

July 2021

Electrochemical Reduction of Hexavalent Chromium in Acetonitrile using Glassy Carbon Electrodes

Temitope Jegede

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_theses

 Part of the [Analytical Chemistry Commons](#)

Recommended Citation

Jegede, Temitope, "Electrochemical Reduction of Hexavalent Chromium in Acetonitrile using Glassy Carbon Electrodes" (2021). *LSU Master's Theses*. 5374.
https://digitalcommons.lsu.edu/gradschool_theses/5374

This Thesis is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Master's Theses by an authorized graduate school editor of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.

ELECTROCHEMICAL REDUCTION OF HEXAVALENT CHROMIUM IN ACETONITRILE USING GLASSY CARBON ELECTRODES

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Master of Science

in

The Department of Chemistry

by

Temitope Oluwaseyi Jegede

B.Tech., Ladoke Akintola University of Technology, 2010

M.Sc., Obafemi Awolowo University, 2016

August 2021

Table of Contents

Abstract.....	iii
Chapter 1. Introduction.....	1
Chapter 2. Experimental.....	7
2.1. Analytical Techniques.....	7
2.2. Analytes and Reagents.....	8
2.3. Electrochemical Methods.....	9
2.4. Optical Methods.....	10
Chapter 3. Results and Discussion.....	11
3.1. Choice of Analyte and Solvent.....	11
3.2. Cyclic Voltammetry at Glassy Carbon Electrodes in Acetonitrile.....	12
3.3. Chromate-dichromate Equilibrium.....	15
3.4. Acid-mediated Reduction of Hexavalent Chromium.....	16
3.5. Homogenous Electron Transfer to Cr(VI).....	19
3.6. Reproducibility Studies.....	21
Chapter 4. Conclusions.....	24
Appendix A. Reuse Permission Request for Figure 1.1.....	25
Appendix B. Reuse Permission for Figure 1.1.....	26
Appendix C. Reuse Permission Request and Permission for Figure 1.2.....	27
Appendix D. Reuse Permission Request for Figure 1.3.....	28
Appendix E. Reuse Permission for Figure 1.3.....	29
Appendix F. Reuse Permission Request for Figure 3.1.....	30

Appendix G. Reuse Permission for Figure 3.1.....	31
References.....	32
Vita.....	36

Abstract

Hexavalent chromium Cr(VI), a form of chromium mainly generated through industrial processes, has attracted great research interests due to its severe toxicity to biological systems. A common way to remove hexavalent chromium from industrial wastes is through reduction to the non-toxic trivalent state. To this end, methods such as chemical reduction, chemical precipitation and coagulation have been used. However, these methods are limited by poor removal efficiency, formation of secondary pollutants (sludge), and are mostly applicable to aqueous solutions. Recently, electrochemical methods have been investigated for reducing hexavalent chromium, but there is a lack of data on the reduction of hexavalent chromium in nonaqueous media. This is a challenge considering the possibility of Cr(VI)-contaminated nonaqueous industrial wastes ending up in water bodies. Therefore, it is crucial to develop methods of treating such wastes before disposal. In this research, an electrochemical method that involves the use of a nonaqueous solvent is presented. Using glassy carbon electrodes and acetonitrile-based electrolyte, a reproducible method of collecting data was established. With the aim of achieving an energy-efficient reduction and making the reduction process electrocatalytic, the effect of Brønsted acids on the reduction process was investigated. In addition, the process of finding suitable electrocatalysts was initiated. Results obtained show reproducible response of glassy carbon electrodes toward hexavalent chromium in acetonitrile and that Cr(VI) reduction proceeds via proton-coupled electron transfer processes.

