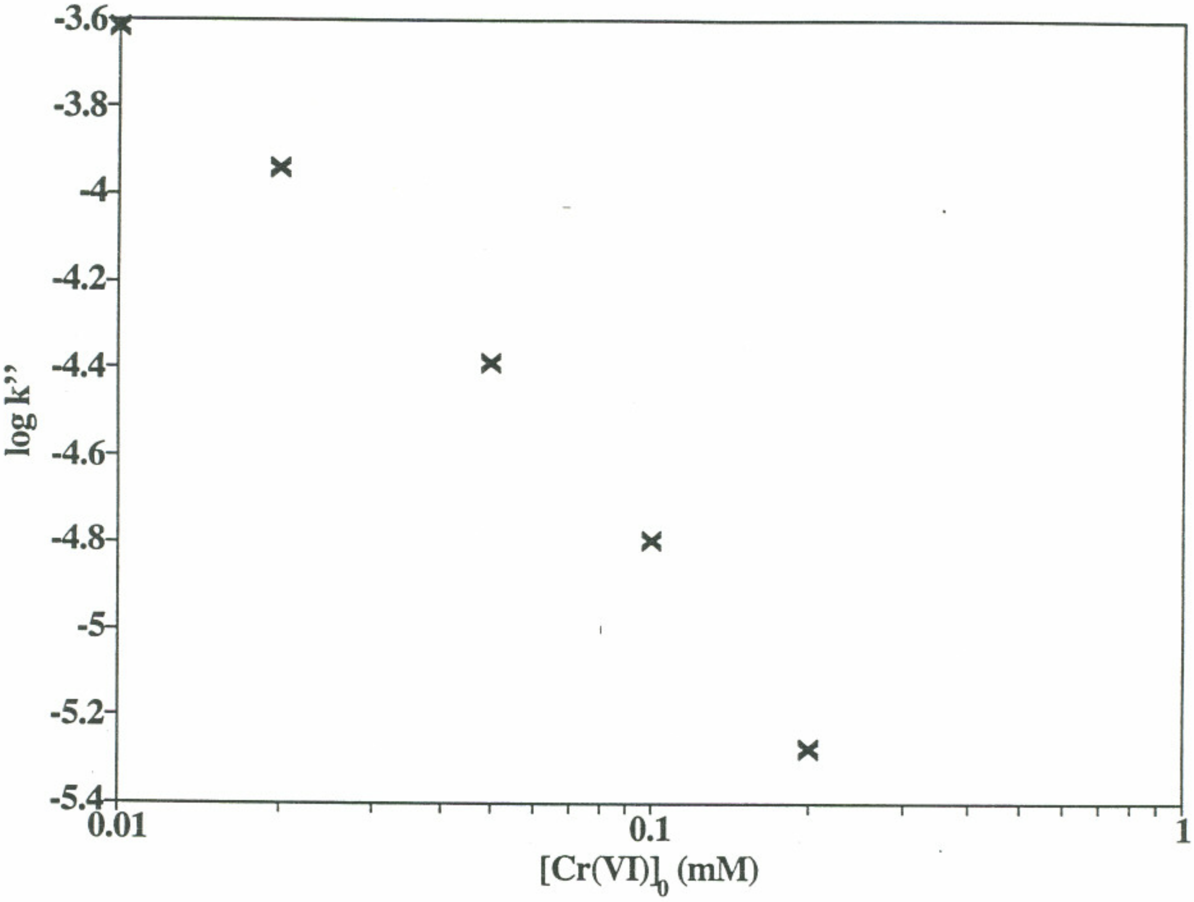


Figure 2.9. Variation in first-order rate coefficients (k'') determined from experiments at various $[Cr(VI)]_0$ using the two-component model. The fraction of SFA oxidized increases with increasing $[Cr(VI)]_0$.

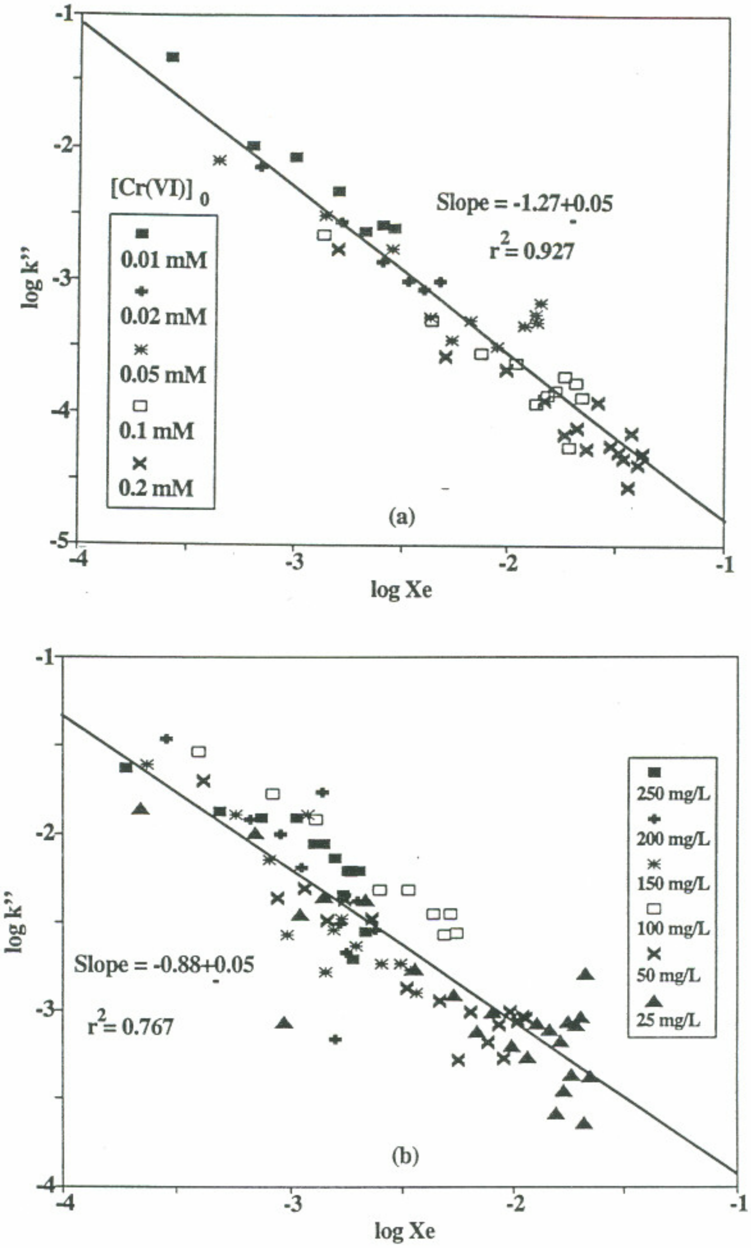


Figure 2.10. Plots of log k'' versus log X_e for (a) the various initial Cr(VI) concentrations with $[SFA]_0$ = 100 mg/L and (b) for various initial SFA concentrations with $[Cr(VI)]_0$ = 0.02 mM. Experiments were performed at pH 2.0. Slope of linear regression of both sets = -1.12±0.04.

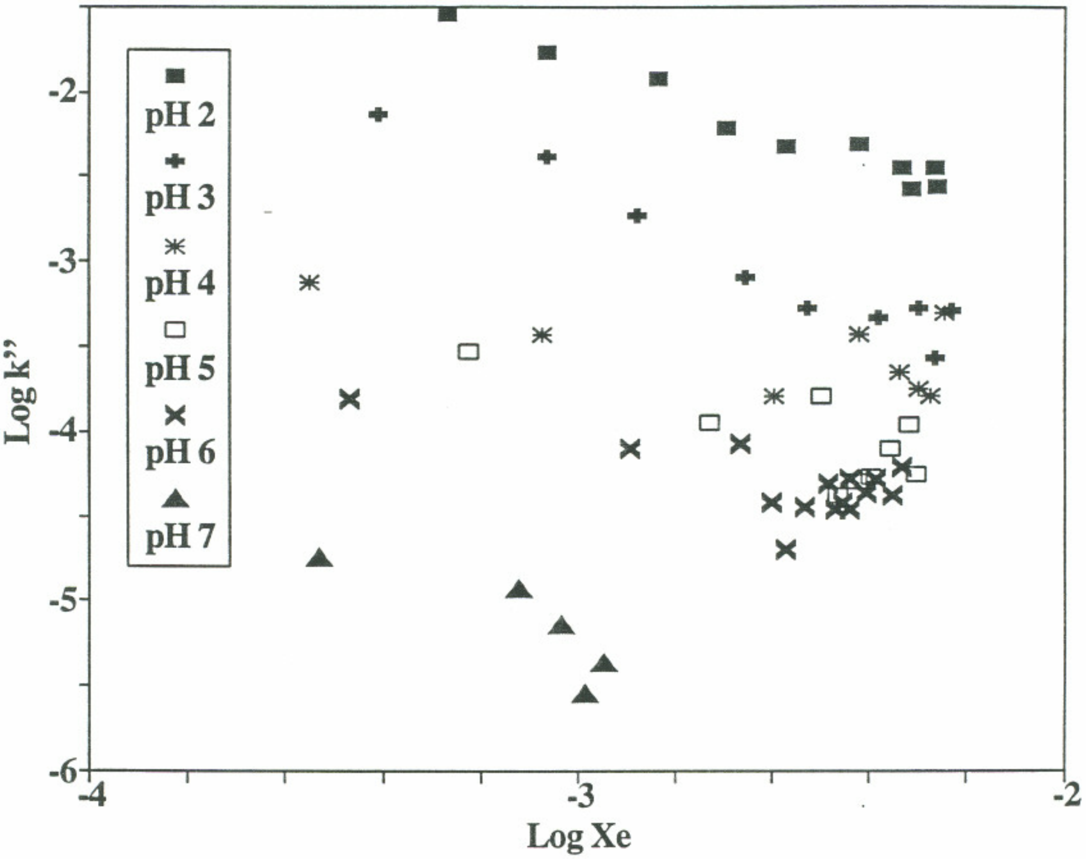
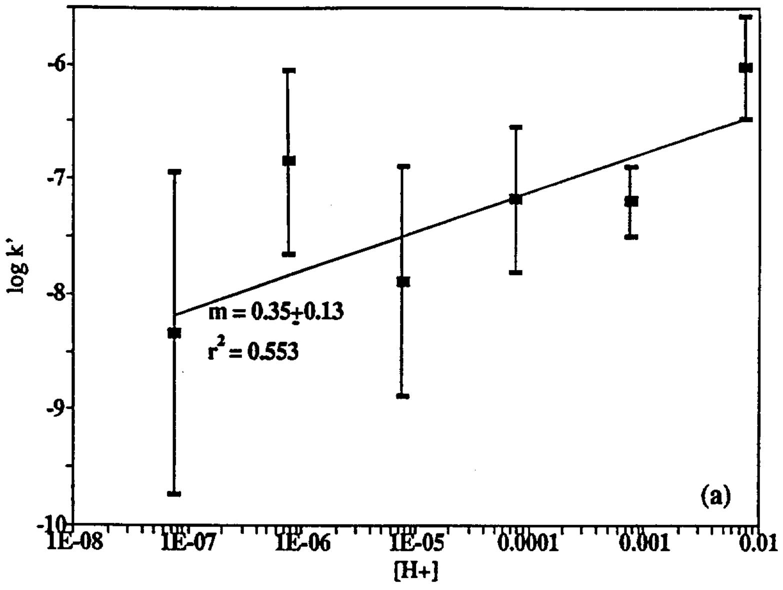


Figure 2.11. Plot of log k'' versus log X_e for various pH experiments.



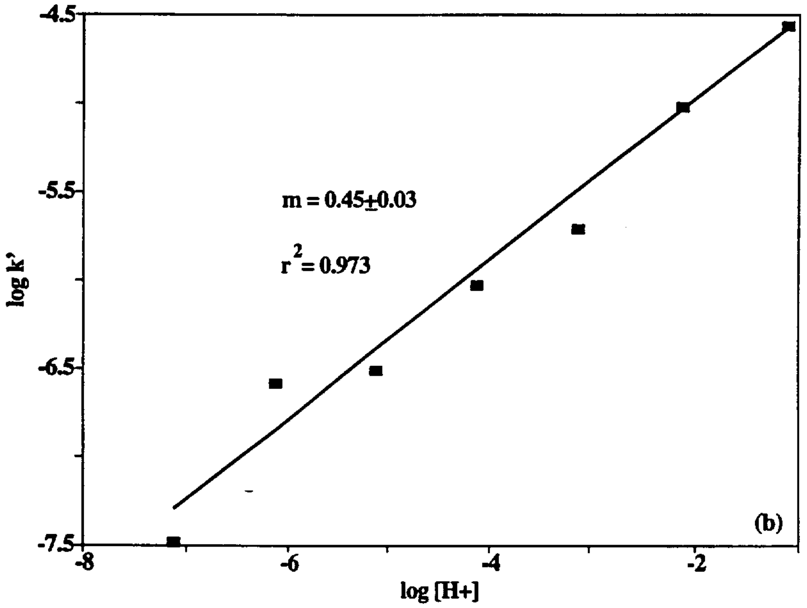


Figure 2.12. Plots of log k' versus [H^+] for various pH experiments. Rate coefficients determined using a) the continuum model and b) the integrated rate equation.

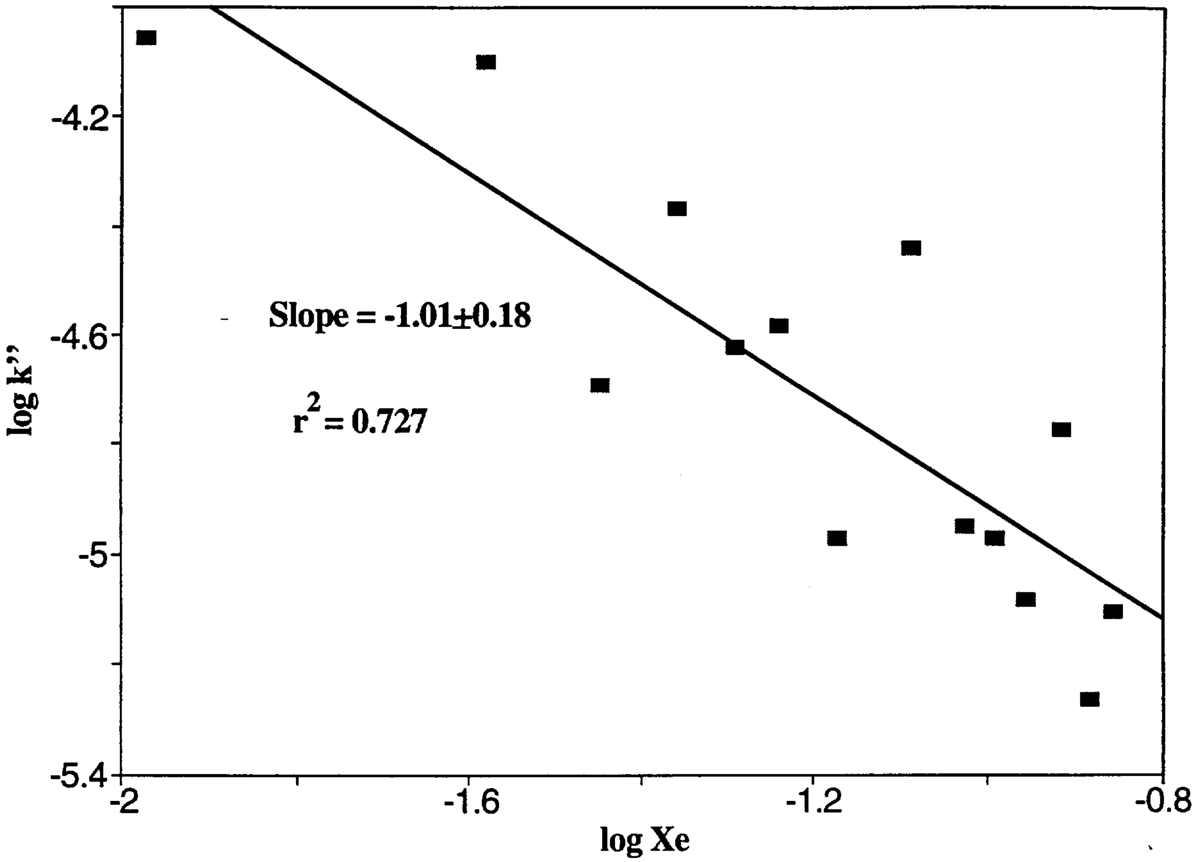


Figure 2.13. Plot of log k'' versus log X_e for experiment with high initial Cr(VI).

