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Effect of Organic Compounds and Copper on Chromium(VI) Reduction: Electrochemical Investigation of Electron Transfer Rates

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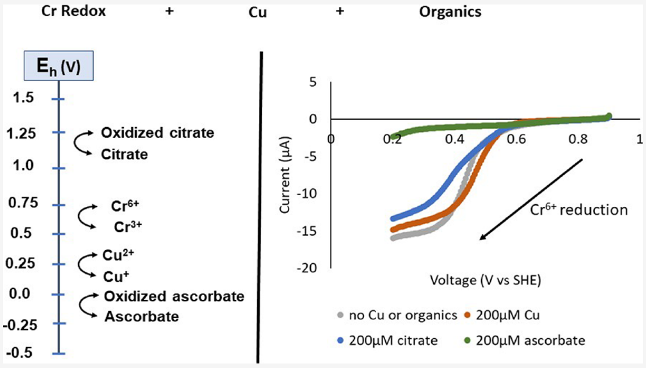
ABSTRACT: Chromium contamination is redox-controlled, with Cr occurring in environmental settings as toxic and mobile Cr(VI) or less toxic Cr(III). The mechanisms and kinetics of Cr(VI) reduction and removal under variable environmental conditions are not fully understood. Here, we measure the charge transfer kinetics of Cr reduction under laboratory-controlled conditions using electrochemical techniques to provide mechanistic insights into the chemical reactions affecting the reduction of Cr(VI). By the addition of common anions, organic compounds, and copper, we determined the impact of each of these constituents on Cr(VI) reduction through voltammetric measurements using a gold rotating disk electrode. Copper acted as an electron shuttle and promoted faster Cr(VI) reduction rates. Sulfate and chloride as well as the organic citrate adsorbed to the electrode and slowed Cr(VI) reduction. The oxidation of certain organics (ascorbate and cysteine as well as oxalate to a lesser extent) was coupled to the reduction of Cr(VI), increasing the Cr(VI) reduction rate, while other organics (glutamate and citrate) were not electrochemically oxidized. Our work on a relatively simple Cr(VI) system illustrates how electrochemical measurements can be applied in an innovative way to provide a more direct measurement of the electron transfer kinetics of environmental and geochemical reactions.



KEYWORDS: *redox, voltammetry, Cr(VI) reduction, kinetics, rotating disk electrode*

■ INTRODUCTION

Chromium (Cr) is a toxic element often found as a contaminant in water and sediments. Cr occurs in the environment in two primary oxidation states: oxidized and mobile Cr(VI) and relatively immobile Cr(III).[1,2] Cr(VI) is toxic and carcinogenic, forming the oxyanion chromate (CrO_4^{2-}) at neutral pH conditions and low concentrations. Chromate is protonated ($HCrO_4^-$ or $H_2CrO_{4(aq)}$) at low pH or forms dichromate ($Cr_2O_7^{2-}$) at higher Cr(VI) concentrations.[1,3,4] Under reducing conditions, Cr(VI) is reduced to Cr(III), which is less toxic and less soluble than Cr(VI). Cr(III) typically strongly adsorbs to solid phases or precipitates as a Cr(III) hydroxide mineral.[1,2] Due to the much less toxic effect of Cr(III) compared to Cr(VI) on human health, Cr(VI) reduction is often utilized to remediate contaminated sites. However, our understanding about how charge transfer kinetics affect the stability of Cr(VI) under environmentally relevant conditions remains lacking.

Cr(VI) reduction to Cr(III) can occur microbially or abiotically with abiotic Cr(VI) reduction often coupled to oxidation of iron(II) or organics.[1,5] Natural organic matter in the environment, such as fulvic or humic acids, can remove Cr by reducing Cr(VI) to relatively insoluble Cr(III). The reduction mechanisms of Cr(VI) by organic matter can be fairly complex, with Cr(VI) being reduced to Cr(V) or Cr(IV) before these intermediates disproportionate, eventually forming Cr(III).[6,7] The reduction of Cr(VI) by solid-phase organics is highly pH-dependent with significantly faster reduction rates at low pH.[1,8,9] At low pH, some of the organic compounds are positively charged, so greater electrostatic attraction of CrO_4^- and $HCrO_4^-$ to these organics can occur, leading to subsequent Cr(VI) reduction. Certain soluble organics, such as ascorbic acid, have been shown to rapidly reduce Cr(VI).[10] Numerous organic compounds, such as citrate and oxalate, bind to Cr(III) and increase its solubility in water, so Cr concentrations may remain high following Cr(VI) reduction by organics. These Cr(III)-organic complexes are thermodynamically favorable versus insoluble Cr(III) hydroxides. Cr(VI) reduction is typically kinetically limited, but certain redox-active elements

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can act as electron shuttles, promoting more rapid Cr(VI) reduction. Copper (Cu), which is often found as a co-occurring contaminant with Cr(VI), can act as one of these electron shuttles, fluctuating between its oxidized Cu(II) form and reduced Cu(I) or Cu(0) states and promoting Cr(VI) reduction in contaminated settings.[11−13] Extensive literature has demonstrated that Fe(II) abiotically reduces Cr(VI) in a pH-dependent reaction.[9,14−18] Organics can also influence the reaction of Fe(II) with Cr(VI) by increasing the solubility and reactivity of Fe(II) and Fe(III).[2,6,9,18−22] Mineral surfaces can also highly impact the mechanisms of Cr(VI) reduction. For example, Cr(VI) reduction by mandelic acid can be catalyzed by the presence of a solid surface, particularly at low pH where the solid surface was positively charged, promoting greater adsorption and reduction of the anionic chromate.[23] These reactions are relevant in reducing waters and sediments rich in organics and/or Fe(II), which could promote Cr(VI) reduction to insoluble Cr(III). The complex interplay among solubility, adsorption/desorption reactions, and electron transfer reactions complicates mechanistic elucidation. One method of simplification is more direct measurement of charge transfer kinetics through electrochemical techniques.