Chapter 1. Introduction

Pollution of the environment by heavy metals poses a significant threat to life and the environment due to their toxic effects at concentrations above permissible levels. Industrial processes have been identified as the major sources of heavy metals, where heavy metals from improperly handled waste find their way to ground water systems, resulting in the contamination of drinking water. Among these heavy metal contaminants is chromium. Although chromium exists in many oxidation states, the environmentally and commercially relevant states are the 0, +3 and +6 oxidation states.¹ The toxicity of chromium depends on its oxidation state; Cr(0) and Cr(III) at moderate concentrations are not considered threats to life or the environment. Hexavalent chromium, on the other hand, is highly toxic and can have carcinogenic effects on biological systems.²⁻⁵ Cr(VI) is generated mainly through anthropogenic processes and is used in applications such as: electroplating, leather tanning, wood preservation, pigment production, and metal finishing.^{1,6,7} Cr(VI) is highly soluble in water and can seep into ground water systems from industrial effluents.^{8,9} Cr(VI) is severely toxic in biological systems due to its participation in intracellular processes that alter enzyme activities, cause DNA damage and cell death. Once in the body, Cr(VI) is readily absorbed by different tissues due to the structural similarity of the chromate anion (CrO_4^{2-}) to the sulfate (SO_4^{2-}) anion and is mistakenly transported across the cellular membrane via the sulphate uptake pathway.^{4,5} Cr(VI), upon entering the cell, is reduced by cell reductants such as glutathione (GSH), ascorbate and NADPH, resulting in the formation of reduced chromium species (Figure 1.1).⁴ Cr(V) and Cr(IV) are short-lived species which can damage DNA via oxidation. Non-oxidative DNA damage can also occur, mostly through the formation of

Cr-DNA adducts.^{4,5} DNA oxidation leads to chromosomal damage and genotoxic mutation (Figure 1.1).⁴ Cr(VI) is toxic, even at low concentrations, while Cr(III) is an essential trace nutrient which is required for normal metabolism of fat, protein and carbohydrates in humans. Cr(III) aids in the conversion of glucose into energy and promotes healthy blood glucose and blood pressure levels.¹⁰

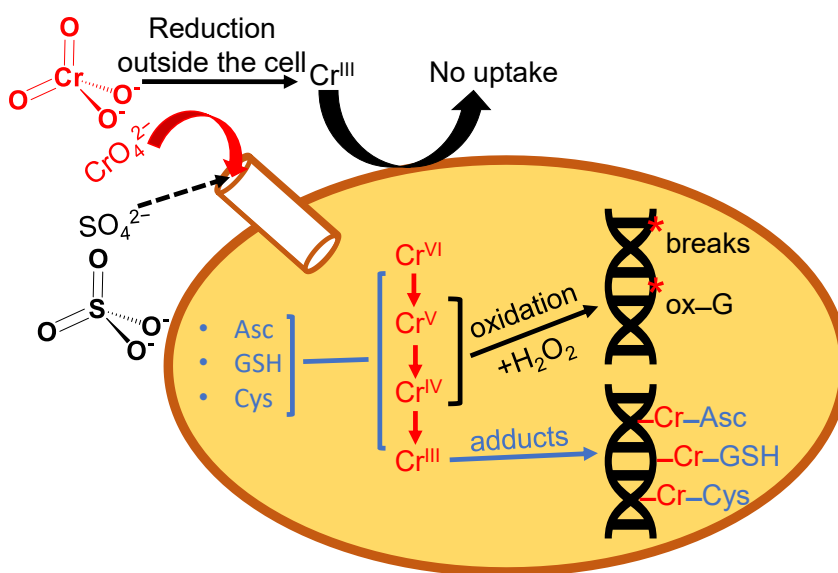


Figure 1.1. Absorption, metabolism, and effects of Cr(VI) on DNA. Adapted from reference⁴ with permission from the American Chemical Society.

The main source of Cr(VI) exposure for humans is through contaminated water. Since Cr(VI)-contaminated non-aqueous industrial wastes can end up in water bodies, it is important to develop methods to remove hexavalent chromium from such wastes before they are disposed.

Conventional methods such as chemical precipitation, coagulation, ion exchange, reverse osmosis and adsorption have been used for the removal of hexavalent chromium.^{3,7,11} However, these methods are limited by high costs, poor removal efficiencies, and formation of secondary pollutants.