CHAPTER 3

Reduction of Cr(VI) in the Presence of Excess Soil Humic Acid

Abstract

Natural organic materials in soils such as humic acids have been shown to reduce the toxic Cr(VI) to the less hazardous and less mobile Cr(III). The kinetics of hexavalent chromium reduction by a soil humic acid (SHA) has been investigated in aqueous solutions where concentrations of Cr(VI), H^+, and SHA were independently varied. Rate experiments were conducted with a large excess of SHA over Cr(VI). Similar experiments were conducted with two other SHAs. Rates of reduction are strongly pH dependent, increasing with decreasing pH. Typical Cr(VI)-SHA reactions display a nonlinear reduction of Cr(VI) with time. The results are modeled by an empirical rate law developed for Cr(VI)-soil fulvic acid reactions describing the effects of varying these parameters on the rates of Cr(VI) reduction. The model is that of a reactive continuum, which treats the SHA as a continuum of reactive groups that

reduce Cr(VI) at varying rates. The rate law which describes this system is

$$R=-k''[HCrO_4^-][SHA][H^+]^m$$

where the exponent m is 0.25±0.03 and the rate coefficient (k') varies with the equivalent fraction (X_e) of SHA that has been oxidized. The apparent rate coefficient can be written as kX_e^n, where k is 3.39×10^{-6} sec^{-1} and n is -1.10±0.05. The log of the rate coefficient varies linearly with the log of X. The Cr(VI)-SHS reactions do not fit the continuum model as well as fulvic acid. Rate coefficients for three SHAs from different soils vary by at most an order of magnitude.

Introduction

Aqueous chromium has been released to the subsurface as a result of its widespread use in a variety of industrial activities (Calder, 1988; Palmer and Wittbrodt, 1991; Burke, 1991; Perlmutter and Lieber, 1985). Since some forms of chromium can be toxic, mutagenic and carcinogenic (Abasi and Soni, 1984; Ono, 1988; Waterhouse, 1975), it is important to understand the behavior of chromium in soil environments. Because both the mobility and toxicity of chromium are dependant upon its oxidation state, redox reactions are very important in determining its fate in the environment.

Although oxidation states of chromium range from -2 to +6 (Cotton and Wilkinson, 1988), only the +3 and +6 states are prevalent in the environment. The more hazardous hexavalent form is generally more mobile than trivalent chromium (van Weerelt et al., 1984). The Cr(VI) oxyanions chromate (CrO_4^{2-}), bichromate ($HCrO_4^-$), and dichromate ($Cr_2O_7^{2-}$) are not strongly sorbed to many soils under alkaline to slightly acidic conditions and hence their mobility is not greatly retarded (Zachara et al., 1989). In contrast, Cr(III) readily precipitates as $Cr(OH)_3$ or as the solid solution $Fe_xCr_{1-x}(OH)_3$ under alkaline to slightly acidic conditions (Rai et al., 1987, Sass and Rai, 1987). Cr(III) can also be immobilized by complexation with organic molecules that are adsorbed to mineral surfaces (James and Bartlett, 1983a & b).

Hexavalent chromium is a strong oxidant which can undergo redox reactions with a number of soil constituents, including minerals, aqueous inorganic ions, simple organic molecules, and humic substances (Palmer and Wittbrodt, 1991). In a study of chromate reduction by various soils, Eary and Rai (1991) concluded that Cr(VI) reduction by organic matter and Fe(II) were roughly equivalent in terms of total reduction capacity. Soil humic substances, which constitute the majority of the organic fraction in most soils, thus represent a significant reservoir of electron donors for Cr(VI) reduction.

Humic substances represent a complex mixture of biogenic molecules consisting of aromatic components extensively substituted with oxygen-containing functional groups (Stevenson, 1985). The three fractions of humic substances, humic acid (HA), fulvic acid (FA) and humin are operationally defined in terms of their solubilities (Aiken et al., 1985). Humic acid is that fraction which is soluble in basic solutions. Humic acids have higher molecular weights and carbon contents than fulvic acids.

The kinetics of Cr(VI) reduction by a soil fulvic acid have been investigated and were discussed in Chapter 2 along with the development of the rate law. Variations in rates of Cr(VI) reduction were determined as a function of reactant concentration and pH. The rate of reduction greatly increases with increasing $[H^+]$, [SFA], and [Cr(VI)]. The empirical rate law developed for the SFA-Cr(VI) reactions treats the SFA as a continuum of reductive groups whose reactivity continuously varies. The rate law which describes this system is of the general form

$$R=-kX_e^n[HCrO_4^-][SFA][H^+]^m \tag{1}$$

where the apparent rate coefficient is a continuously varying parameter that is a function of the equivalent fraction of SFA that has been oxidized (X_e). The apparent rate coefficient varied with the inverse of X_e over a range of 0.00016 to 0.05 and the exponent m is 0.45±0.03. The non-integer value for m is not surprising considering the empirical method from which it was derived.

In this chapter, we describe a series of laboratory experiments in which the kinetics of Cr(VI) reduction by a soil humic acid (SHA) has been studied. The rate experiments were conducted with an excess of SHA over Cr(VI) to study the reactivity of the most easily oxidized components of the SHA. The major goals of these experiments were to determine the variability of Cr(VI) reduction rates as a function of pH, Cr(VI) concentration, and SHA concentration and to determine how well the data can be modeled by an empirical rate law developed for Cr(VI)/soil fulvic acid (SFA) reactions. Results for two additional SHAs were also compared to the model.

Experimental Section

Materials. Three humic acids obtained from the International Humic Substances Society (IHSS) collection of reference humic materials were used in the experiments. These materials were used because their properties such as composition and NMR spectra (Thorn et al. 1989, 1991) were readily available. The elemental compositions of the SHAs are summarized in Table 3.1. Experiments were conducted in foil-wrapped glass reaction vessels with ultrapure (~18 mega-ohm) water. All chemicals were reagent grade.

Table 3.1 Elemental Composition of IHSS Humic Acids. Data From Thorn et al., 1992 and IHSS; unpublished.

Sample	C	H	O	N	S	P	Ash
Soil HA	57.99	3.78	33.69	4.18	0.41	0.32	0.90
Summit Hill HA	54.13	4.91	35.39	5.03	0.60	0.40	1.52
Peat HA	56.82	4.06	34.91	3.74	0.68	0.11	1.92

Analytical and Experimental Methods. The experimental procedures used are identical to those used to develop the Cr(VI)-SFA rate law. A detailed description of these procedures can be found in Chapter 2. Briefly, a modified Walkley-Black (1934) method was used to determine the quantity of reducing equivalents per milligram of SHA. These tests completely oxidize the SHA in concentrated sulfuric acid and Cr(VI). The number of reducing equivalents in the SHA is calculated by dividing the difference between initial and final Cr(VI) concentrations by the mass of SHA added to the reaction vessel.

The rate of reduction of Cr(VI) by SHA was determined by measuring the time-dependent concentration of Cr(VI) using a diphenylcarbazide (DPC) colorimetric method described in Chapter 2. These experiments were performed in triplicate tests at room temperature (25±2°C) with 20 to 400 times excess SHA as determined from the modified Walkley-Black tests. The background electrolyte was 0.1 $\underline{M}$ LiCl.

Rate experiments at various pH values determined the effect of $[H^+]$ on the rate of Cr(VI) reduction by SHA. Aliquots (20 ml) of a stock solution containing 100 mg/L of SHA were equilibrated for 24 hours at pH 2, 3, 4, 5, 6 or 7 before being spiked with 0.02 mM Cr(VI). The pH was maintained within 0.1 pH unit by additions of either H_2SO_4 or LiOH. For pH 5 and below the pH drift was < 0.05 units. A second set of rate experiments similar to those just described but at a fixed pH of 2.0 and with initial Cr(VI) concentrations of 0.01, 0.02, 0.05, 0.1 and 0.2 mM was conducted to determine variations of reduction rates as a function of Cr(VI) concentration. A third set of batch experiments was also performed at pH 2.0 and an initial Cr(VI) concentration of 0.02 mM, but with initial SHA concentrations of 25, 50, 100, 150, 200, and 250 mg/L. Similar batch experiments were also used to determine differences in rates of Cr(VI) reduction by SHAs from various soil types at pH 3.0.

The applicability of the rate law was tested by conducting an experiment at a higher Cr(VI) concentration than had been used previously. The experiment monitored Cr(VI) reduction rates in 40 mL solutions of 100 mg/L SHA spiked with 0.8 mM Cr(VI).

Results

SHA Reducing Capacity. The modified Walkley-Black tests are a measure of the quantity of Cr(VI) reducible by SHA under extremely acidic conditions. The concentrations of reducing equivalents available in the IHSS reference SHAs as determined by the modified Walkley-Black tests is given in Table 3.2. These measurements are used to determine the initial SHA concentration ($[SHA]_0$) and allow for calculation of the fraction of SHA that has been oxidized during the rate experiments. The number of reducing equivalents available per carbon is calculated by dividing the number of reducing equivalents per mg of SHA by the mass of carbon (Table 3.2).

Less than 5% of the SHA reducing equivalents were oxidized in all of the rate experiments. Thus, the rates of reduction determined in these tests represent the rates of reduction by the most reactive groups in the SHA. One would expect the rates to decrease as a larger fraction of the SHA were to be oxidized, with only the more recalcitrant components remaining.

Table 3.2 Reducing Capacities of the IHSS Reference Humic Substances as Determined from the Walkley-Black Tests.

Sample	reducing equivalents (μeq/mg SHA)	change in charge on carbon
Soil Humic Acid	131±21	2.7
Summit Hill Humic Acid	156±12	3.3
Peat Humic Acid	135±18	3.0

pH Effects. Reduction of Cr(VI) was observed at all values of pH in the range 2 to 7. As with many organic compounds, the rates of reduction are strongly pH dependant, the rate increasing with decreasing pH (Figure 3.1). Typical Cr(VI)-SHA reactions are characterized by a nonlinear decrease of [Cr(VI)] and a decrease in the rate of reduction with time. Plots of log relative Cr(VI) concentration (log C/C_0) versus time display an early rapid decrease (Figure 3.2), indicating that the reactions are not first-order with respect to Cr(VI). The rapid initial decrease is likely due to the presence of functional groups that are much more reactive than the bulk of reduction sites in the humic acid. Other possible explanations for this initial drop could be adsorption or complexation. One would not expect complexation or adsorption of humic acid containing predominantly negatively charged functional groups with the anionic chromate species.

Chromate-ester formation is believed to be a precursor to the reduction of Cr(VI) by organics (Cotton and Wilkinson, 1988; Stone et al. 1993). Chromate-ester formation for phenols has been suggested to be rapid and reversible, as well as relatively independent of pH (Elovitz, 1993). Elovitz (1993) found that chromate-phenol ester formation is essentially instantaneous in the pH range 2 to 5. Our results at early times are very pH dependent, and although the initial decrease in Cr(VI) concentration is rapid, it is not instantaneous. Additionally, the strong binding of

Cr(VI) to DPC should complex the Cr(VI) which is weakly bound by the chromate esters. Our results show strong pH dependence at early times, which is when complexation/ester formation is expected to occur. Thus, it is likely that the observed rapid decrease of Cr(VI) is due to reduction rather than complexation or esterification.

Effect of Initial Cr(VI) Concentration. The relative Cr(VI) reduction rate at pH 2 decreases with increasing initial Cr(VI) concentrations in the range $[Cr(VI)]_0$ = 0.01 mM to 0.2 mM (Figure 3.3a). The shape of the curves in Figure 3.3a is similar to those in Figure 3.2 in that there is an initial rapid drop in Cr(VI) concentration. A family of curves was obtained rather than a single curve, emphasizing that the reduction cannot be modeled as a simple first-order reaction with a constant rate coeffiecient.

Effect of SHA Concentration. The rate of Cr(VI) reduction at pH 2 increases with increasing SHA concentration in the range $[SHA]_0$ = 25-250 mg/L. The reaction is characterized by a non-linear Cr(VI) loss with time. As is the case with both various pH and various initial Cr(VI) concentration, plots of log relative Cr(VI) concentration versus time show an initial rapid drop (Figure 3.3b).

Reduction at Higher Cr(VI) Concentration. The experiments with 0.8 mmol/L initial Cr(VI) show a nonlinear rapid loss of Cr(VI) at the beginning, followed by a much slower reduction of chromate (Fig. 3.4). This is similar to the behavior observed in experiments with much smaller concentrations of chromate.

Reaction Rates for Various SHSs. Rates of chromate reduction by the three SHAs at pH 3.0 were examined. The reaction of Cr(VI) and SHA occurs in a similar fashion for all of the SHAs studied. A typical Cr(VI)-SHA reaction is characterized by a non-linear decrease in Cr(VI) concentration over time (Fig. 3.5). The initial Cr(VI)-SHS reaction rate is rapid, followed by a much slower rate of Cr(VI) reduction. The rate of reduction is greater for the peat SHA than for the other two SHAs studied. The reaction rate for the peat SHA is nearly identical to that of the SFA at early times, but the rate for the SFA slows down at later times relative to the peat SHA. A comparison of chromate reduction by the SHA and SFA from the same soil show that the SFA reduces Cr(VI) at a rate roughly twice that of the SHA.

Discussion

The key objective of this study is to determine if a rate law for developed for Cr(VI)/SFA reactions can be applied to Cr(VI)/SHA reactions. The complete development of the rate law is detailed in Chapter 2. A brief summary of the rate law is presented here.

The reactive continuum model treats the SHS as a continuous series of reactive components that react at varying rates. The rate law developed for SFA is based on Cr(VI)-organic reactions at a constant pH that follow a rate law of the general form

$$R=\frac{d[Cr(VI)]}{dt}=-k'''[org][HCrO_4^-] \qquad (2)$$

where [org] denotes the concentration of the organic (Wiberg, 1965). With a complex macromolecule such as humic acid, we expect the reaction of Cr(VI) with each moiety to follow the general rate equation given in eq. 2. The reaction is first-order with respect to both the organic and bichromate. In the continuum model the overall rate is the sum of many individual reactions, thus the apparent first-order rate coefficient varies as a function of the reducing equivalent fraction (X_e) of the SHA which has been oxidized. The distribution of reactivities of the SHA can be empirically derived from our experiments. For a fixed pH, we assume reactions that follow a rate law of the form

$$R=-k''[SHA][HCrO_4^-] \tag{3}$$

where k'', the observed rate coefficient, is a function of X_e. Since we define our concentrations of SHA in terms of Cr(VI) reducing equivalents we can calculate the fraction of SHA oxidized from the amount of Cr(VI) reduced during the experiments.

The observed rate coefficient at a given X_e was calculated for the SHA data using a central difference approximation between sampling intervals. The range of the total fraction of SHA oxidized was controlled using various $[Cr(VI)]_0$ or various $[SHA]_0$. We expect that plots of log k'' versus log X_e for experiments at a constant pH to display a linear relationship. An order with respect to X_e can be calculated from the slope of the line (n), and the rate coefficient (k') from the y-intercept of the line. A plot of log k'' versus log X_e for the various $[Cr(VI)]_0$ experiments (Figure 3.6a) displays a linear relationship with a slope of -0.80±0.17 (Table 3.3). A similar plot for the various $[SHA]_0$ experiments (Figure 3.6b) also displays a linear relationship for each independent test, with an overall slope of -1.25±0.07 (Table 3.3). The overall slope of all the data combined is -1.10±0.05.