Electrochemistry can provide greater insight into the mechanisms of Cr(VI) reduction through a more direct measurement of charge transfer kinetics. Voltammetric techniques, where the voltage of a working electrode is systematically changed and the resulting current is measured, allows one to observe at what reducing potential and at what rate Cr(VI) reduction occurs under laboratory controlled conditions.[3,4] Gold has been commonly used as an electrode due to its high electrical conductivity (rapid charge transfer) and its chemical stability (lack of oxide formation).[24] Cr(VI) reduction on gold working electrodes is influenced by the supporting electrolyte and pH of the Cr(VI) solution with the greatest current produced using nitric acid and very acidic pH (pH of 0.5).[25,26] The variation between different electrolytes may be due to the preferential adsorption of certain electrolytes to the gold surface influencing Cr(VI) reduction.[25] Many electrochemical studies on Cr(VI) reduction have focused on the detection of Cr(VI) but not on how variable chemistry impacts Cr(VI) reduction.

The objective of this study is to determine how common anions, organic compounds, and copper influence Cr(VI) reduction using aqueous voltammetric methods. Few electrochemical studies have investigated the influence of aqueous chemistry on the electron transfer kinetics of Cr(VI) reduction.[3,5] The novelty of this study is to directly measure charge transfer kinetics involving Cr(VI) reduction reactions in the presence of environmentally relevant anions and ligands as well as Cu as a potential electron shuttle. Heavy metals, such as copper, often co-occur with Cr(VI) in contaminated settings. Copper is utilized in our experiments as a model redox-active metal that can interact with Cr(VI). Mechanistic insights are gained on how co-occurring constituents impact Cr(VI) reduction.

■ MATERIALS AND METHODS

Electrochemistry Experiments. All electrochemical measurements were performed using a WaveDriver 10 potentiostat and a Pine Research MSR rotator that allows rotating disk electrode (RDE) experiments. We utilized a gold RDE working electrode, a Ag/AgCl reference electrode, and a graphite counter electrode for all experiments. Initial testing with a glassy carbon RDE working electrode did not provide enough signal of Cr(VI) reduction at our experimental parameters. The gold RDE electrode was cleaned with an alumina slurry and washed with DI water before each day of the experiments and when the electrochemical signal was shifting due to film formation. For each experiment, we performed linear voltammetry where we decreased the voltage and measured the resulting change in current due to chemical reactions. All experiments used a scan window of 0.7 to 0.0 V versus a Ag/AgCl reference electrode (0.9 to 0.2 V versus a standard hydrogen electrode (SHE)). This range minimizes the oxidation of the gold electrode (not observed until ∼1.1 V versus SHE)[27] and the reduction of water to hydrogen gas (some seen at ∼0.3 V versus SHE).[27,28] In the context of other environmental contaminants, the range of potentials explored here encompass the redox potentials for Fe(III) reduction to Fe(II) (∼0.7 V at pH 2) and selenite reduction to selenide (∼0.4 V at pH 2).[29,30] This scan window clearly captures the reduction of Cr(VI) in all experiments. For each experiment, we ran cyclic voltammograms until a steady state was reached where the current produced during each voltammetric scan did not change over time. The uncertainty of each experiment was approximately 1 μA as shown by the reproducibility of an experiment with 10 mM nitric acid and no added organics (Figure S1). For our experiments, we used a scan rate of 20 mV/s and an RDE rotation rate of 900 rpm. We tested the impact of scan and rotation rates (Figures S2 and S3) and found that these rates were optimal for our experimental parameters.

The Cr(VI) solution used for our experiments contained 50 μM Cr(VI) added as sodium chromate to represent environmentally relevant conditions. The solution also had a chloride concentration of 1.0 mM to promote some adsorption of chloride to the electrode, which prevented drifting of the electrochemical signal and allowed better data consistency and interpretation with the addition of other chemicals. Our Cr(VI) solution also contained 10 mM nitric acid for most experiments, which provided a strong signal of Cr(VI) reduction. The nitric acid decreased the pH of the solution to 2.1, which was necessary to consistently measure electrochemical Cr(VI) reduction.

We also tested the effect of other electrolytes on electrochemical Cr(VI) reduction by using 10 mM hydrochloric acid or 10 mM sulfuric acid instead of nitric acid (Table 1). These results (see below) led us to further test the impact of these electrolytes by using our 10 mM nitric acid solution with an additional 50 mM sodium sulfate (pH adjusted by adding 15 mM nitric acid).

Table 1. Experimental Parameters of Electrolyte Experiments

Cr(VI) concentration (μM)	electrolyte concentration (mM)	pH	electrolytes
50	10	2.1	sulfuric acid, hydrochloric acid, and nitric acid

We tested the effect of organic compounds as well as copper on Cr(VI) reduction (Table 2). We attempted to avoid the precipitation of Fe or Cr solids, which can negatively impact electrochemical methods, by not adding Fe to the Cr(VI) solution, which is at dilute concentrations. To our Cr(VI) solution (50 μM Cr(VI), 1.0 mM sodium chloride, and 10 mM

Table 2. Experimental Parameters of Organic and Cu Experiments

Cr(VI) concentration (μM)	nitric acid concentration (mM)	pH	added constituents (200 μM)
50	10	2.1	none, glutamic acid, citric acid, oxalic acid, ascorbic acid, cysteine, and Cu(II) sulfate

nitric acid), we added 200 μM glutamic acid, citric acid, oxalic acid, cysteine, or ascorbic acid. These organic compounds were chosen based on their variable reducing power, with ascorbic acid being most easily oxidized. With the amount of nitric acid added to the Cr(VI) solutions, the pH of the solutions did not change more than 0.01 pH units following the addition of glutamate, citrate, oxalate, cysteine, ascorbate, or Cu(II). Two hundred micromolar of each organic compound was added in order to not overwhelm the chemical system while providing enough to fully react with 50 μM Cr. We also tested how Cu influenced Cr reduction by adding 200 μM Cu(II) sulfate to the Cr solution.

For each of these additions, we also tested the electrochemical effect of each organic (or Cu) without any Cr in solution. These background samples helped to establish at what potential the oxidation of these organics occurred (see the Results and Discussion). For Cu, both the reduction and oxidation of Cu was observed (see the Results and Discussion).

The addition of oxalic acid and Cu produced faster rates of Cr(VI) reduction (see below), so we also tested if these constituents could promote Cr(VI) reduction at higher pH where Cr(VI) reduction was difficult to measure. We first tested a 1 mM nitric acid and 9 mM sodium nitrate solution with 50 μM Cr(VI) at pH 3.0 without any addition of oxalic acid or Cu. We then added 200 μM oxalic acid or Cu(II) sulfate to determine if more measurable Cr(VI) reduction was attained.