Owing to their sensitivity, cost-efficiency, ease of operation, and scalability, electrochemical techniques have been widely applied for the treatment of many environmental pollutants.^{12–16} Compared to the conventional methods, electrochemical techniques are faster and more environmentally benign as contaminants can be detected or reduced within a short period of time with minimal generation of secondary waste.^{17,18} Consequently, the removal of hexavalent chromium in aqueous media via electrochemical reduction using different electrodes have been reported in literature.^{8,20,21} However, there is a lack of information on the electrochemical reduction of Cr(VI) in non-aqueous media. This is a challenge as Cr(VI)-contaminated nonaqueous industrial wastes can end up in water bodies. This can be avoided by treating such wastes at the source at which they are generated, allowing for the reclamation and reuse of chromium instead of its release to the environment.

Non-aqueous electrochemistry can be effective for the removal of hexavalent chromium in nonaqueous waste for many reasons. First, compared to water, polar aprotic solvents, such as dimethylformamide and acetonitrile, used as solvents in non-aqueous electrochemistry offer solubility and miscibility to a wide range of organic compounds and salts. Also, non-aqueous solvents have wider potential window which allows for electrochemical investigations beyond the potential window of water. Moreover, the reduction of hexavalent chromium in water is complicated by its speciation in water. A diagram showing the speciation of hexavalent chromium in water is presented in Figure 1.2.⁶ Depending on pH, temperature and total chromium concentration, hexavalent chromium exists in different forms in water.⁶ $\text{Cr}_2\text{O}_7^{2-}$ is the predominant form at high total

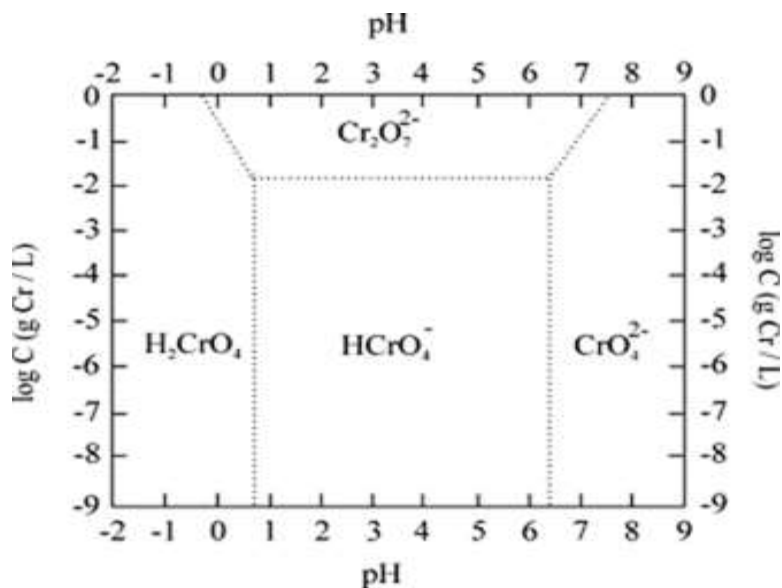


Figure 1.2. Cr(VI) speciation dependence on pH and concentration in water at 25 °C. Reprinted from reference⁶, originally adapted from reference²¹ with permission from Elsevier.

chromium concentrations and acidic to neutral pH, while at low concentration and neutral to basic pH, the predominant form is CrO_4^{2-} . At more acidic pH, CrO_4^{2-} is protonated to form HCrO_4^- and H_2CrO_4 . The chromate-dichromate equilibrium is presented as: $2\text{CrO}_4^{2-} + 2\text{H}^+ \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$ (Equation 1.1). Polar aprotic non-aqueous solvents, unlike water, do not supply H^+ required to keep chromate and dichromate species in equilibrium, hence chromate-dichromate equilibrium is not expected to be a problem. Therefore, non-aqueous electrochemistry could allow the fundamental study of the electrochemical reduction of hexavalent chromium without interference from H^+ or H_3O^+ equivalents. To reduce hexavalent chromium in non-aqueous media, a suitable procedure must be developed, the mechanism of the reduction process must be understood and ways to make the reduction more efficient must be explored. The focus of this research is to develop an energy-efficient method to facilitate the transfer of protons and electrons that will aid in the reduction of hexavalent chromium to benign trivalent chromium in non-aqueous media. To have a fundamental understanding of the electrochemical processes

involved in the reduction of Cr(VI) in nonaqueous media, cyclic voltammetry experiments are carried out using glassy carbon as working electrode.