The apparent rate coefficients, k', obtained from the intercepts of the k'' versus X_e plots include the effects of $[H^+]$. to obtain the dependence on $[H^+]$ and the appropriate rate constant, k, we must analyze the experiments with different pH values. Initially, we attempted to obtain the dependence of the rate equation on $[H^+]$ by first plotting log k'' versus log X_e (Figure 3.7). This plot yields an array of subparallel lines, one for each pH, with slopes of n and intercepts of log k'. As is the case for the previously discussed experiments, the reaction order (n) of these experiments is close to -1. In principle, the order with respect to $[H^+]$ can then be obtained as the slope of the log of the intercepts of these curves, log k' versus log $[H^+]$. However, the

Table 3.3: Calculated apparent rate coefficients (k') and reaction order (n) with respect to X for each set of triplicate experiments conducted.

pH	$[SHA]_0$	$[Cr(VI)]_0$	n	k'	r^2
2	25	0.02	-0.97±0.16	-5.68±0.24	0.98
2	50	0.02	-1.06±0.15	-5.66±0.32	0.97
2	100	0.02	-0.89±0.12	-5.86±0.22	0.98
2	150	0.02	-1.02±0.17	-5.84±0.51	0.93
2	200	0.02	-1.12±0.21	-6.04±0.26	0.98
2	250	0.02	-1.19±0.32	-6.00±0.21	0.99
2	100	0.01	-0.55±0.06	-5.65±0.21	0.99
2	100	0.02	-1.02±0.16	-5.75±0.40	0.93
2	100	0.05	-0.99±0.16	-5.98±0.28	0.97
2	100	0.1	-1.02±0.12	-6.17±0.23	0.98
2	100	0.2	-1.12±0.15	-6.39±0.24	0.97
2	100	0.02	-0.80±0.12	-5.28±0.24	0.98
3	100	0.02	-1.31±0.34	-6.30±0.31	0.95
4	100	0.02	-0.92±0.23	-6.51±0.16	0.91
5	100	0.02	-0.33±0.12	-6.93±0.35	0.96
6	100	0.02	-1.04±0.12	-6.99±0.23	0.99
7	100	0.02	-1.25±0.35	-7.10±0.41	0.97

standard errors in the parameters obtained in the linear regression were large and the regression line only explained 40% of the variation in the data. These large variances are primarily the result of successive approximations in the data set.

To overcome this numerical limitation, we calculated the rate coefficients from the experimental data using the integrated form of the rate equation. This method allowed us to obtain more precise results because the data is smoothed by the regression process. A reaction order with respect to $[H^+]$ was determined from the slope of the linear regression of the plot of log k' versus $[H^+]$ (Figure 3.8). When we apply this model to our data, the order with respect to $[H^+]$ is 0.25±0.03. The non-integer value for an order with respect to $[H^+]$ is not surprising considering the empirical nature in which it was derived. It suggests that the parallel reactions involve different numbers of electron transfers. Elovitz (1993) found that the rate dependence of Cr(VI) reduction by phenols was governed by three parallel redox pathways involving zero, one and two protons. Oxidation products of that study indicate that both one- and two-electron transfers occur.

We now can include $[H^+]$ in the rate law to yield

$$R=-kX_e^n[HCrO_4^-][SHA]_0(1-X)[H^+]^m \tag{4}$$

where $n = -1.10\pm0.05$ and $m = 0.25\pm0.03$. The rate coefficient, k, is obtained from the y-intercepts in Figure 3.6 and has a value of 3.38×10^{-6} sec^{-1}. The bichromate and pH are measurable system parameters and [SHA] and X_e can be calculated from measured parameters. The rate law given by Equation 4 describes a system where the reaction rate is dependant upon the fraction of organic material that has been oxidized. The only calculated parameters in the rate law are the rate coefficient k, and the reaction orders with respect to X_e and H^+. The rate equation should be valid for fractions of up to 5% of the soil humic substance being oxidized.

The experiment at 0.8 mM $[Cr(VI)]_0$ was designed to test the rate law under conditions outside of the concentration range for which the rate parameters were calculated. A plot of the log of the apparent rate coefficient versus the log of the fraction of SHS oxidized shows a linear relationship (Fig. 3.9), with a slope of -1.18±0.26. The data display a slower rate of reduction than that predicted by the rate law using the rate coefficient computed from earlier experiments (Fig.3.4). The rate coefficient determined from the best fit of the data shows that the form of the rate law is correct.

The data for the experiments with SHAs from different soils show good agreement with the analytical solution (Figure 3.5). Rate coefficients for each of the SHAs were calculated assuming that the order with respect to $[H^+]$ was the same as that calculated for the reference SHA (0.25) and that the order with respect to X_e is -1.0 (Table 3.4). The rate law more accurately models the data for the fulvic acid than the data for any of the humic acids.

Table 3.4 Calculated apparent rate coefficients (k') and reaction order with respect to X_e for the various soil humic substances studied.

Sample	n	k'	r^2
Soil Humic Acid	-1.04±0.19	-7.23±0.58	0.77
Summit Hill Humic Acid	-0.77±0.21	-6.73±0.29	0.67
Peat Humic Acid	-0.67±0.25	-6.13±0.21	0.60
Soil Fulvic Acid	-0.96±0.07	-5.78±0.19	0.97

The rate coefficients do not positively correlate with elemental composition (Table 3.1), SHS reducing capacities (Table 3.2) or carbon distributions determined from quantitative NMR spectra of the humic materials (Table 3.5). Elemental composition, functional group analysis and NMR spectral characterization have shown that peat humic acids tend to be similar to those from mineral soils (Mathur and

Farnham, 1982; Thorn et al., 1992) even though they come from vastly different environments. Although their origins are quite different, the rates at which they reduce chromium is not as varied as might be expected. The reason for this may be that the reactive functional groups responsible for chromate reduction occupy similar sites on the humic molecule regardless of its origin. Alternatively, the similarity in rates may me due to the method of isolation from the soils.

Table 3.5. Carbon distributions of humic and fulvic acids determined from quantitative NMR spectra. Numbers represent percent of total spectrum. Data from Thorn et al. 1989.

Sample	Ketone/ Quinone	Carboxyl	Aromatic	Hetero- Aliphatic	Aliphatic
Soil Humic Acid	6	18	54	5	16
Summit Hill HA	7	19	35	14	25
Peat HA	5	20	51	5	19
Soil Fulvic Acid	12	25	31	9	22

Plots of log relative Cr(VI) concentration versus time for the SHAs (Fig. 3.10) are slightly concave downwards, suggesting an apparent increase in the reduction rates at later times. Data for all three of the humic acids show the same systematic bias compared to the values computed by the rate law. This bias would appear to reflect the autocatalytic behavior previously discussed. All three of the SHAs studied display this apparent autocatalytic behavior. One possible explanation for this behavior is that the extremely large humic molecules are broken up by the initial reduction reactions, allowing for additional reaction sites to become available for reduction by the chromate molecule, thus increasing the Cr(VI) reduction rate. This autocatalytic effect would be expected to be diminished as the fraction of organic oxidized increases, since at some point further breakdown of the large molecules would not yield additional reduction sites.

Summary and Conclusions

Soil humic acid can effectively reduce Cr(VI) in aqueous solution in the pH range 2-7, with the Cr(VI) reduction rate increasing with decreasing pH, increasing $[SHA]_0$ and increasing $[Cr(VI)]_0$. The rate of reduction is non-linear and can be adequately described by a reactive continuum model. In this model, the rate coefficient is a continuously varying parameter, the value of which is determined by the fraction of SHA which has been oxidized. The model is valid in the pH range 2-7, Cr(VI) concentrations from 0.02 to 0.2 mM and SHS concentrations from 25 to 250 mg/L. The rate law was shown to adequately describe Cr(VI) reduction by SHA's from different soils. The humic acids do not fit the rate law as well as fulvic acid, for which the rate law was established.

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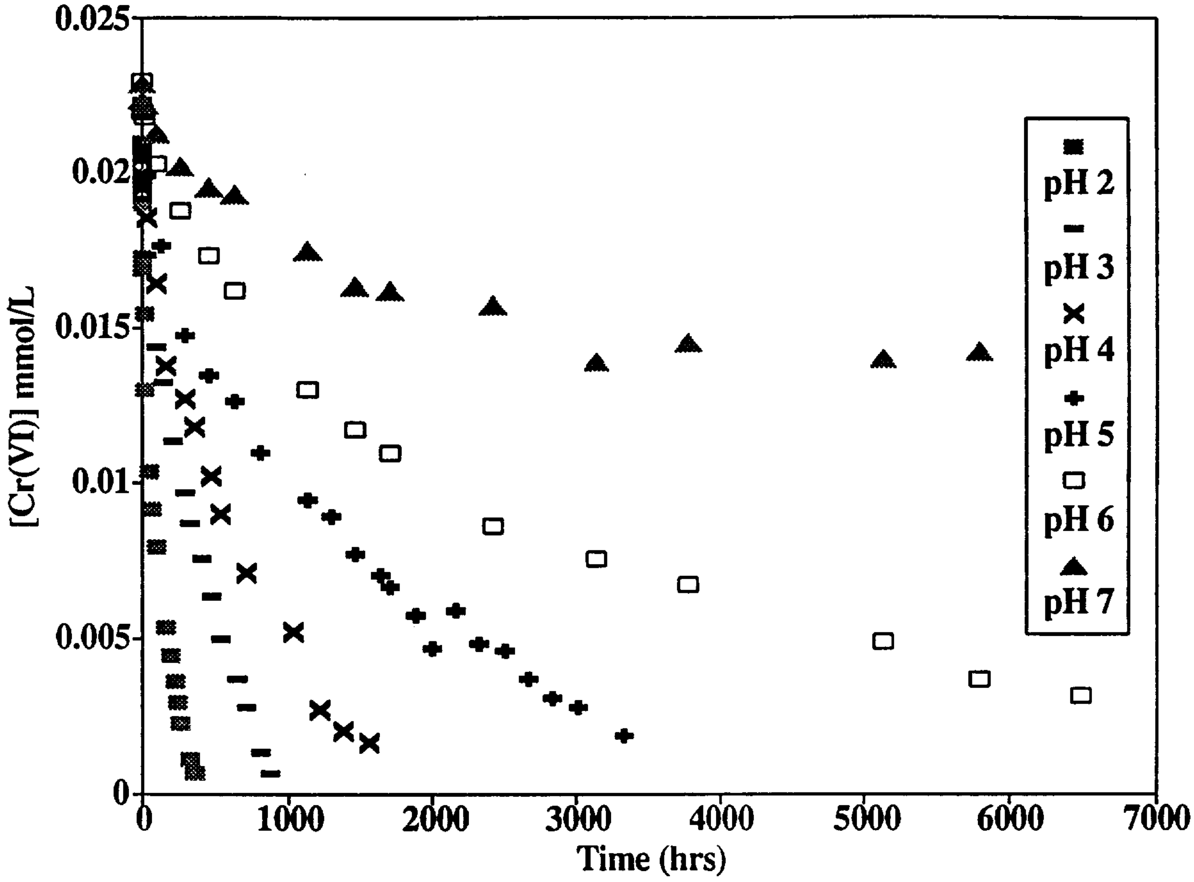

Figure 3.1. Reduction of Cr(VI) by soil humic acid. Plot of Cr(VI) as a function of time for batch experiments at various pHs. $[Cr(VI)]_0$ = 0.02 mM, $[SHA]_0$ = 100 mg/L, I = 0.1M. Points represent means of triplicate samples.

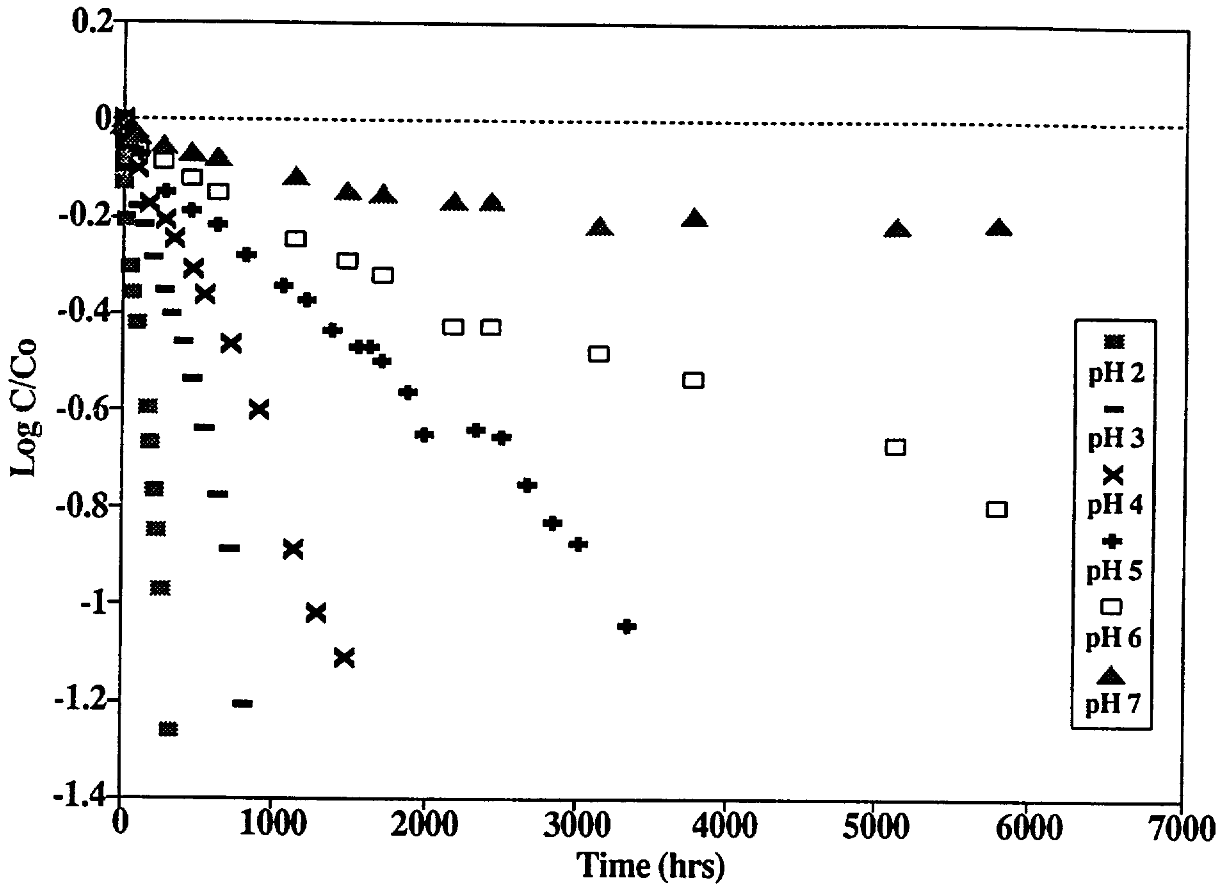

Figure 3.2. Pseudo-first-order plots of log relative Cr(VI) concentration versus time for Cr(VI)/SHA reactions at various pHs.

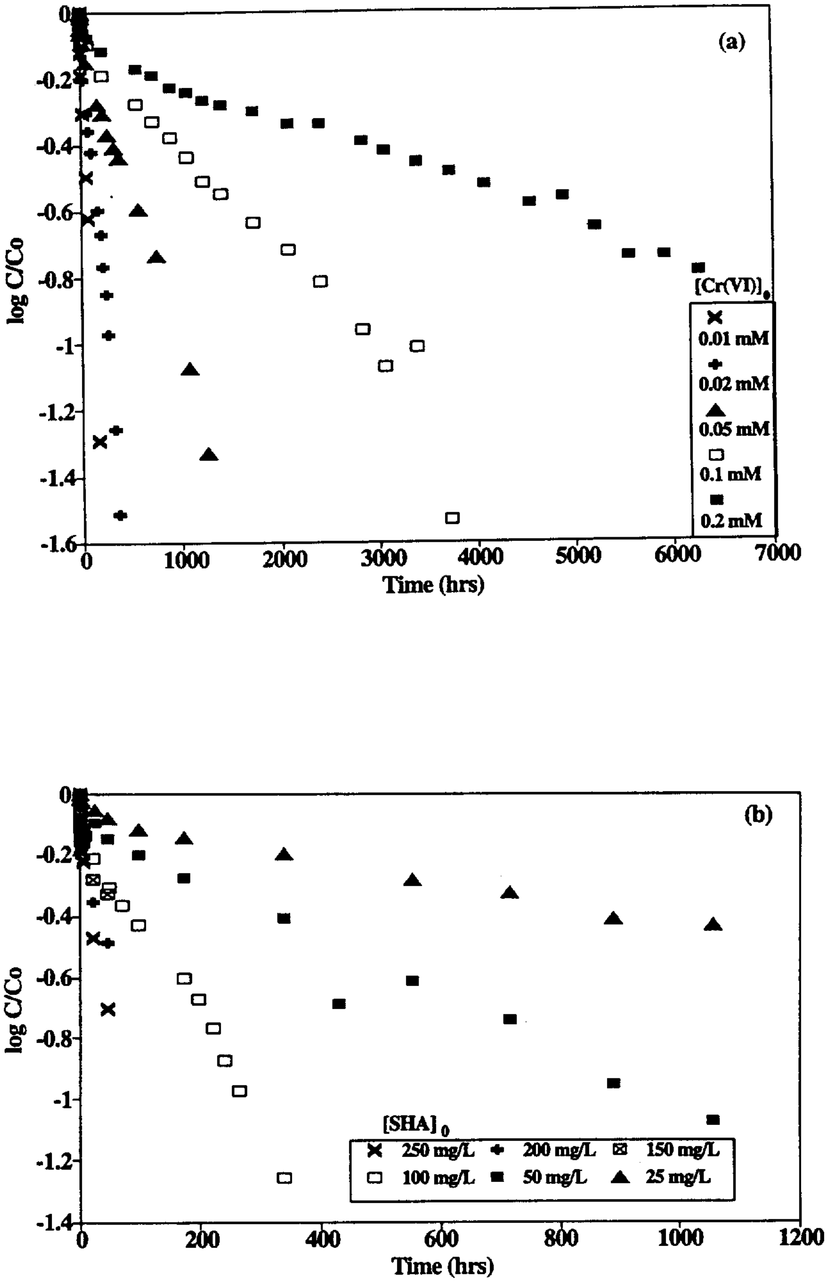

Figure 3.3. Pseudo-first-order plots of log relative Cr(VI) concentration versus time for experiments at a) various $[Cr(VI)]_0$ and b) various $[SHA]_0$. Reactions were performed at pH 2 and $I = 0.1M$.