For experiments that provided distinct voltammograms from Cr(VI) reduction without organics or Cu, we acquired voltammograms at different RDE rotation rates (100, 150, 250, 400, 900, and 1600 rpm) to perform Koutecky−Levich analysis (Table 3). Koutecky−Levich analysis can be applied to RDE experiments with sluggish kinetics to estimate the electron transfer rate constant.[31] By plotting the inverse of the measured current at a certain voltage versus the RDE rotation rate to the power of −1/2, we obtained a general estimate of the electron transfer rate constant (k_h).[31] The electron transfer rate constant was equal to the reciprocal of the y-intercept divided by $nF\pi r^2C_A$.

$$\frac{1}{I_c} = \frac{1.61\upsilon^{1/6}\omega^{-1/2}}{nF\pi r^2 {D_A}^{2/3} C_A} + \frac{1}{nF\pi r^2 C_A}\frac{1}{k_h} \tag{1}$$

where I_C = measured current (A), D_A = diffusion coefficient of Cr(VI) (1.132×10^{-5} cm^2/s),[32] υ = viscosity of the solution (100 cm^2/s), ω = rotation rate (rad/s), n = number of electrons involved before the rate-determining step (1 electron for Cr(VI) to Cr(V)), F = Faraday constant (9.65×10^4 A s/mol), r = radius of the RDE (0.25 cm), C_A = Cr(VI) concentration (5×10^{-8} mol/cm^3), and k_h = heterogeneous electron transfer rate constant (cm/s).

Table 3. Koutecky−Levich Analysis of Cr(VI) Reduction Experiments in a Nitric Acid Solution with no Organics (or Cu), with Citrate, with Oxalate, and with Cu

	no organics	citrate	oxalate	copper
slope (related to diffusion layer thickness)	2.7×10^5	3.0×10^5	4.4×10^5	3.4×10^5
y-intercept (related to electron transfer rate constant)	4.6×10^4	1.4×10^5	3.5×10^4	2.1×10^4
electron transfer rate constant (cm/s)	2.3×10^{-2}	7.7×10^{-3}	3.1×10^{-2}	4.9×10^{-2}
percent difference in electron transfer rate constant (from no organics experiment)		67% slower	33% faster	113% faster
R^2	0.987	0.996	0.988	0.996

We used a single electron for n because, most likely, the number of electrons transferred to Cr(VI) before the rate-determining step is 1. Once the relatively stable Cr(VI) is reduced to Cr(V), Cr(V) can either be easily reduced further or disproportionate, eventually forming Cr(III).[2,3] A previous electrochemical study suggested that Cr(VI) reduction to Cr(V) occurred at a gold electrode before disproportionation reactions led to the production of Cr(III).[4] Even if more electrons are transferred to Cr(VI) before the rate-limiting step, this study provides a direct comparison of electron transfer rates during Cr(VI) reduction under variable environmental conditions. We compared the electron transfer rate constants of experiments with no organics or copper with citrate, with oxalate, and with Cu at a chosen voltage of 0.45 V versus SHE. Linear relationships of the inverse of the measured current versus the rotation rate to the power of −1/2 were observed for each of these experiments at a voltage of 0.45 V. We selected a voltage of 0.45 V since Cr(VI) reduction is increasing at this potential and a linear behavior of $\frac{1}{I_c}$ versus $\omega^{-1/2}$ is observed at that potential. We also performed Koutecky−Levich analysis at 0.35 V to confirm that the same general trends were observed at more reducing potentials (Figure S4 and Table S1).

XPS Measurements. To test for deposition of Cr and Cu minerals during Cr(VI) reduction in the presence of Cu, we utilized X-ray photoelectron spectroscopy (XPS) to analyze near-surface (5−10 nm)

elemental composition of the electrode. Following our electrochemical experiments that included both Cr(VI) and Cu(II), the electrode was quickly washed with DI water before XPS analysis.

While our experiments were designed to prevent the precipitation of Cr(III) hydroxides, XPS allowed us to check if Cr(III) still precipitated. We tested if any underdeposition of Cr(0) or Cu(0) occurred during experiments that included Cu. The gold RDE electrode used for Cr(VI) reduction with Cu(II) added was tested for copper (Cu(II), Cu(I), and Cu(0)) and chromium (Cr(VI), Cr(III), and Cr(0)) measured at their 2p spectra using a Kratos AXIS-UltraDLD XPS.

UV-Vis Experiments. In addition to electrochemical experiments where the reducing potential was changed to induce Cr(VI) reduction, we also conducted several experiments where we tested for chemical Cr(VI) reduction without any electrical forcing. For these experiments, we used the same chemical parameters as our electrochemical experiments with 10 mM nitric acid, 1.0 mM sodium chloride, and 50 μM Cr(VI). To this solution, we added 200 μM glutamic acid, citric acid, oxalic acid, cysteine, ascorbic acid, or Cu(II) sulfate to test for Cr(VI) reduction by these species. These experiments were conducted in duplicate.

Cr(VI) concentrations were measured by UV-vis spectroscopy on a Cary 50 Bio spectrophotometer using a wavelength of 370 nm.[33] This method does not require adding a reactant to the Cr(VI) solution, but it directly measures the Cr(VI) in solution. The addition of organic compounds or Cu(II) did not impact the measured absorbance of Cr(VI). Testing with 10, 50, and 100 μM Cr(VI) solutions at our experimental pH of 2.1 revealed a consistent linear relationship between absorbance and Cr(VI) concentration. The Cr(VI) concentration of each sample was calculated by comparing the absorbance of the sample to the absorbance of the bracketing analyses of the 50 μM standard solution. Cr(VI) concentration of each Cr solution was measured at 10 min, 30 min, 2 h, 4 h, 2 days, and 7 days after the addition of an organic compound or Cu(II).