To compare and understand the chemistry involved in the reduction of hexavalent chromium in non-aqueous media and water using glassy carbon electrodes, we considered literature reports on the reduction of hexavalent chromium in water using glassy carbon electrodes. For example, Welch *et al.*,⁶ in 2005, reported that the electrochemical reduction of hexavalent chromium in water at glassy carbon electrodes yielded irreproducible results and that expensive noble metal electrodes are required for Cr(VI) reduction. However, in a recent study, Stern *et al.*²² reported a method for obtaining reproducible Cr(VI) detection/reduction in water at glassy carbon electrodes. Stern *et al.*²² also reported that the reduction of hexavalent chromium at glassy carbon electrodes was dependent on pH. No electrochemical response was obtained for the addition of chromate to water in the presence of KCl electrolyte within the potential window studied. However, a reduction peak was observed on the addition of acid, and the peak potential shifted to more positive values as more acid was added, indicating an acid dependent rate limiting chemical step. Moreover, during the titration of chromate into a 0.1 M citric acid buffer at pH 4.75, Stern *et al.* reported a loss of linearity in current response at high chromate concentrations, and a sharp shift in peak potential to less negative values at about 3 mM chromate concentration (Figure 1.3). These changes in peak currents and peak potentials were attributed to the equilibrium between chromate and dichromate (Equation 1.1). Following up on this previous work, herein is described a method for obtaining reproducible cyclic voltammetric data for Cr(VI) detection/reduction in a non-aqueous medium using glassy carbon electrodes, allowing for a better understanding of the

reduction process. The effect of Brønsted acids on the behavior of Cr(VI) and electrocatalysis using small molecular catalysts are also evaluated. This research is important for the development of a cheap, energy efficient and environmentally benign method for removing Cr(VI) from non-aqueous sources.

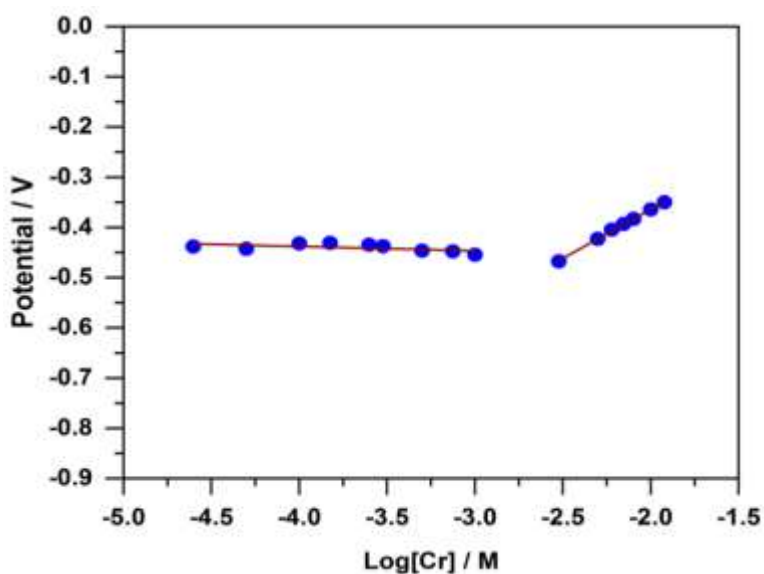


Figure 1.3. Evolution of cathodic peak potential with chromate concentration in 0.1 M citric acid buffer at pH 4.75. Figure from reference²² with permission from the copyright holder.

Chapter 2. Experimental

2.1. Analytical Techniques

To have a fundamental understanding of the electrochemical processes involved in the reduction of Cr(VI) in nonaqueous media, cyclic voltammetry experiments are carried out using glassy carbon as working electrode.