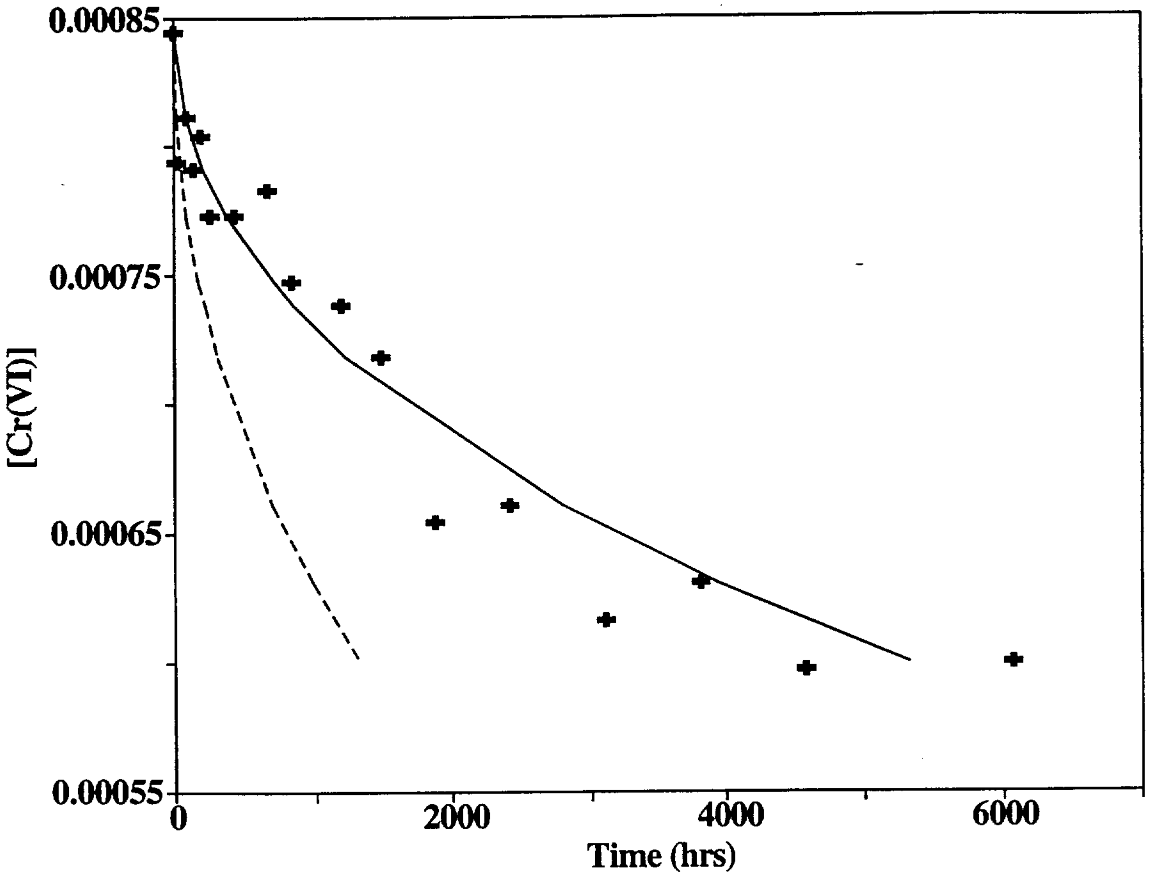

Figure 3.4 Reduction of Cr(VI) by SHA at pH 2.0 and $[Cr(VI)]_0$ = 0.8 mM, $[SHA]_0$ = 100 mg/L. Solid line is best fit analytical solution, dashed line is analytical solution using previously calculated k.

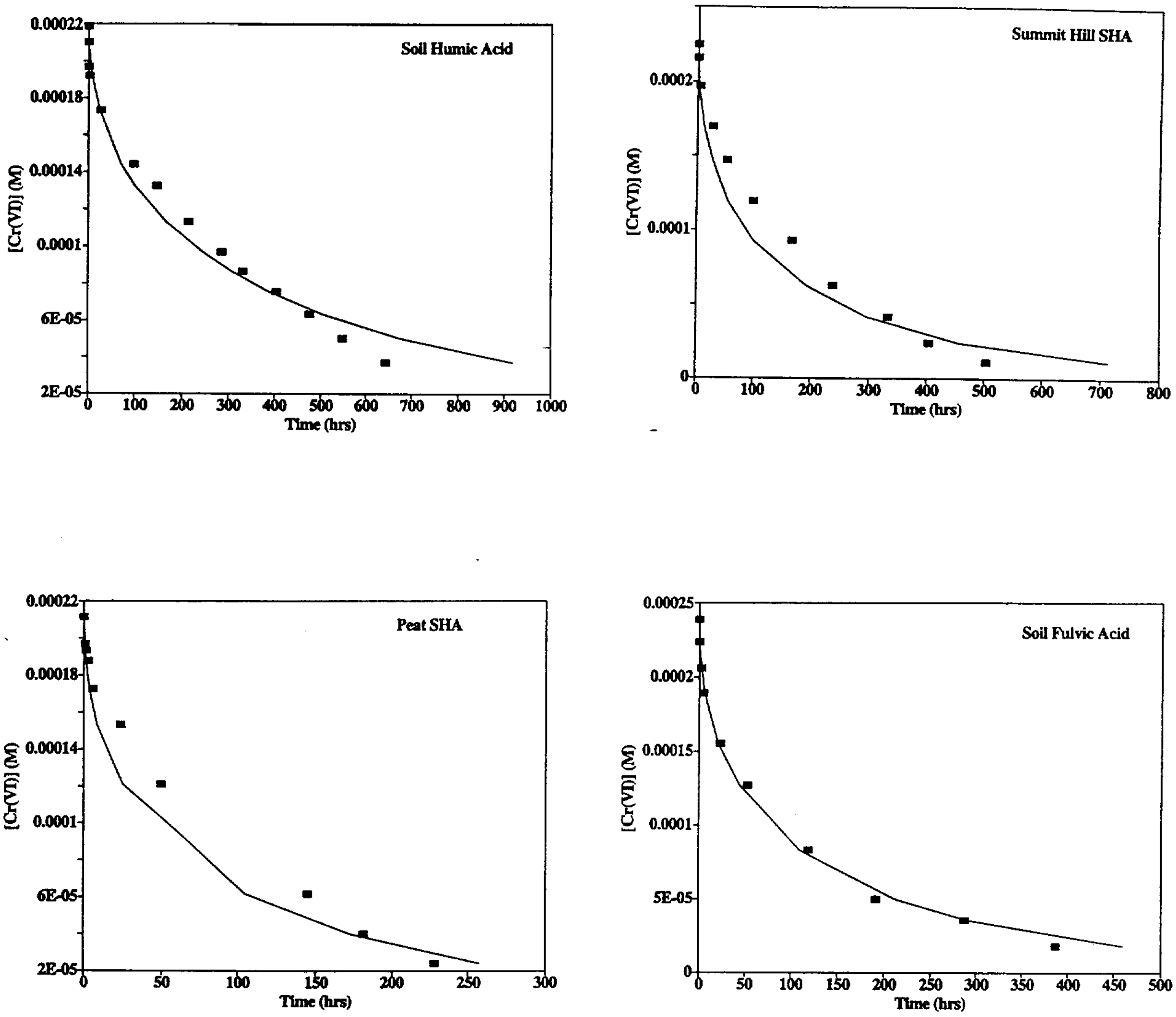

Figure 3.5 Reduction of Cr(VI) by three SHAa and a SFA at pH 3.0 $[Cr(VI)]_0$ = 0.02 mM, $[SHS]_0$ = 100 mg/L.

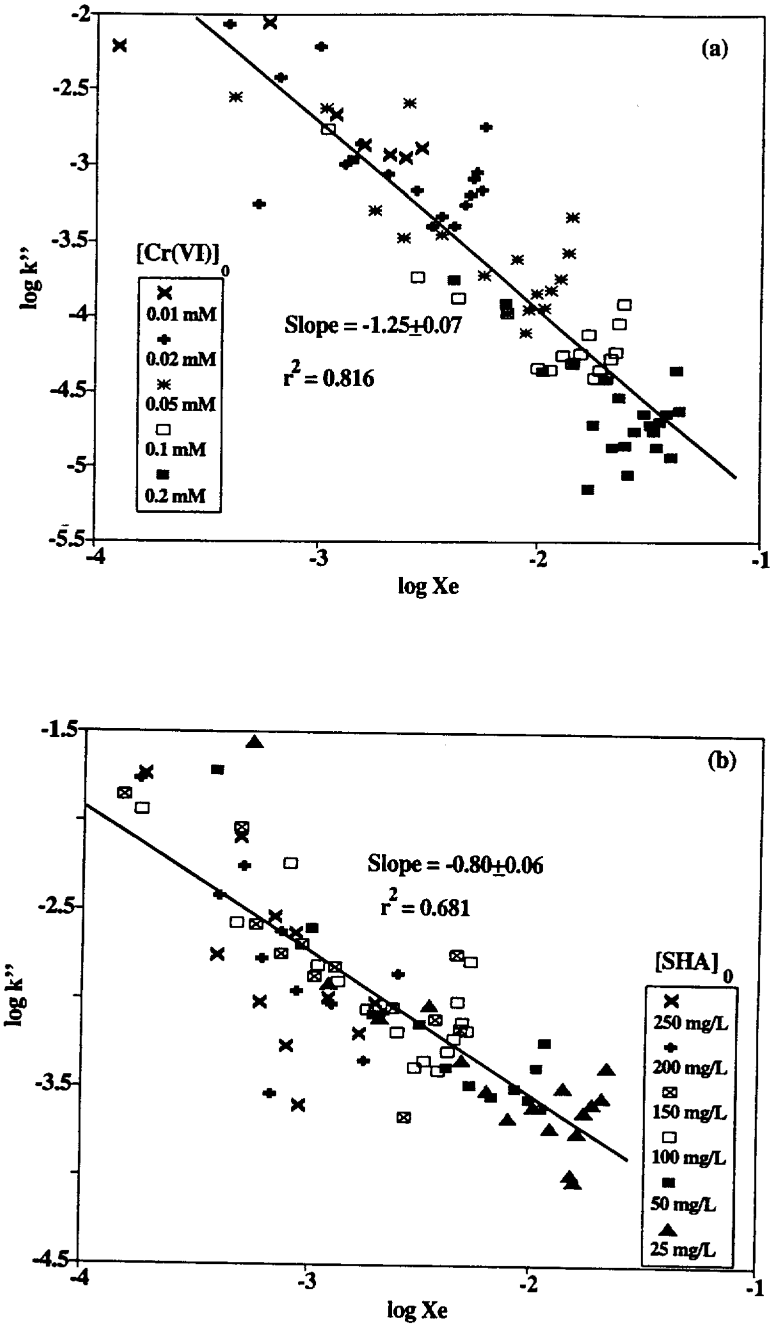

Figure 3.6. Plots of log k'' versus log X_e for (a) the various initial Cr(VI) concentrations with $[SFA]_0$ = 100 mg/L and (b) for various initial SFA concentrations with $[Cr(VI)]_0$ = 0.02 mM. Experiments were performed at pH 2.0.

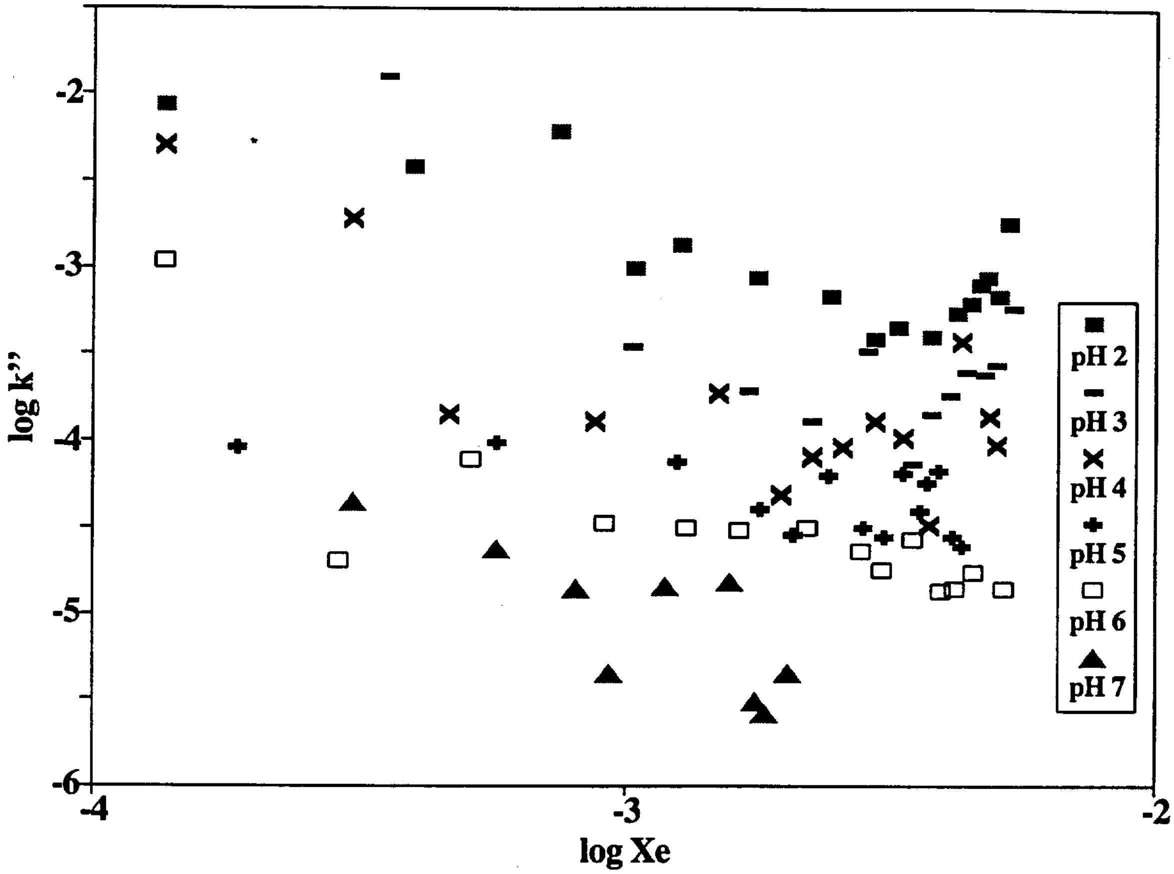

Figure 3.7. Plot of log k'' versus log X_e for various pH experiments.