■ RESULTS AND DISCUSSION

Effect of the Electrolyte. The type of primary electrolyte used in our electrochemical experiments affected the resulting linear voltammograms. We tested how 10 mM nitric acid, 10 mM hydrochloric acid, and 10 mM sulfuric acid affected Cr(VI) reduction. The pH of the 10 mM hydrochloric acid and nitric acid were both 2.1, while 10 mM sulfuric acid was slightly more acidic at pH 1.9. Cr(VI) reduction with hydrochloric acid and sulfuric acid produced a similar voltammetric scan shape, but Cr(VI) reduction occurred at a lower potential for hydrochloric acid. Chloride has a larger diffusion coefficient (2.030×10^{-9} m^2 s^{-1}) than sulfate (1.070×10^{-9} m^2 s^{-1}),[34] so we would expect Cr(VI) reduction to proceed earlier with hydrochloric acid if diffusion was a major factor. Faster diffusion likely leads to the steeper slope of the change in current seen in chloride and nitrate versus sulfate (Figure 1). The discrepancy in onset potential between hydrochloric acid and sulfuric acid is likely due to the small difference in pH, with lower pH typically promoting Cr(VI) reduction at less reducing potentials.[4,25]

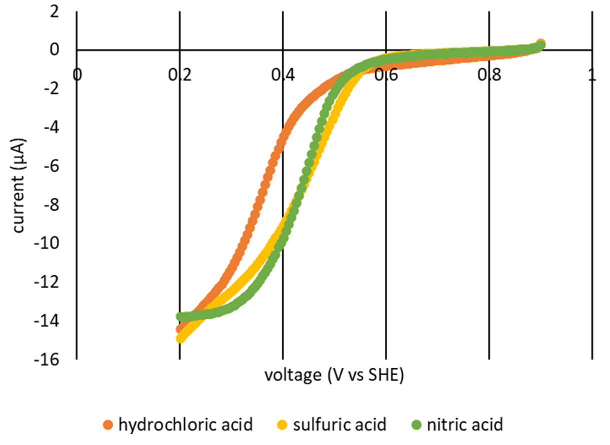

Figure 1. Effect of electrolyte on Cr(VI) reduction. A 50 μM Cr(VI) solution included either 10 mM of hydrochloric acid (pH of 2.1), 10 mM sulfuric acid (pH of 1.9), or 10mM nitric acid (pH of 2.1).

Using 10 mM nitric acid produced a significantly different voltammetric scan from hydrochloric acid and sulfuric acid (Figure 1). While hydrochloric and sulfuric acids resulted in the current consistently becoming more negative as the voltage was decreased, nitric acid produced a more rapid increase in negative current at 0.3 V and then a plateau after the potential reached 0.15 V (Figure 1). Cr(VI) can complex with chloride and sulfate, particularly at low pH.[35,36] However, in our 10 mM Cl^- or SO_4^{2-} solution at pH ~2, these species would be relatively minor (<5%) versus the major $HCrO_4^-$ species, which should still dominate the electrochemical behavior. Sulfate, chloride, and/or nitrate could influence the formation of a reactive Cr(VI) species on the electrode surface, generating the distinctive behavior of Cr(VI) reduction in 10 mM nitric acid. The distinct electrochemical behavior of the nitric acid solution may also have been due to less nitrate adsorbing to the electrode than sulfate or chloride (Figure 1). At our experimental pH of 2.1, a gold electrode has a potential of zero charge of approximately 0.2 V (versus SHE),[37−39] so the gold surface should remain positively charged across our voltammetric scan of 0.9 to 0.2 V. Anions, such as sulfate, chloride, and nitrate can adsorb to the gold electrode with nitrate adsorbing less to gold than sulfate and chloride.[27,40] Adsorption of sulfate or nitrate to the electrode should make the electrode less positively charged, so the electrostatic attraction of Cr(VI) to the electrode would decrease, possibly slowing Cr(VI) reduction rates. In addition, the adsorption of electro-inactive sulfate and chloride to the electrode should decrease the available surface sites for Cr(VI) reduction. We observed that a less reducing potential was necessary for Cr(VI) reduction with nitric acid than hydrochloric acid. In addition, the current reached a steady value once the amount of reactive Cr(VI) reached a steady state. With the loss of electrode surface area and electrostatic charge due to the adsorption of sulfate and chloride, the reactive Cr(VI) may not have reached a steady state value, so the current continued to decrease as the potential was shifted.

By adding 50 mM sodium sulfate to our 10 mM nitric acid solution, we further tested the effect of the electrolyte on Cr reduction. To keep the pH at 2.1, we also added another 15 mM of nitric acid. During this experiment, significantly less negative current was produced versus the 10 mM nitric acid or sulfuric acid solution (Figure 2). We did not observe a loss of current in subsequent electrochemical experiments, so if sulfate reduction to elemental sulfur occurred, it did not negatively affect the electrode surface. The loss of current in the 50 mM

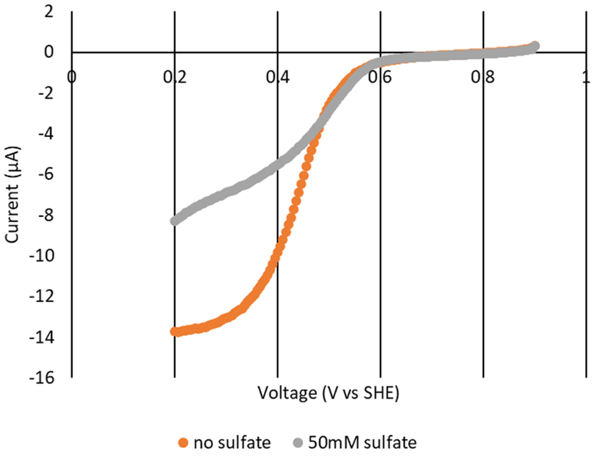

Figure 2. Impact of adding 50 mM sulfate to a 10 mM nitric acid and 50 μM Cr(VI) solution. Nitric acid (15 mM) was added (final concentration of 25 mM HNO_3) to keep the pH at 2.1.

sulfate experiment strongly suggests that adsorption of sulfate to the gold electrode prevents Cr(VI) contact with the electrode and subsequent reduction to Cr(III).

Effect of Organic Compounds on Cr Reduction. UV−vis experiments indicated how Cr(VI) reduction proceeded without electrochemical potential forcing. We observed Cr(VI) reduction by two of the five added organic compounds. No Cr(VI) reduction was induced by addition of glutamate, citrate, or oxalate (Figure 3 and Table S2). Ascorbate, a known antioxidant, rapidly reduced Cr(VI) with only 2% of Cr(VI) remaining in solution after 10 min of reacting with ascorbate (Figure 3). The reduction of Cr(VI) coupled to the oxidation of cysteine was slower but still significant. Seventy-eight percent of Cr(VI) was reduced by cysteine over 2 days (Figure 3).

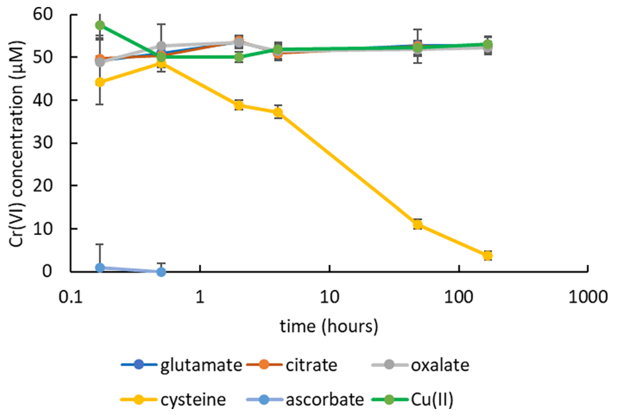

Figure 3. Cr(VI) concentrations over time with addition of 200 μM of each constituent. Error bars represent two standard deviations of either the duplicate samples or of the 50 μM Cr(VI) standard, whichever is larger. Glutamate and citrate plot on top of each other.

During electrochemical experiments, the addition of organic compounds to our 10 mM nitric acid solution influenced Cr(VI) reduction through enhanced rates, rapid removal, or adsorption to the electrode. Citrate led to a slower increase in negative current, similar to that seen with Cr(VI) reduction in sulfuric or hydrochloric acid solutions (Figure 4A). Using Koutecky−Levich analysis, we estimated the charge transfer rate of Cr(VI) reduction with versus without citrate (Figure 5 and Table 3). Assuming that the diffusion rate of Cr(VI) did not change with the addition of citrate, the charge transfer rate of Cr(VI) reduction in nitric acid solution was 67% slower with citrate added than without citrate (Table 3).

When we added 50 mM sodium sulfate to the nitric acid solution, the addition of citrate produced no change in the linear voltammogram (Figure S5A). Since the addition of a sorbent leads to no citrate effects, this strongly suggests that citrate is only influencing Cr(VI) reduction by adsorbing to the electrode. Citrate should be either neutrally or negatively charged at pH 2.1, so it should adsorb to the positively charged gold electrode. When we performed background electrochemical experiments of a citrate solution without Cr(VI), no oxidation peak for citrate was observed. Glutamate did not cause any electrochemical shifts with Cr(VI) reduction. Glutamate would be either neutrally or positively charged at pH 2.1, so little to no glutamate should adsorb to the electrode.

On the other hand, oxalate oxidation was detected in background nitric acid experiments near 0.7 V. This potential is at the most oxidizing range of our experiments. With Cr(VI) included in solution, oxalate promoted faster Cr(VI) reduction with a reduction rate 33% faster than without oxalate (Figure 4B and Table 3). However, with the addition of 50 mM sulfate to solution, no effect of oxalate was observed (Figure S5B). No Cr(VI) reduction was detected in UV−vis experiments with oxalate (Figure 3). The oxalate requires adsorption to the gold electrode in order to be oxidized, which is coupled to Cr(VI) reduction. Previous studies also demonstrate how adsorption of the oxalate ion to the working electrode is necessary for oxidation.[41,42]

Cysteine and ascorbate did not require adsorption to promote Cr(VI) reduction. As suggested by the UV−vis experiments where these organics induced Cr(VI) reduction with no electrical forcing, Cr(VI) is rapidly reduced by these organics and little to no Cr(VI) reduction occurs directly on the electrode. The impact of these organics on our electrochemical experiments was quite drastic. With these antioxidants included in our Cr(VI) solution, little to no evidence of Cr(VI) reduction was observed (Figure 4C). The chemical reduction of Cr(VI) directly by ascorbate and cysteine appears to outcompete the electrochemical reduction of Cr(VI) on the gold electrode. The initial oxidizing potential of the electrode may promote the oxidation of these organics, which is coupled to Cr(VI) reduction, but little to no Cr(VI) reduction occurs directly on the electrode while these organics are present.

The oxidation potential of organics can strongly influence how quickly these organics can reduce Cr(VI). Background experiments with ascorbate or cysteine and no Cr(VI) observed the oxidation of ascorbate at 0.55 V and oxidation of cysteine at 0.7 V (Figure 6). If these organics can be easily oxidized, then their oxidation can be coupled to fast Cr(VI) reduction. Many environmentally relevant organics, such as humic and fulvic acids, are less easily oxidized but may still promote Cr(VI) reduction.[8,9]

Our electrochemical experiments did not detect any changes in Cr(VI) reduction potential due to the formation of Cr(III) organic compounds. Cr(III) can complex with organics such as citrate and glutamate, which are thermodynamically favorable to Cr(III) hydroxide solids. However, the addition of glutamate and citrate did not promote greater Cr(VI) reduction. Slightly more favorable thermodynamics with formation of Cr(III)−organic species do not appear to increase the rate of Cr(VI) reduction.

Role of Cu in Cr(VI) Reduction. Copper has been shown to act as an electron shuttle, promoting both Cr(VI) reduction and Cr(III) oxidation depending on redox conditions.[11−13] Our electrochemical experiments provide further evidence of how Cu can promote Cr(VI) reduction. With the addition of Cu(II) to our nitric acid solution, Cr(VI) reduction occurred at a higher potential (Figure 4D). This change in potential was also observed when 50 mM sulfate was included in the Cr(VI) solution, so this effect was not due to adsorption, which is consistent with the positive charge of Cu (Figure S5C). Background cyclic voltammetry experiments with no Cr(VI) indicate that Cu(II) is electrochemically reduced to Cu(I) or Cu(0) at 0.55 V (Figure S6). During the oxidation sweep, the Cu(I)/Cu(0) is oxidized back to Cu(II) at a potential of 0.45 V. Cr(VI) reduction with Cu begins at 0.55 V, which is ~0.05 V higher than without Cu (Figure 4D). The reduction rate of Cr(VI) is approximately 113% faster with Cu included in