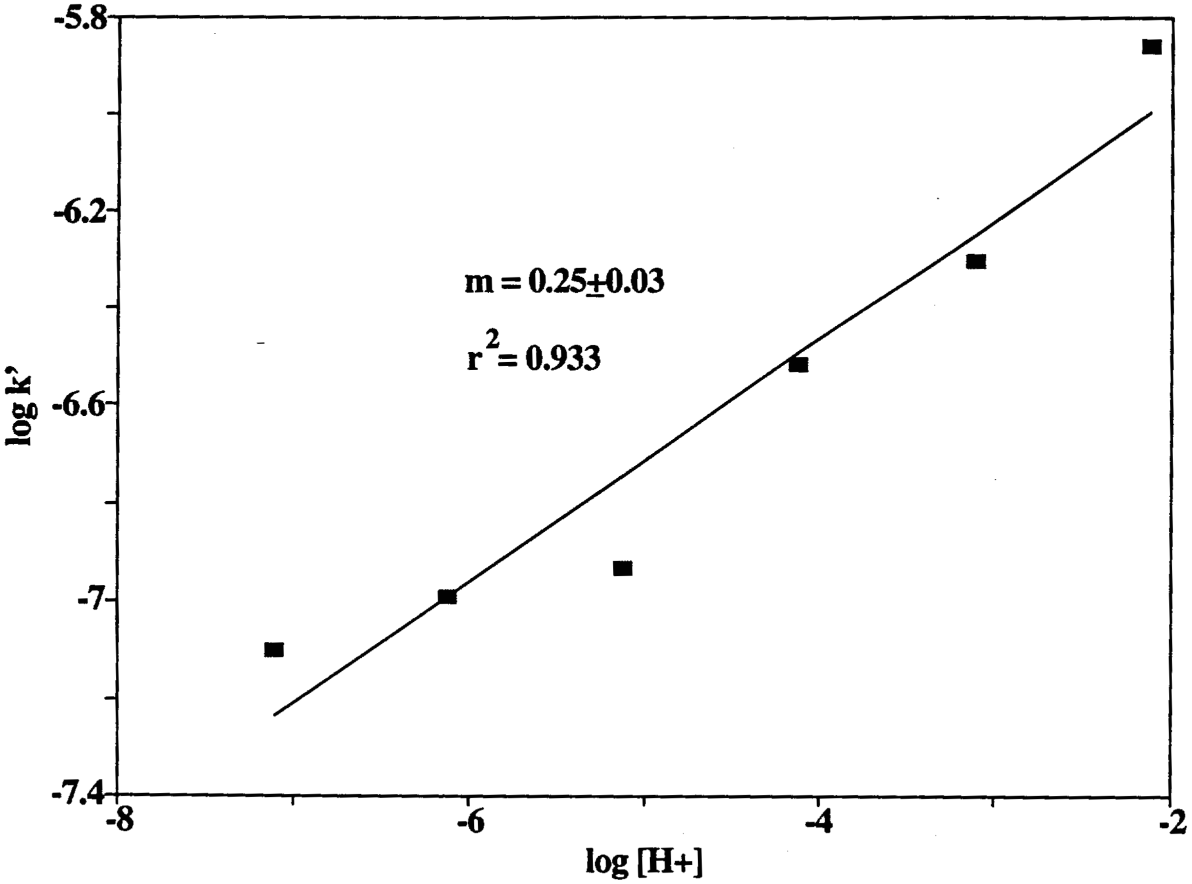

Figure 3.8. Plot of log k' versus[H^+] for various pH experiments. Rate coefficients determined using the integrated form of the rate equation.

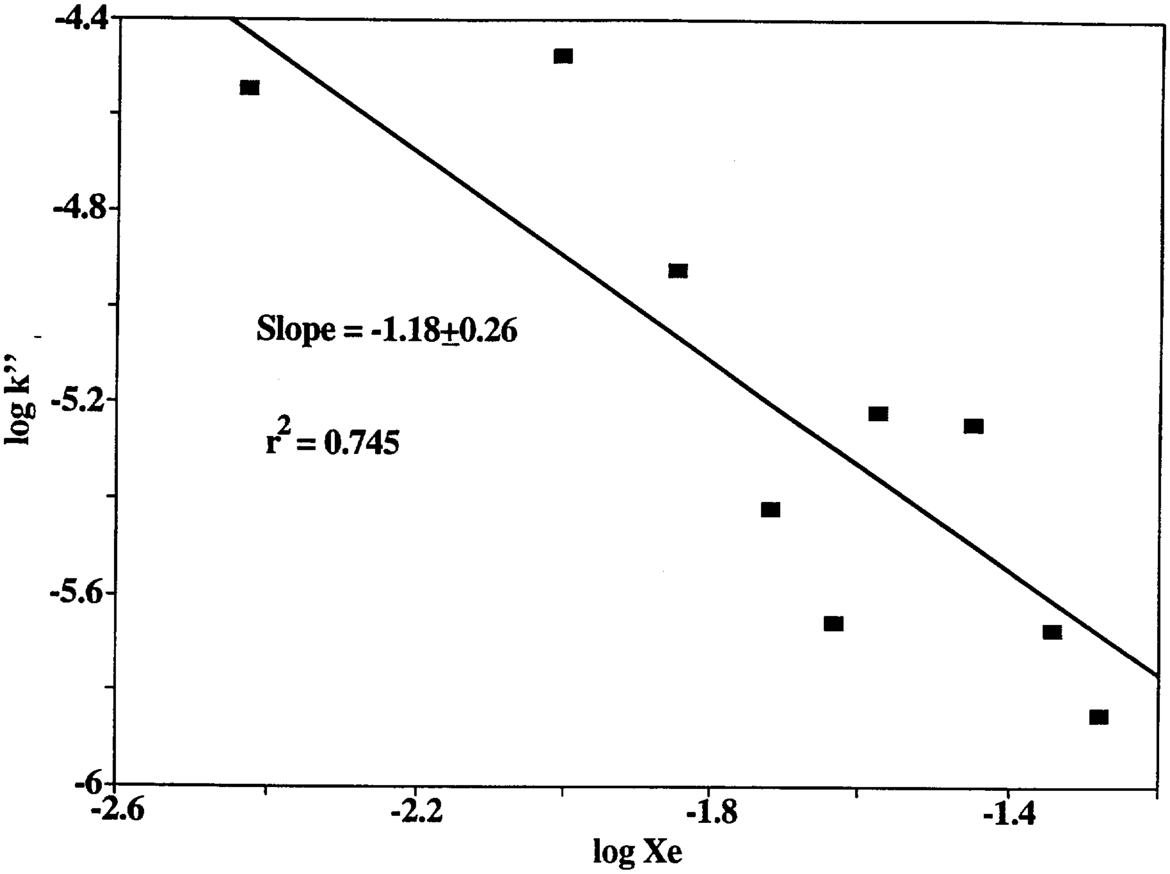

Figure 3.9 Plot of log k'' versus log X_e for $[Cr(VI)]_0$ = 0.8 mM at pH 2.0.

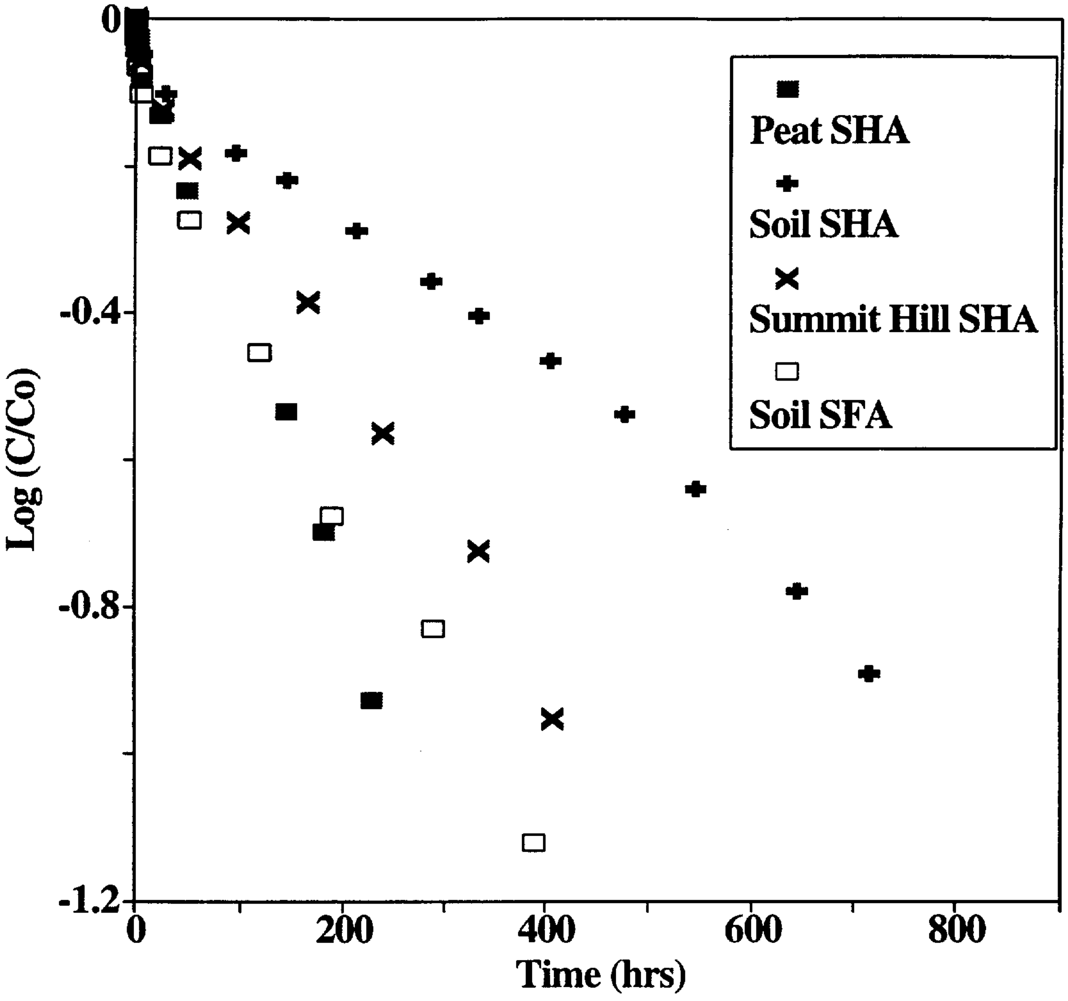

Figure 3.10 First-order plot of Cr(VI)/SHA reactions for various SHAs.

CHAPTER 4

Effect of Temperature, Ionic Strength and Electrolytes on the Reduction of Hexavalent Chromium by Soil Humic Substances

Abstract

The kinetics of hexavalent chromium reduction by excess soil humic substances (SHSs) was investigated in aqueous solutions where the temperature, ionic strength, background electrolyte, Cr(III), and Fe(III) were independently varied. Typical Cr(VI)-SHS reactions display a non-linear reduction of Cr(VI) with time, that is modeled as a continuum of components whose reactivity decreases as a greater fraction of the SHS is consumed. Cr(VI) reduction rates increase with increasing temperature. Arrhenius plots for Cr(VI) reduction yield activation entropies of 60±4 and 64±3 kJ mol^{-1} for soil humic acid and soil fulvic acid respectively. Rates of Cr(VI) reduction are not significantly altered due to changes in either background electrolyte or ionic strength. The presence of aqueous Cr(III) slightly inhibits the rate

of chromate reduction by soil humic acid, but has no effect on reduction by soil fulvic acid. Ferric iron greatly increases the rate of Cr(VI) reduction, even when only a small amount of Fe(III) is added to the system. A redox cycle where Fe is alternately reduced by SHS and oxidized by Cr may be established in these systems.

Introduction

Numerous industrial activities, including metallurgy, leather tanning, electroplating, lumber treating, and electricity generation produce significant quantities of chromium wastes. Leakage, unsuitable storage or improper disposal practices at these sites have led to many instances where chromium has been released to the subsurface (Calder, 1988; Palmer et al. 1988; Palmer and Wittbrodt, 1991). Because chromium can be acutely toxic, carcinogenic, and teratogenic (Abasi and Soni, 1984; Nieboer and Shaw, 1988; Ono, 1988; Waterhouse, 1975; Yassi and Nieboer, 1988), it is necessary to understand the processes governing the transport and transformation of chromium in the environment. Since both the mobility and toxicity of Cr depend on its oxidation state, redox reactions involving Cr are extremely important in determining its fate in the environment and potential risk to human health.

Chromium occurs in the environment in two stable oxidation states. The hexavalent form is more toxic (vanWeerelt et al. 1984) and generally more mobile than trivalent chromium (Bartlett and James, 1988). Cr(VI) species are weakly sorbed to many soils under alkaline to slightly acidic conditions (Zachara et al. 1989), thus can be very mobile in subsurface environments. In contrast, Cr(III) readily precipitates as $Cr(OH)_3$ or as the solid solution $Fe_xCr_{1-x}(OH)_3$ under alkaline to slightly acidic conditions (Rai et al. 1987; Sass and Rai, 1987). Aqueous Cr(III) can also be immobilized by chelation to organic molecules adsorbed to mineral surfaces (James and Bartlett, 1983a & b).

Cr(VI) is a strong oxidant that can be reduced to Cr(III) in soils by aqueous ions, mineral surfaces, simple organic molecules, or soil humic substances (Palmer and Wittbrodt, 1991). In a study of chromate reduction by various soils, Eary and Rai (1991) concluded that Cr(VI) reduction by organic matter and Fe(II) were roughly equivalent. Humic substances are present in virtually all soils and constitute the major dissolved and particulate organic fraction in most soils. Soil humic substances (SHSs) thus may represent a significant donor reservoir of electrons for Cr(VI) reduction.

The rates of Cr(VI) reduction by soil fulvic acid (SFA) and soil humic acid (SHA) were examined in chapters 2 and 3 respectively. Reaction of Cr(VI) with excess SHS is characterized by a nonlinear loss of Cr(VI) with time. The rate of Cr(VI) reduction decreases with time due to the depletion of Cr(VI) and the reduced reactivity of the SHS as it becomes oxidized. An empirical rate law for soil fulvic acid (SFA) and soil humic acid (SHA) was developed in which the rate of reaction was dependant on the mole fraction of humic substance oxidized. This rate law was generated from experiments in which the H^+, Cr(VI), and SHS concentrations were independently varied and apply to the first 5% of oxidizable SHS. As is the case with many organic-Cr(VI) reactions, the rate of reduction dramatically increases as the pH decreases. The empirical rate law treats the SHS as a continuum of reactive groups such that the rate of reduction follows

$$R=-kX_e^n[HCrO_4^-][SHS]_0(1-X_e)[H^+]^m \tag{5}$$

where X_e is the equivalent fraction of SHS oxidized. The results of those studies indicate that SFA reduces Cr(VI) more rapidly than SHA does.

The background electrolyte for experiments used to develop the rate law was LiCl. Lithium ion was used as the background cation because it does not exhibit site-specific binding with humic acid (Bonn and Fish, 1993). Lithium is rarely the major background cation would be a rare case in natural groundwaters. Thus, we conducted experiments using cations that more commonly contribute to the ionic strength of natural waters. The dependence of reduction rates on the background electrolyte was investigated using two monovalent (Li^+, K^+), and two divalent (Ca^{2+}, Mg^{2+}) cations.

Changes in ionic strength of the solution or the valence of the background electrolyte can cause conformational modifications in the SHS (Swift, 1989). Bonn (1992) suggests that significant humate conformational changes occur when divalent cation concentrations are greater than 2 mM. We suspected that these conformational changes would make the reactive functional groups either more or less accessible to Cr(VI), thereby altering the rate of reduction. The ionic strength dependence of Cr(VI) reduction by SHSs was studied in the ionic strength range 0.05 - 0.5 M.

The reduction of Cr(VI) by SHSs ultimately results in the formation of trivalent chromium. This Cr(III) can affect the rate of reduction by binding portions of the humic materials into complexes, potentially making them more resistant to oxidation. Experiments were conducted to determine the effects on Cr(VI) reduction rates due to the presence of various amounts of Cr(III).