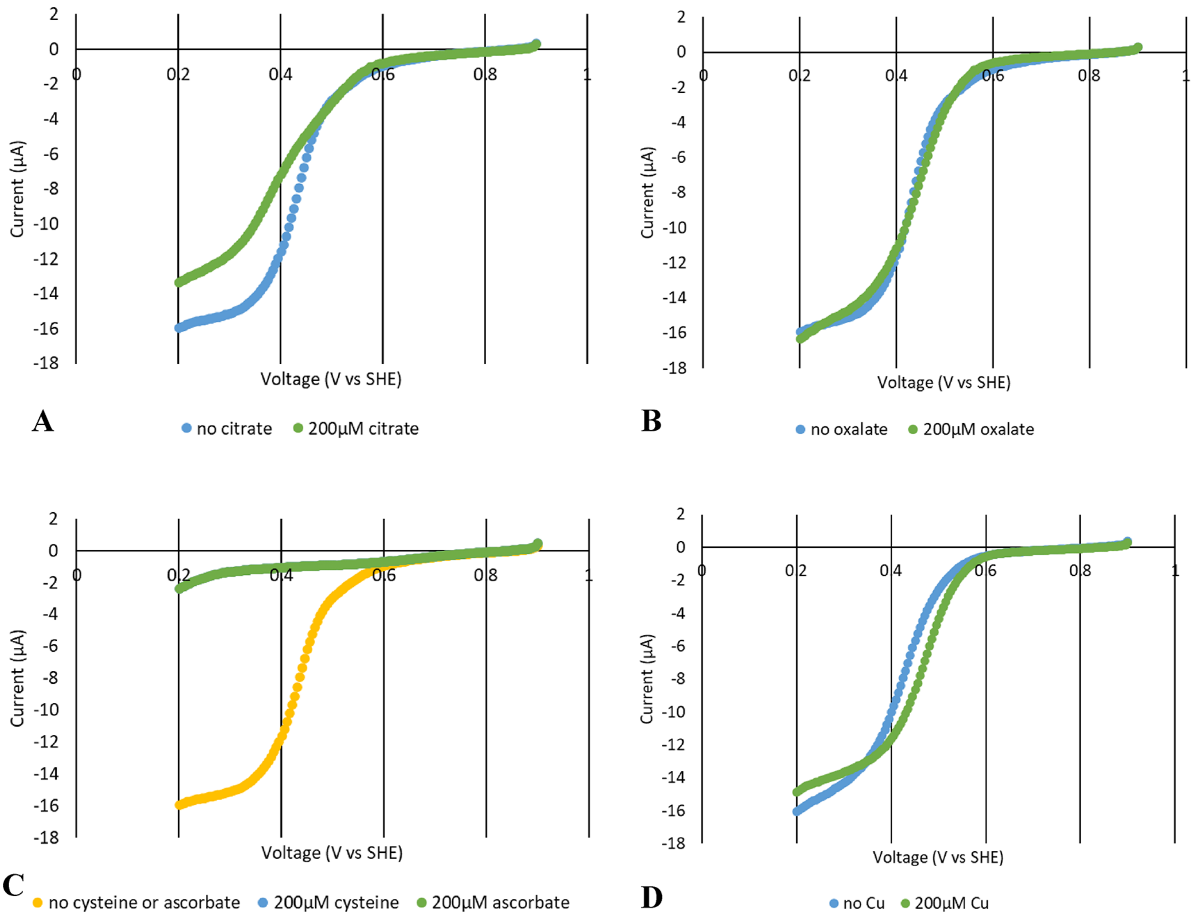

Figure 4. Effect of adding 200 μM (A) citrate, (B) oxalate, (C) cysteine or ascorbate, or (D) Cu(II) sulfate to the nitric acid and Cr(VI) solution. Please note that Cr(VI) solutions with 200 μM cysteine or ascorbate plot on top of each other, which is also consistent with nitric acid solution blanks with no Cr(VI).

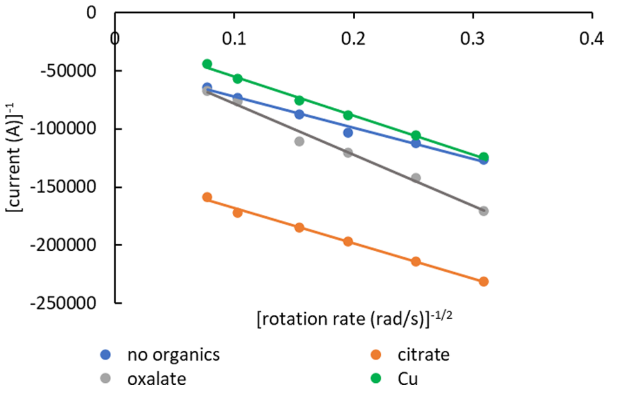

Figure 5. Koutecky–Levich analysis of Cr(VI) electron transfer rates across a range of rotation rates (100, 150, 250, 400, 900, and 1600 rpm) at a voltage of 0.45V, illustrating the impact of citrate, oxalate, and Cu on Cr(VI) reduction in a nitric acid solution.

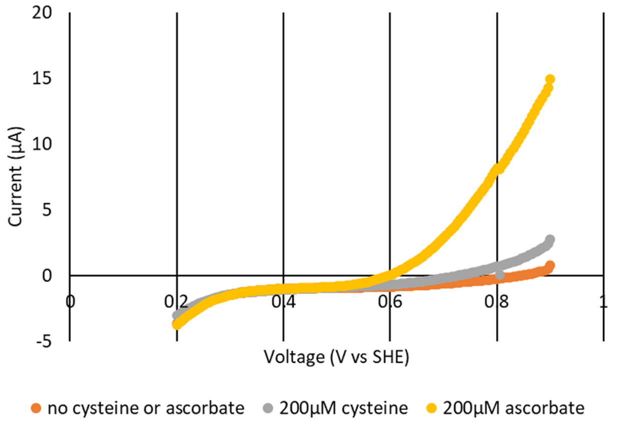

Figure 6. Effect of 200 μM cysteine and ascorbate on nitric acid solution with no Cr(VI) added.

solution (Table 3). The reduced Cu may promote Cr(VI) reduction by forming a readily reducible complex with Cr(VI) that is then reduced at the electrode surface. Another possibility is the direct interaction of reduced Cu with Cr(VI). If Cu(II) is reduced to Cu(I) at the electrode surface, the oxidation of Cu(I) to Cu(II) can promote Cr(VI) reduction to Cr(V), which disproportionates to Cr(III).

No copper was detected by XPS analyses on the electrode following the experiment, which suggests that Cu(0) underdeposition appears to be minimal. No Cu(II) or Cu(I) was detected by XPS, indicating that the adsorption of these species to the gold electrode was minimal. However, chromium represented 11% of the material detected on the electrode surface (Figure S7 and Table S3). A trivial amount of this chromium may have been due to Cr(VI) adsorption to the electrode. Chromium was primarily present (95% of chromium detected) as Cr(III) hydroxide due to Cr(III) precipitation (Figure 7 and Figure S7). While our experiments were designed to prevent precipitation of Cr(III) hydroxides, higher

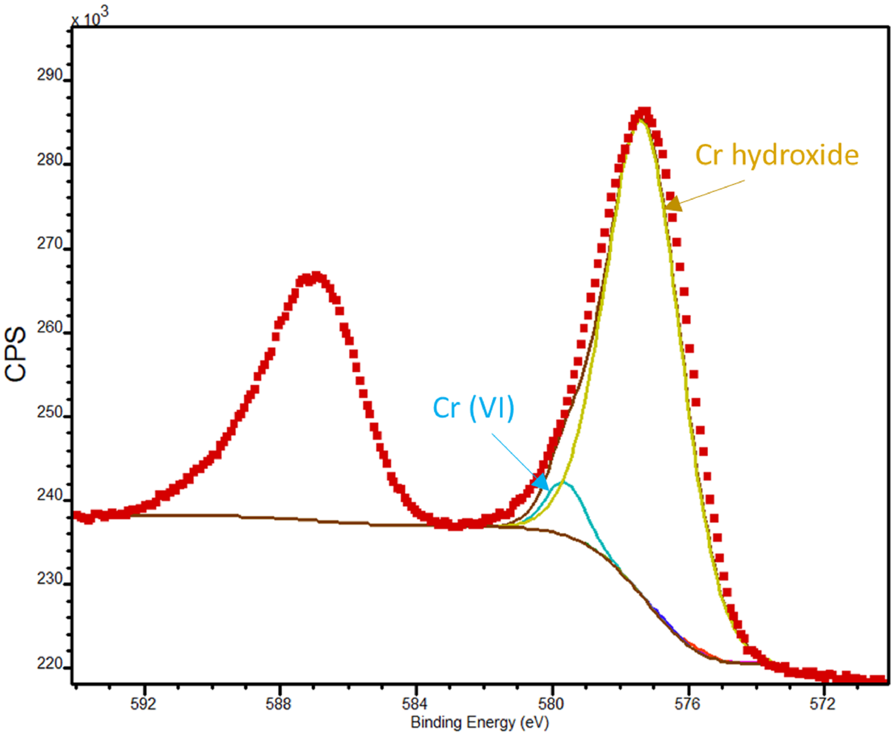

Figure 7. XPS scan of chromium 2p spectra on gold electrode following an electrochemical Cr(VI) experiment. Cr is primarily detected (94.5%) as Cr(III) hydroxide with trivial amount (5.5%) of Cr(VI) possibly present.

local Cr(III) concentrations near the electrode likely led to conditions promoting the stability of Cr(III) species. Our experiments typically required several cyclic voltammetric scans before reaching the steady state, which may have been due to the deposition of solids such as Cr(III) hydroxides. Once this steady state was achieved, the signal remained constant without loss of current due to solid deposition.

Effect of pH. Under our experimental pH conditions of 2.1, the electrode was positively charged, resulting in electrostatic attraction of $HCrO_4^-$. With surface contact of Cr(VI) to the electrode, electrochemical Cr(VI) reduction could proceed. When the pH of the electrochemical experiments was increased to 3.0, Cr(VI) reduction was barely detected with a current that was ~0.5 μA more negative than the baseline (Figure 8). Since the electrode was not positively charged at pH 3.0, Cr(VI) was not as strongly attracted to the electrode, decreasing the rate of subsequent electrochemical reduction. In addition, Cr(III) hydroxide precipitation appeared to accelerate at this higher pH with subsequent electrochemical experiments highly altered following experiments at pH 3.0 if the electrode was not immediately cleaned with alumina (Figure S9).

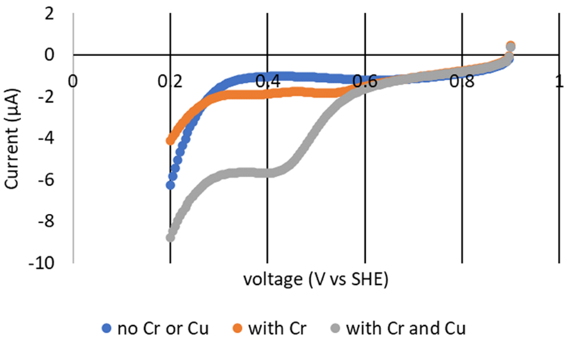

Figure 8. A solution of 1 mM nitric acid and 9 mM sodium nitrate at pH 3.0 that included no Cr(VI) or Cu(II), 50 μM Cr(VI), or 50 μM Cr(VI) and 200 μM Cu(II). Cr(VI) reduction is barely detectable at pH 3.0 without the addition of Cu(II).

The addition of 200 μM oxalic acid or Cu(II) sulfate promoted greater Cr(VI) reduction at pH 3.0 with a measurable current produced. With the addition of Cu, the current became ~4 μA more negative due to the oxidation of reduced Cu being coupled to greater Cr(VI) reduction (Figure 8). When oxalic acid was added, the pH of the experiment dropped slightly to 2.9, which slightly increased Cr(VI) reduction rates. The negative current increased significantly, likely due to the oxidation of oxalate, promoting greater Cr(VI) reduction (Figure S10). At a pH of 2.9−3.0, oxalate and Cu can promote significant Cr(VI) reduction through improved electron transfer kinetics. At more neutral pH conditions, oxalic acid may not adsorb strongly enough to the electrode to promote Cr(VI) reduction. However, as a noncomplexed cation, Cu should continue to promote Cr(VI) reduction.