Humic substances have been shown to reduce ferric iron to ferrous iron (Szilagyi, 1973a & b; Deng and Stumm, 1993). In turn, ferrous iron can reduce Cr(VI). The rate of Cr(VI) reduction by ferrous iron at low pH is much more rapid than reduction by humic substances. Chromate reduction by Fe(II) at low pH is rapid, with the reaction going to completion in less than five minutes (Eary and Rai, 1988). In contrast, the rate of Cr(VI) reduction by humic and fulvic acids is much slower, even at pH 2 (see Chapters 2 and 3). Thus, we would expect the rate of Cr(VI) reduction to increase in the presence of iron. While the reduction of both Fe(III) and Cr(VI) by SHSs are known to occur, it is unlikely that the reduction mechanisms are identical. The Fe^{3+} cation has a very different association mechanism with humic substances than would the chromate anion. As such, one would expect that Cr(VI) reduction by humic-reduced iron and by SHS would not be competing reactions. If the chromium reduction reactions by iron and by SHS are not competitive, then the rates of reduction of chromium by iron and by SHS should be additive. We conducted a series of experiments to determine how the addition of Fe(III) alters the rate of Cr(VI) reduction by SHSs.

The objective of this chapter is to describe the effects of temperature, ionic strength, and dissolved electrolytes on the rate of reduction of Cr(VI) by a soil fulvic acid and a soil humic acid. Experiments were conducted in the temperature range 4 to 55°C. Ionic strength was varied from 0.05 to 0.5 M. Several mono- and divalent cations were examined as background electrolytes. Additionally, experiments were conducted to determine the response of the system to the presence of Cr(III) or Fe(III).

Experimental Section

Materials. Soil fulvic acid and soil humic acid were obtained from the International Humic Substances Society (IHSS) collection of reference humic materials (ref. # 1R102F and 1R102H). These materials were used because the properties of these humic substances such as composition and NMR spectra (Thorn et al., 1989, 1991) were readily available. Solutions were prepared with ultrapure (~18 mega-ohm) water from a Barnstead Nanopure water purification system. Chemicals were all of reagent grade. The glass reaction vessels were foil-wrapped to prevent photoreactions.

Analytical and Experimental Methods. The reduction of Cr(VI) by a SHS was determined by measuring the time-dependent concentration of Cr(VI) in batch reaction vessels. Most of these experiments were performed at room temperature (25±2°C) in triplicate. These reduction experiments were conducted with excess SHS over chromium as determined from the modified Walkley-Black tests reported in chapters 2 and 3.

Aliquots (20 ml) of a stock solution containing 100 mg/L of SHS were equilibrated for 24 hours at pH 2.0 and then spiked with Cr(VI). The pH in all experiments was 2.0±0.056. Cr(VI) concentrations were measured over time by a diphenylcarbazide (DPC) colorimetric method described in Chapter 2. The Fe(II) concentration was measured in the experiments spiked with Fe(III) using a 1,10 phenanthroline method (APHA, 1989; Tamura et al, 1974).

The effects of background electrolyte composition was studied using both mono- and divalent cations (Li^+, K^+, Ca^{2+}, and Mg^{2+}). For experiments with various ionic strengths, temperatures or trivalent cations, the background electrolyte was LiCl. The rate of Cr(VI) reduction as a function of ionic strength was studied in the range $I = 0.05 - 0.5$ M. The rate of reduction as a function of temperature was studied in the range 277-328 K at pH 2.0.

The rate of Cr(VI) reduction by SHSs in the presence of a trivalent cation was examined using either Cr(III) or Fe(III). Rate experiments were conducted in the Cr(III) concentration range 0.0 - 0.4 mM. To determine the extent to which Cr(III) may increase the resistance of SHS to oxidation, we pretreated the humic matter in various solutions of Cr(III) for 24 hrs. prior to reaction with Cr(VI). The rate of Cr(VI) reduction was studied at two [Fe(III)] (0.002 mM and 0.012 mM) to determine how the reduction rate changes in the presence of an ion known to be reduced by SHS (Szilagyi. 1973, 1971) and oxidized by chromium (Bartlett and James, 1988). Initial Cr(VI) concentration for all the rate experiments was 0.02 mM. The ionic strength was 0.1 M for all sets of experiments other than the various ionic strength set.

Results and Discussion

The results of these experiments are consistent with those described in Chapters 2 and 3, in that the reaction is characterized by a non-linear loss of Cr(VI) with time. The reaction is initially rapid then becomes slower as more of the SHS is oxidized. All of the experiments follow the general rate law given by Equation 1.

Temperature Effects. Raising the temperature from 277 to 328 K greatly increases the rate of Cr(VI) reduction by SHS as pH 2.0 (Figure 4.1). Rate coefficients, k, were computed at 277, 288, 298, 308 and 328 K using the rate law given by Equation 1. A regression analysis of the integrated form of the rate equation yields a slope from which the rate coefficient is calculated.

We assumed that the temperature dependence of the rate coefficients followed

$$k=\frac{k_B T}{h}e^{\Delta S^{*}/R}e^{-\Delta H^{*}/RT} \qquad \textbf{(6)}$$

(Lasaga, 1981) where $\Delta H^{\neq}$ is the heat of activation and $\Delta S^{\neq}$ is the entropy of activation, T is temperature in kelvins, k_B is Boltzman's constant ($1.38\text{x}10^{-23}$ JK^{-1}), h is planck's constant ($6.63\text{x}10^{-34}$ J-sec), and R is the gas constant (8.314 $J(K\text{-}mol)^{-1}$. The heats and entropies of activation were calculated from the slopes and intercepts of plots of ln (k/T) versus 1/T (Figure 4.2, Table 4.1). Because of the empirical manner in which the rate coefficients were derived, the activation parameters must be taken as composite values for all reactions including the rate limiting step. As such, they do not necessarily describe the activation energy of an elementary reaction.

The computed activation enthalpies for SFA and SHA are not statistically different at the 95% confidence level as calculated from a t-test (Davis, 1973). This could imply that the rate limiting step is the same for both SFA and SHA. This makes sense if the SFA and SHA contain the same reactive functional groups, albeit at different concentrations. These computed heats of activation are 1.2 to 1.5 times larger than those reported for Cr(VI) reduction reactions by simple organic compounds with hydroxyl or sulfhydryl functional groups (Elovitz, 1993).

The entropy of activation ($\Delta S^\ddagger$) is often used as an indicator of the configuration of the activated complex. A large negative number such as those calculated for the SHSs indicates that the reactant molecules are separated by short bonds. Such bonding would be consistent with the idea that the decomposition of the chromate ester is the rate limiting step. The activation energies are relatively large and greatly in excess of those required for diffusion (21 kJ mol^{-1}), suggesting that transport processes are not the rate limiting factor in our experiments.

Table 4.1. Activation Data for Cr(VI) Reduction by IHSS Reference Soil Humic Acid and Soil Fulvic Acid at pH 2. $[Cr(VI)]_0$ = 0.02 mM, $[SHS]_0$ = 100 mg/L, T = 4-55°C.

	$\Delta H^{\neq}$ (kJ mol^{-1})	$-\Delta S^{\neq}$ (kJ mol^{-1} K^{-1})	E_a (kJ mol^{-1})
SHA	60±4	-226±8	63±4
SFA	64±3	-228±6	66±3

Effect of Varying Ionic Strength and Background Electrolyte. Plots of [Cr(VI)] versus time display little difference in rates of reduction as the ionic strength is varied over the range [LiCl] = 0.05 - 0.5 M (Fig. 4.3). The mean values of the measurements for both SFA (Fig. 4.3a) and SHA (Fig. 4.3b) were identical within the analytical error.

Plots of [Cr(VI)] versus time (Figure 4.4) show very little variation in Cr(VI) reduction rates by SFA or SHA as the background cation changes. These results suggest that conformational changes in the humic substances due to the presence of various cations do not significantly affect the resistance of the SHS to oxidation by the chromate species. Perhaps this is because cation binding is primarily an electrostatic phenomena and one would not expect the chromate anions to behave in the same manner as cations. In addition, it is likely that groups that are responsible for cation binding, predominantly the carboxylic acid groups, are not the same groups involved in reduction reaction reactions (e.g., alcoholic and phenolic groups), suggesting that Cr(VI) interacts with the more hydrophilic components of the SHS which are always accessible to the aqueous chromate regardless of the conformation of the macromolecule.

Role of Cr(III) in Chromate Reduction by SHSs. Plots of [Cr(VI)] versus time show that the pretreatment with Cr(III) does not alter the rates of reduction by SFA (Figure 4.5a) but appears to have a slight inhibiting effect on the rate of Cr(VI) reduction by SHA (Figure 4.5b). Rate coefficients for these experiments calculated using Eq. 1 differ by only 30% between experiments with 0.01 and 0.4 mM initial Cr(III), a minor change relative to the effects of temperature or pH. These results suggest that the sites which reduce the Cr(VI) are not greatly affected by conformational changes in those that complex the trivalent chromium.

Effect of Fe(III) on Chromate Reduction by SHSs. The reduction of Cr(VI) by both SFA and SHA increases with the addition of Fe(III) to the system (Figure 4.6). When Cr(VI) is present there is no measurable Fe(II), but after all of the Cr(VI) is reduced, Fe(II) appears (Fig. 4.7a & b). This indicates that the reduction of Cr(VI) by Fe(II) is relatively rapid. As expected, control blanks containing Fe but no Cr(VI) show that SFA reduces Fe(III) in solution faster than SHA does (Fig. 4.7). No special precautions were taken to eliminate dissolved oxygen from these systems, since at pH 2 the oxidation of ferrous iron by chromate is much more rapid than by oxygen (Eary and Rai, 1988).

The iron experiments were conducted with both an excess of Fe(III) over Cr(VI) and with a deficit of Fe(III) versus Cr(VI). One would expect the ferric iron to be reduced to ferrous iron by the SHS and then reoxidized by the Cr(VI). Results of the experiment with only an equivalent fraction of 3% as much Fe as Cr indicate that the iron is set into a cycling process, being alternately reduced by the SHS and then oxidized by the Cr(VI) (Fig. 4.8). If the Fe(III) were reduced by the SHS and oxidized by the Cr(VI) only once before being complexed by the SHS, then after the initial loss of Cr(VI) due to reduction by Fe, the rate of Cr(VI) reduction would reflect that of reduction by SHS alone. An unexpected result of these experiments is that some of the added iron is almost immediately reduced and in turn reduces the Cr(VI) extremely rapidly. The reaction is so fast that the initial Cr(VI) measurements (<10 min. after Cr and Fe addition) show a 30% Cr(VI) loss for SFA and 15% loss for SHA. In contrast, when no Fe is present, less than 10% of the Cr(VI) is reduced by SFA and less than 5% of the Cr(VI) is reduced by the SHA in the first 30 minutes. As can be seen from the plots of [Cr(VI)] versus time, the initial measurement of Cr(VI) is significantly lower than the amount added, suggesting that the Fe(III) is immediately reduced by the SHS and then is available to reduce the Cr(VI).

These results can have important implications in natural systems, where dissolved iron typically is at low concentrations. Even a relatively minor amount of iron in a system can significantly alter the rate of Cr(VI)/SHS reactions. These results illustrate the nature of redox cycling and the importance of knowing reaction rates. Other reactants in addition to Cr, Fe, and SHSs can be included in the redox cycle. For example, a MnO_2 solid could be present to reoxidize Cr(III) to Cr(VI).

Summary and Conclusions

The reduction of Cr(VI) by SFA and SHA was investigated in solutions where the temperature, ionic strength, and background electrolyte were varied. Results of experiments with monovalent (Li^+, K^+), and divalent (Ca^{2+}, Mg^{2+}) cations, demonstrate that the rates of reduction are not greatly altered by variations in background cations. Experiments using various amounts of LiCl show no significant changes in Cr(VI) reduction rates with varying ionic strength. These results indicate that the empirical rate laws developed in previous chapters are applicable over a wider range of conditions than previously discussed.

Experiments at various temperatures show a significant temperature dependence of the reactions, with activation enthalpies of 68 kJ/mol for SFA and 62 kJ/mol for SHA. While the rate laws were developed at 25°C, groundwaters are generally cooler than this temperature. The results presented here allow for temperature corrections to be made for various conditions.

The role of Cr(III) in the reduction of Cr(VI) was also investigated. It appears that the presence of Cr(III) does not inhibit the reduction of Cr(VI) by SFA and only slightly inhibits the rate of reduction by SHA. The slight slowing of reduction rates by SHA in the presence of Cr(III) is unlikely to be important in most environments. At most natural pH values (4-10), Cr(III) generally precipitates as hydroxide solids, thus the levels of aqueous Cr(III) are very low. The presence of a Cr(III) solid may have an effect on Cr(VI) reduction rates, but has not been addressed.

The rate of Cr(VI) reduction by SFA and SHA was investigated in the presence of Fe(III). The rate of Cr(VI) reduction increases greatly with the addition of ferric iron to the system. The Fe(III)-Fe(II) redox couple appears to act as an electron transfer catalyst for the reduction of Cr(VI) by SHSs. A reaction sequence occurs where the iron is involved in a redox cycle, being alternately reduced by the SHS then oxidized by the Cr(VI). Natural systems often have only a minor quantity of Fe in solution. These results indicate that only a small fraction of Fe can catalyse a larger quantity of Cr.

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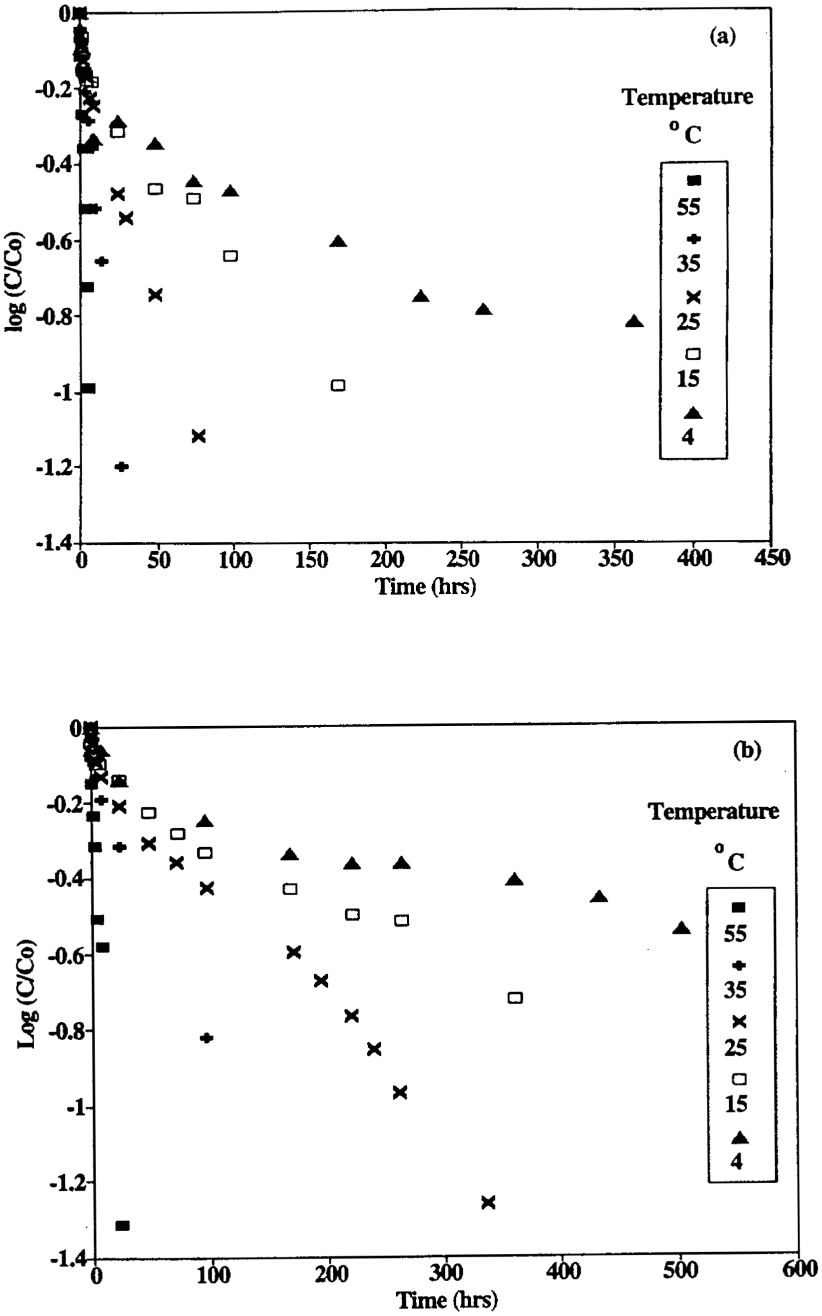


Figure 4.1. Reduction of Cr(VI) by a) soil fulvic acid and b) soil humic acid at various temperatures (4, 15, 25, 35, 55°C). First-order plots of log relative [Cr(VI)] versus time. $[Cr(VI)]_0 = 0.02$ mM, $[SHS]_0 = 100$ mg/L, $I = 0.1$ M, pH = 2.0.

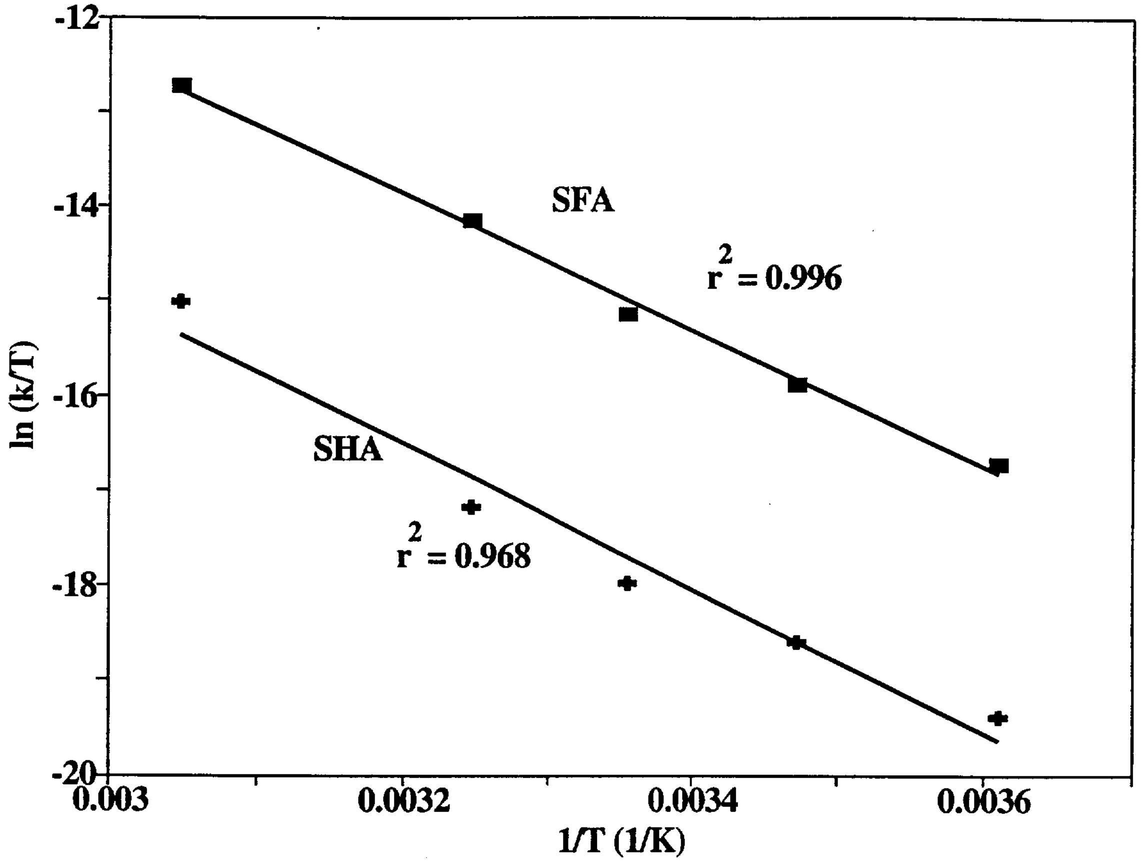
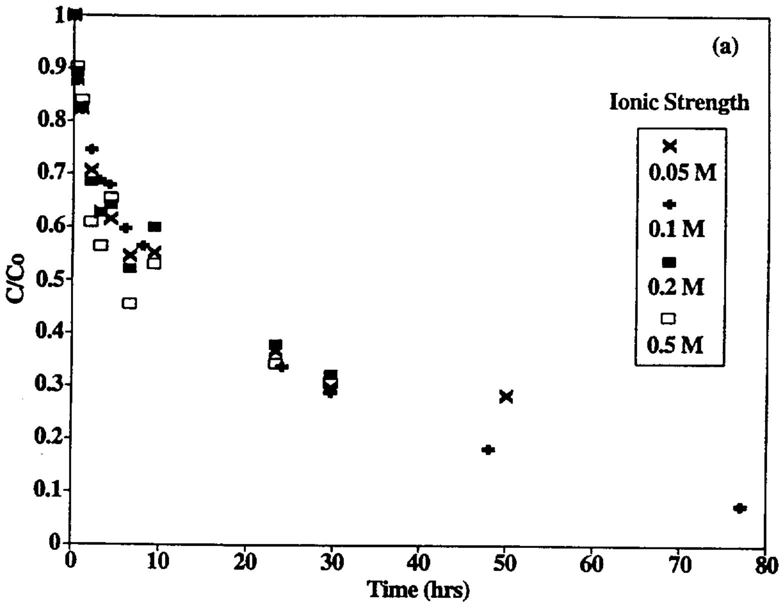


Figure 4.2. Influence of reaction temperature on the observed rate coefficients for Cr(VI) reduction by SHS. Plots of ln (k_{exp}/T) versus 1/T for 4, 15, 25, 35, and 55°C. Curves fitted by a weighted least-squares linear regression. Heats (ΔH‡) and entropies (ΔS‡) of activation computed from slopes and intercepts, respectively.



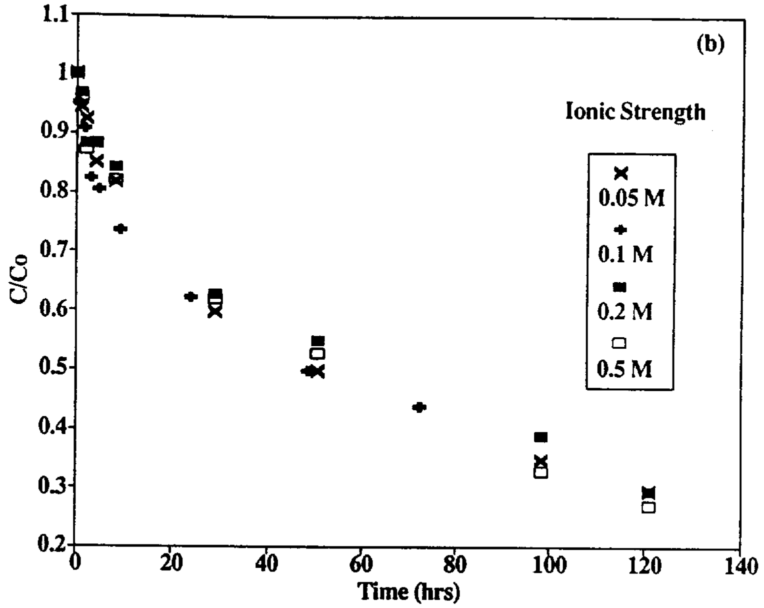
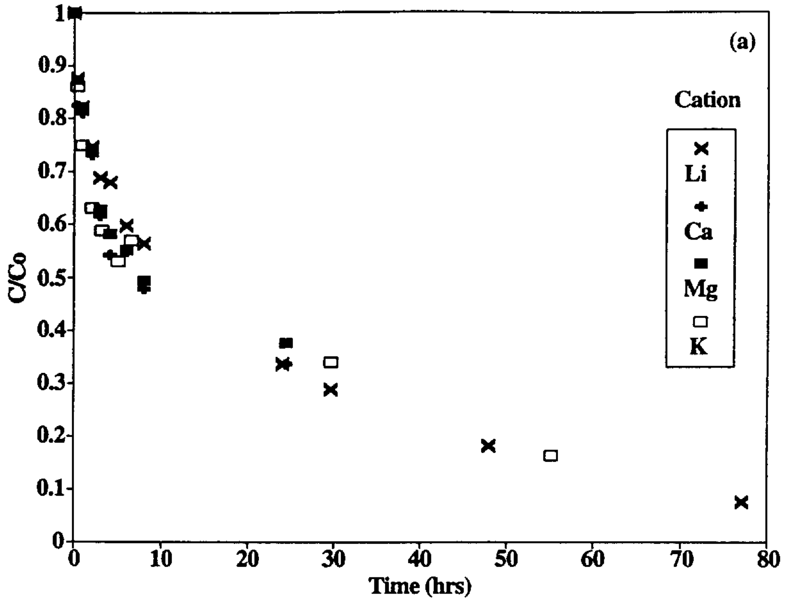


Figure 4.3. Reduction of Cr(VI) by a) soil fulvic acid and b) soil humic acid in solutions of various ionic strengths in the range I = 0.05 - 0.5 M. Points represent means of triplicate measurements. $[Cr(VI)]_0$= 0.02 mM, $[SHS]_0$= 100 mg/L, pH = 2.0.



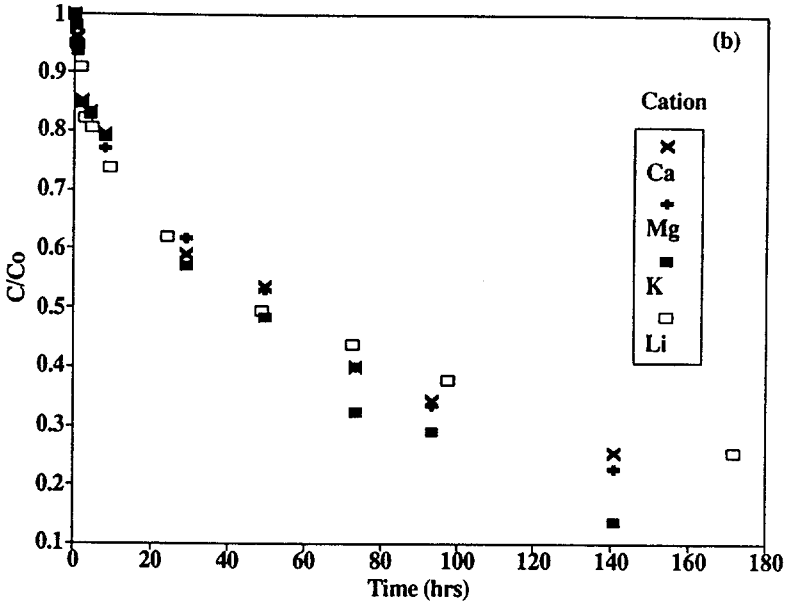


Figure 4.4. Reduction of Cr(VI) by a) soil fulvic acid and b) soil humic acid in solutions with various cations for the background electrolyte. $[Cr(VI)]_0 = 0.02$ mM, $[SHS]_0 = 100$ mg/L, $I = 0.1$ M, pH 2.0.

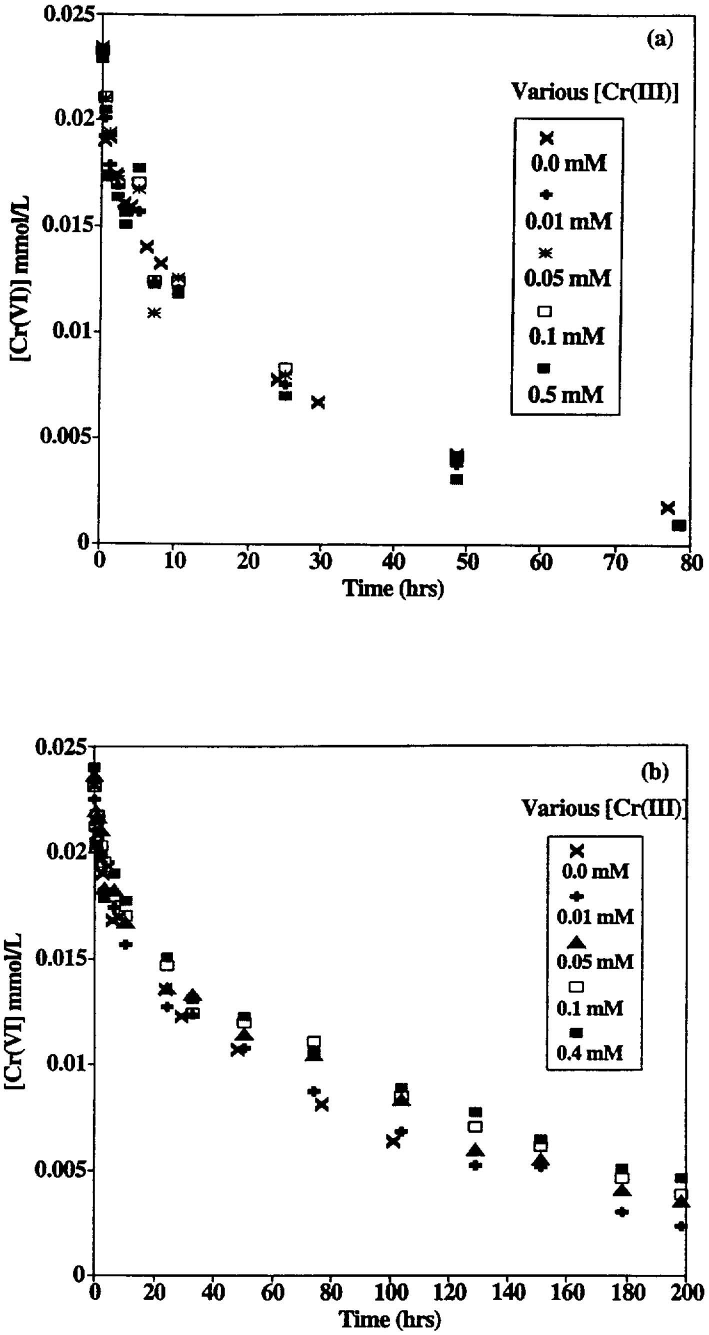


Figure 4.5. Reduction of Cr(VI) by a) soil fulvic acid and b) soil humic acid in solutions with various initial concentrations of Cr(III). $[Cr(VI)]_0$= 0.02 mM, $[SHS]_0$= 100 mg/L, I = 0.1 M, pH = 2.0.

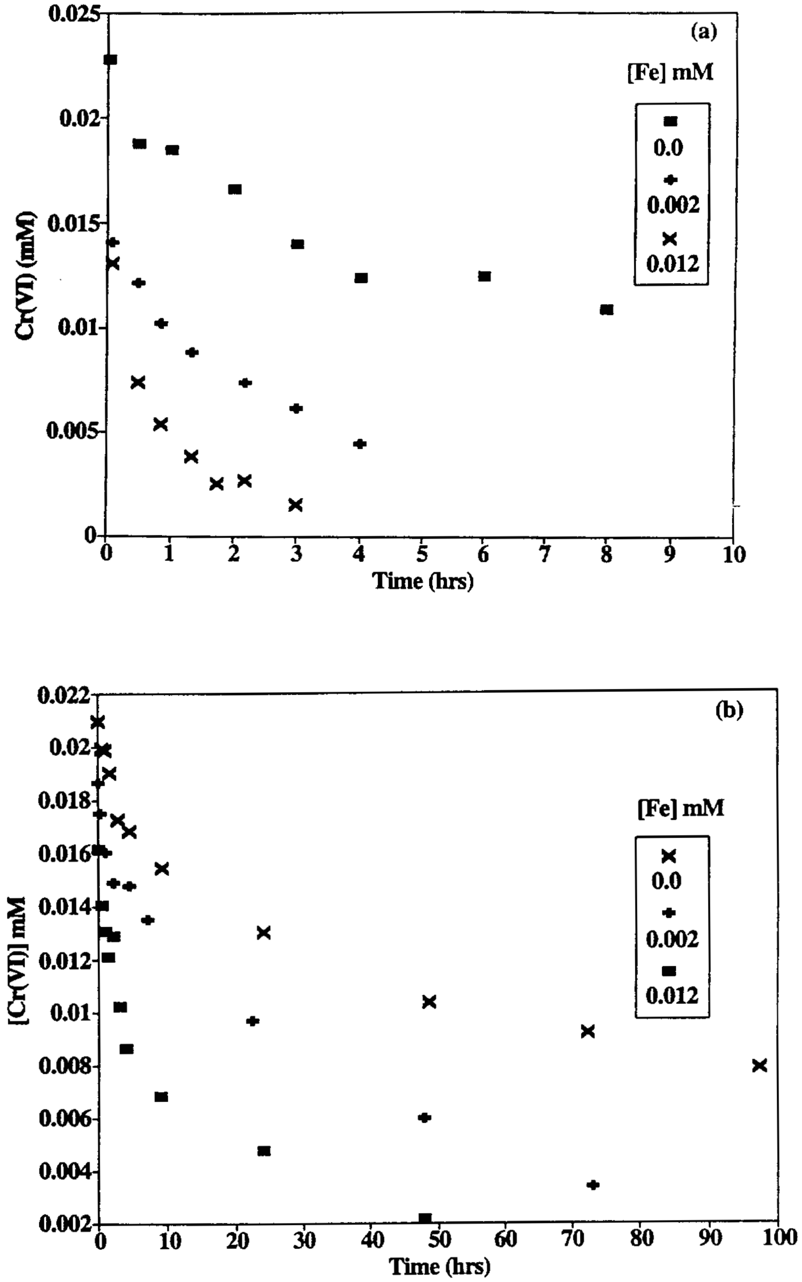


Figure 4.6. Reduction of Cr(VI) by a) soil fulvic acid and b) soil humic acid in solutions with various initial concentrations of Fe(III). $[Cr(VI)]_0 = 0.02$ mM, $[SHS]_0 = 100$ mg/L, $I = 0.1$ M pH = 2.0.