Environmental Implications. This electrochemical study provides greater insight into the charge transfer rates of Cr(VI) reduction. Electron transfer reactions at the surface of our working electrode are heterogeneous,[43] so adsorption of anions to the electrode influences electron transfer rates. These electrochemical reactions provide mechanistic insights on comparable homogeneous reduction reactions in solution[43] as well as heterogeneous charge transfer reactions on mineral surfaces. By multiplying our electron transfer rate constants, estimated utilizing the analysis of Koutecky−Levich, by the surface area of the electrode and dividing this rate by the volume of solution, we obtained a bulk Cr(VI) reduction rate constant ranging from 7.6×10^{-6} to 4.8×10^{-5} s^{-1}. During each voltammetric scan, less than 0.2% of Cr(VI) is reduced, so the aqueous Cr(VI) concentration should not change significantly during our experiments. These electron transfer rates are controlled by the small electrode surface area since Cr(VI) needs to contact the electrode surface to promote Cr(VI) reduction. The bulk reduction rate constant for Cr(VI) on Cu metal has been measured at approximately 2.4×10^{-3} s^{-1} for a Cu mesh with a surface area ~7 times that of our electrode.[44] Cr(VI) removal by zero-valent iron has been measured at an apparent rate constant of 6.6×10^{-5} s^{-1}.[45] Bulk Cr(VI) reduction rates by aqueous reductants are typically faster since Cr(VI) reduction is homogeneous and not controlled by the surface area of the reductant but typically by the aqueous concentration of reductant. Cr(VI) reduction by Fe(II) under acidic conditions has a rate constant of $\sim 7 \times 10^{-3}$ s^{-1} at an Fe(II) concentration of 1 mM,[46] while Cr(VI) reduction by ascorbic acid under neutral pH conditions has been measured at a rate constant of $\sim 10^{-2}$ s^{-1} at an ascorbic acid concentration of 2.75 mM.[47]

Cr(VI) reduction is not instantaneous with Cu promoting faster Cr(VI) reduction at more oxidizing conditions. With Cu, Cr reduction occurred at a potential ~0.05 V higher and at a rate 113% faster than without Cu (Figure 4D and Table 3). Cr(VI) reduction can also be coupled to oxidation of organics to induce Cr(VI) reduction. While Cr(VI) reduction by ascorbate and cysteine was too rapid to measure electrochemically, oxalate promoted Cr(VI) reduction at a rate 33% faster versus without oxalate (Table 3). Organic compounds and electron shuttles promote Cr(VI) reduction under our experimental conditions and at a wide range of environmental conditions.

Our experiments were conducted at a pH of 2.1 to 3.0, lying in the lower pH range of acid mine drainage, which can result in waters with pH values between 2 and 6.[48] These acidic conditions promote positively charged surfaces of reducing minerals, such as Fe(II) sulfides and Fe(II)-containing clays. Naturally occurring anions, such as chloride and sulfate, can adsorb to these positively charged surfaces, decreasing reduction rates of Cr(VI).

Less Cr(VI) reduction occurs on mineral surfaces when the pH of environmental waters is closer to neutral.[1] Under neutral pH conditions, mineral surfaces typically become negatively charged, so chromate ions are not electrostatically attracted as easily as observed at acidic pH. Instead of being controlled by reducing minerals, Cr(VI) concentrations are more influenced by aqueous reductants, such as fulvic acids and Fe(II). As we observed in our experiments with cysteine and ascorbate, organic compounds can lead to rapid reduction and removal of Cr(VI). Cr(VI) reduction by organics may slow but can continue to proceed at circumneutral pH.[10] Natural organic compounds can also form colloids, which bind with iron and chromium, inducing Cr(VI) reduction.[49] In addition, organic compounds function as ligands for metals, such as iron or copper, which can increase their solubility and reactivity with Cr(VI).[9,11,18] As a non-complexed cation or complexed with organic ligands, copper should remain as an electron shuttle when the pH of environmental waters is close to neutral,[12] promoting Cr(VI) reduction.

The geochemical insights gained from this electrochemical study provide foundational knowledge for future research at more neutral pH. Our simplified Cr(VI) system has provided insights into how ions, metals, and organic compounds influence the electron transfer rates of Cr(VI) reduction at controlled redox potentials. We can combine this knowledge with knowledge gained from batch or column experiments conducted at more neutral pH to better understand how Cr(VI) is reduced and removed at higher pH. Reactive transport models constructed using electrochemical data in addition to other experimental data may be utilized to better predict contaminant transport and develop remediation alternatives for chromium.

Similar electrochemical studies may be applied to other redox-active elements, such as copper, arsenic, selenium, and uranium. Recent research has demonstrated the usefulness of electrochemistry in studying the fluctuation of oxidation states, effect of reducing mineral surfaces, and influence of organics on the uranium and selenium systems.[50−52] Electrochemical measurements can provide better quantitative data on adsorption and redox reactions during redox changes than other geochemical tools.

■ CONCLUSIONS

Electrochemical measurements of Cr(VI) reduction provide a more direct analysis of electron transfer rates under changing redox conditions. Our experiments at acidic pH represent an acid mine drainage system but can provide insight into neutral pH settings. Under acidic conditions, adsorption of naturally occurring anions, such as sulfate and chloride, to the reducing surface slows Cr(VI) reduction. Citrate can also adsorb to the reducing surface, decreasing Cr(VI) reduction rates. The oxidation of oxalate, cysteine, and ascorbate can be coupled to Cr(VI) reduction with rapid Cr(VI) reduction observed with cysteine and ascorbate. Copper can promote more rapid Cr(VI) reduction at more oxidizing conditions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.2c00309.

> Reproducibility of voltammetric scans; impact of changing scan rate and rotation rate; Koutecky−Levich analysis at 0.35 V; effect of adding citrate, oxalate, or Cu to a Cr(VI) solution containing sulfate; background experiment with Cu(II); XPS survey scan of electrode; XPS scan of chromium spectra $p_{1/2}$ and $p_{3/2}$; voltammetric scans before and after pH 3.0 experiments; effect of oxalate on electrochemical Cr(VI) reduction at pH 3; UV−vis absorption and concentration data; composition of electrode following electrochemical Cr(VI) reduction (PDF)

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Notes

The authors declare no competing financial interest.

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