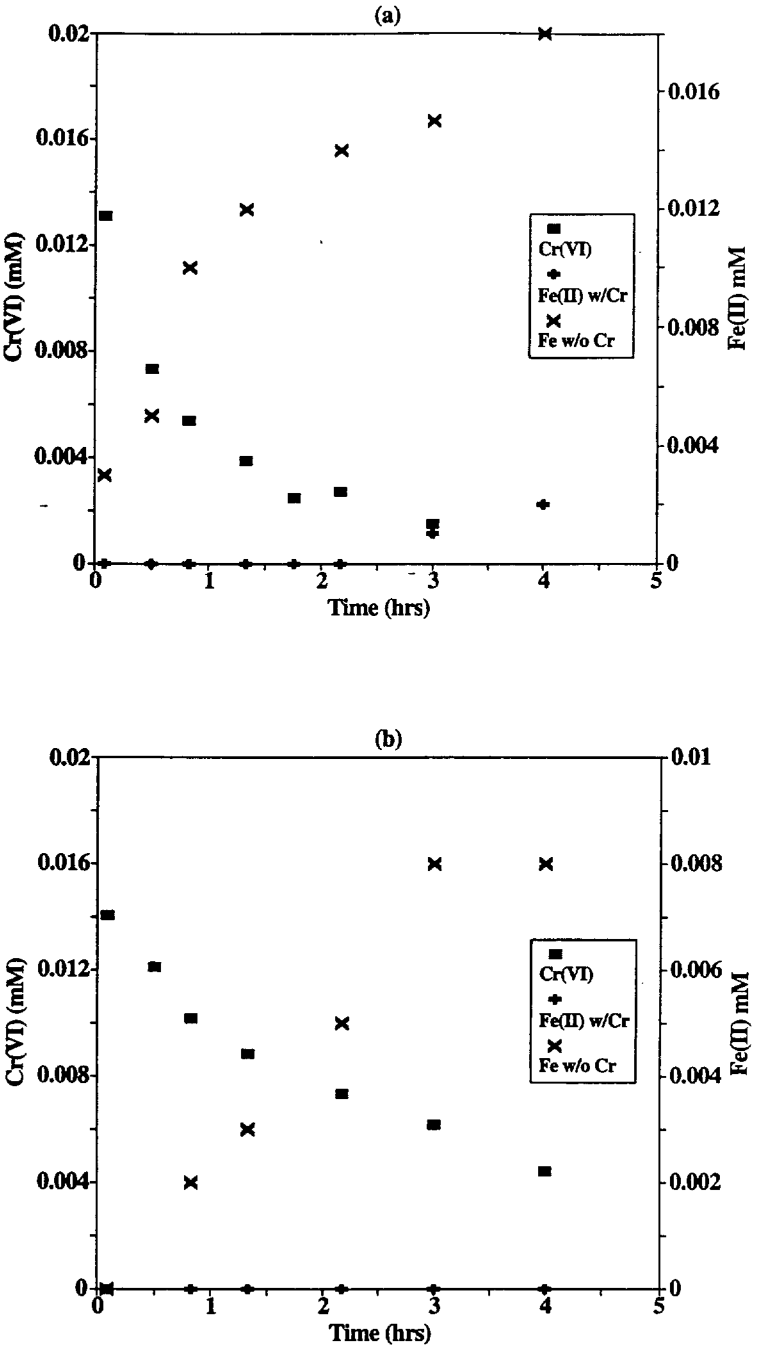


Figure 4.7. Ferrous iron concentration versus time for experiments where Fe(III) was added to solution. $[SHS]_0$ = 100 mg/L, I = 0.1 M pH = 2.0.

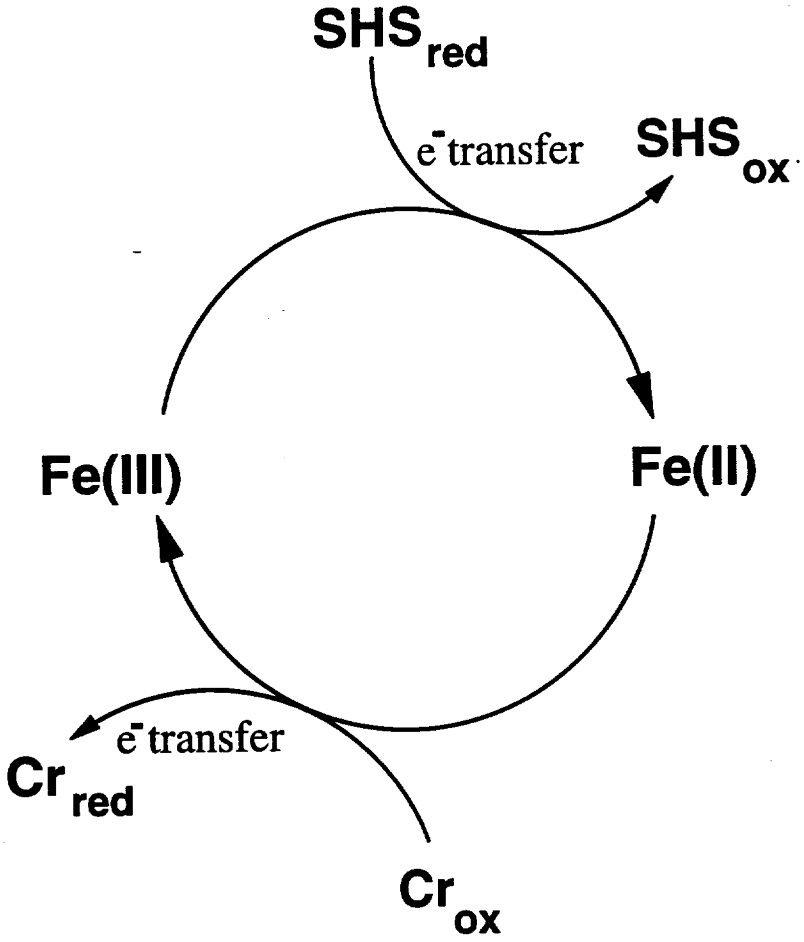


Figure 4.8. Description of redox cycling of iron in a system with chromium and SHS present. Since only one electron transfer occurs for each redox reaction with iron, the chromium can be in either the +6, +5, or +4 state.

CHAPTER 5

Summary and Conclusions

The results presented in this thesis provide a comprehensive study of aqueous phase interaction between soil humic substances (SHSs) and hexavalent chromium under conditions typical of many chromium-contaminated sites. Many sites have high levels of Cr(VI) contamination, some into the thousands of ppm range, making chromium a dominant player in redox reactions occurring in the subsurface. Studies of redox reactions between Cr(VI) and SHSs are not prevalent in the environmental literature. There is a small body of research concerning Cr(VI) reactions with natural organic matter, but most of this analysis is directed toward reactions occurring at very low levels of Cr(VI), concentrations that are more typical of natural conditions or slightly contaminated sites. The research described here has addressed the need for kinetic data concerning Cr(VI)/SHS redox reactions under environmental conditions. The results enable us to work toward the inclusion of redox reaction terms in transport models for chromium.

The overall goal of this research project was to gain an understanding of the propensity for Cr(VI) reduction by soil humic substances under environmental conditions. The primary questions addressed were; 1) what are the timescales on which the reactions occur and are these timescales environmentally relevant, 2) can the kinetics of transformation be predicted with a simple model, and 3) what are the environmental conditions that affect the rates of transformation. Because of the heterogeneous nature and complexity of humic substances, analysis of reaction products was not practical. Thus, an empirical rather than a mechanistic approach was used to answer these questions.

A rate law is developed for soil fulvic acid-Cr(VI) reactions in Chapter 2 for conditions where there is an excess of SFA over chromium. An excess of humic substances over chromium can be the case even when only a small fraction of the soil consists of organic matter. The rate law developed is for a continuum of reactive constituents, whose reactivity changes as the humic material evolves during the reaction. The factors that most influence the reaction rate are pH and the fraction of SHS that has been oxidized. The rate equation is valid over a range of pH and reactant concentrations. The applicability of the rate law to Cr(VI)-SHA reactions is discussed in Chapter 3.

The effects of temperature, ionic strength and various electrolytes on the rate of Cr(VI) reduction by a SFA and a SHA are presented in Chapter 4. The knowledge of reaction rates over a wide temperature range allows us to adjust the model for environmental conditions. Rates of reduction are not significantly altered due to changes in either background electrolyte or ionic strength. The presence of Cr(III) slightly inhibits the rate of reduction by soil humic acid, but not that of soil fulvic acid. Ferric iron increases the rate of Cr(VI) reduction, even when only a small amount of Fe(III) is added to the system. It appears that the Fe participates in a redox cycle, alternately reduced by the SHS then oxidized by the Cr(VI).

An empirical rate expression is a useful tool for accounting for Cr(VI)/SHS reactions in the environment provided it adequately predicts the reaction rate over wide ranges of solution conditions. Many contaminated sites have high Cr (VI) concentrations and low pH in the plume, resulting in steep chemical gradients. For example, contamination at the United Chrome Products site in Corvallis, Oregon was due primarily to leaking plating baths, creating a near source Cr(VI) concentration of nearly 20,000 mg/L and a pH of approximately 2 (CH2M Hill, 1990). However, the acidity is not spatially coincident with the chromate plume. The low pH is attenuated by the soil exchange capacity within tens of meters of the source while the Cr(VI) plume extends approximately a hundred meters down gradient. The Cr(VI) plume thus includes a pH range from 2 to 7. In order to be useful, a reaction model must be robust and include wide variation in solution conditions. In an environment where pH is well buffered and nearly constant, the empirical rate law yields reasonable estimates of Cr(VI)/SHS reaction rates over a wide range of solution concentration. However, because the reaction varies with respect to [H^+], predictions across a large pH gradient may exhibit a greater degree of uncertainty. Such complexities notwithstanding, we can use the rate law an experimentally determined rate constants to quantify the characteristic time scales of Cr(VI) reduction reactions and put them in the context of time scales of other environmental processes.

Reaction Timescales

The results of our kinetic investigations show that Cr(VI) can be readily reduced to Cr(III) by SHSs on timescales comparable to environmental transport timescales. The data show that the rates of these reactions can vary by many orders of magnitude, depending on reactants and solution conditions. Reaction rates are most strongly affected by pH and the fraction of humic that has been oxidized. The log k'-$\{H^+\}$ profiles for SFA and SHA (Figures 2.10 and 3.6 respectively) show that the rates can vary by more than two orders of magnitude over the pH range 2-7. Reduction rates were shown to vary by over three orders of magnitude over just a small fraction (<5%) of oxidizable SHS.

Rates of groundwater transport can vary over several orders of magnitude. The timescales of Cr(VI)-SHS reactions overlaps the timescales for groundwater transport. Both are on the order of days to months. As such, these reactions are fast enough to be environmentally significant, yet slow enough that we cannot assume instantaneous reactions or chemical equilibrium. Therefore, we must include these redox reactions in Cr(VI) transport models in order to accurately predict the movement of Cr(VI) in the subsurface. In addition to reduction reactions, we must also consider oxidation reactions, such as the oxidation of Cr(III) to Cr(VI) by MnO_2, that occur on a similar timescale.

Application of Results to Environmental Situations

The results of this study show that Cr(VI) can be reduced to Cr(III) by soil humic substances in moderately acidic to neutral solutions. It is useful to examine the conditions under which these reactions would occur in the field in order to gain an understanding of the environmental relevance and application of the experimental results. The conclusions of these studies can have important implications for remediation strategies at chromium-contaminates sites. Locales with high levels of contamination can have much of the Cr(VI) removed using traditional pump-and-treat methods. However, at some point the chromium concentrations will begin "tailing", thus rendering the remediation measures inefficient and cost-prohibitive. In such cases, or at sites where initial contamination levels are low, the approach of "natural attenuation" may be a viable option. Various tests used to determine the Cr(VI) reduction potential of a soil provide little information on the timescales over which these transformations will occur in the environment. Natural attenuation can only be considered if the reduction kinetics are on a timescale that is less than the timescale for transport of the Cr(VI) from the source to some point of compliance. The results of this research indicate that Cr(VI) reduction by SHSs and groundwater transport can be of the same timescales. Thus, these reactions may be important as a major contributor to the natural attenuation of Cr(VI) at some sites.

Implications for Further Research

This study sheds light on an important process that can occur in chromium-contaminated soils. While the reduction of Cr(VI) by SHSs is only a small part in the overall cycling of chromium in the environment, it is an important reaction worthy of additional study. As illustrated by the experiments with iron present, small perturbations in the system can have drastic results on the reaction rates. Since iron is relatively insoluble at slightly acidic to neutral conditions, rates of reduction in the presence of trace amounts of Fe at more neutral pH values should be determined. Other processes such as reactions with mineral surfaces, should also be considered.

In conclusion, this thesis project provided new and significant information concerning reactions between Cr(VI) and soil humic substances under conditions typically found in the environment. The results indicate that SHSs have a profound effect on the environmental fate of Cr(VI).

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VITA

The author was born July 7, 1959 in Flint, Michigan, and was raised in the Buicktown suburbs. He had a keen interest in science even at an early age, with a distinct bent toward the earth sciences. The decision to pursue a career in geology was a combination of his interest in earth science and a love of the outdoors. He followed his desires to Houghton, in the state's upper peninsula, where he obtained a Bachelor of Science in Geology at Michigan Technological University in May, 1981. He spent the summer after graduation conducting heavy metals exploration in Michigan and Wisconsin before venturing north to Alaska.

He studied economic geology in Fairbanks, where he received a Master of Science in Geology from the University of Alaska in May 1985. His thesis was "Paleomagnetism and Petrology of St. Mattthew Island, Bering Sea, Alaska". His explorations of the Great White North, a geologist's paradise, with an endless variety of terranes, outcrops and geologic structures, included field work for his research and exploration for a variety of mineral deposits. Disillusioned by the dim prospects for the mining industry in the states, this geologist decided to pursue other venues.

A move from Fairbanks to Portland, Oregon occurred in August 1985 and the author spent the next six months travelling in New Zealand. Upon return, he took a temporary position as a geologist for the Geotechnical Group of the Oregon Department of Transportation. He began studying hydrogeology in the spring of 1987, taking classes part-time, first at Portland State University, then at the Oregon Graduate Center. In July 1988 he began full-time studies in the Department of Environmental Science and Engineering. After working on various projects concerning the transport and transformation of chromium, he completed his degree with this thesis.

List of Publications

Palmer, C.D. and P.R. Wittbrodt, Processes Affecting the Remediation of Chromium-Contaminated Sites. *Environmental Health Perspectives*. Vol. 92, pp. 25-40, **1991.**

Wittbrodt, P.R., D.B. Stone, and D. Turner. Paleomagnetism and Geochronology of St. Matthew Island, Bering Sea, Alaska. *Can. J. Earth Sci.* Vol.26 pp. 2116-2129 **1989**.