Cyclic voltammetry is an electroanalytical technique used for the study of electroactive species. Cyclic voltammetry is usually the first technique in the electrochemical study of a compound, electrode surface, or a biological material since it is a useful technique for obtaining quick information about the thermodynamics of redox processes and electron transfer kinetics.²³

Cyclic voltammetric experiments are carried out using a vessel known as an electrochemical cell (shown in Figure 2.1). The electrochemical cell consists of a working electrode where the redox reaction of interest occurs, a reference electrode, which has a

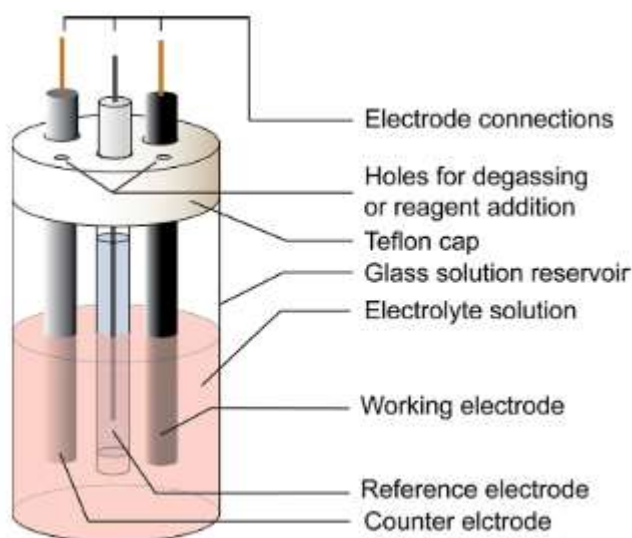


Figure 2.1. A schematic describing a typical electrochemical cell for cyclic voltammetry experiments. Figure from reference²⁴ with permission from the American Chemical Society.

well-defined and stable equilibrium potential, to which the potential of the working electrode is referenced, and a counter electrode to complete the electrical circuit.²⁴

In cyclic voltammetry experiment, a potential is applied to the working electrode using a potentiostat, and this potential is varied with time. The current passing through the working electrode is then measured as a function of the applied potential and a plot of current versus applied potential is generated. This plot is known as a voltammogram.^{23,24}

Ultraviolet and visible (UV-vis) spectroscopy involves the measurement of light absorption by a sample and is a useful tool to differentiate components of a sample based on their absorption bands as different molecules absorb radiation at different wavelengths. In UV-Vis experiments, a plot of absorbance against wavelength is generated. This plot is known as a UV-vis spectrum.²⁵

2.2. Analytes and Reagents

Acetonitrile (Millipore Sigma, 99.8%) was degassed with three freeze-pump-thaw cycles and dried over activated molecular sieves. Bis (tetrabutylammonium) dichromate (Sigma-Aldrich, 99%) and phenol (TCI Chemicals, 99.5%) were dried at room temperature under vacuum for 8 hours. Dichloromethane (BDH Chemicals, 99.5%), N,N-Dimethylformamide (Acros, 99.8%), Tetrahydrofuran (Millipore Sigma, 99.5%), Pyridinium dichromate (Sigma-Aldrich, 98%), Ammonium chromate (Alfa Aesar, 98%), Ammonium dichromate (Alfa Aesar, 99.9%), Ferrocene (Alfa Aesar, 99%), benzoic acid (Acros, 99.6%), and salicylic acid (TCI Chemicals, 99.5%) were used as received. Tetrabutylammonium hexafluorophosphate [NBu₄][PF₆] (TCI Chemicals, 98%) was

recrystallized from hot ethanol, filtered, washed with cold ethanol, and dried at room temperature under vacuum for 24 hours.

2.3. Electrochemical Methods

To prevent oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) which are competing reactions, electrochemistry was carried out in a nitrogen-filled glovebox with a Bio-Logic SAS potentiostat using a three-electrode cell system. The cell was composed of a disposable 20 mL borosilicate glass scintillation vial with a Teflon cap bearing openings for the three electrodes and openings for degassing or reagent addition. The three-electrode system contained a glassy carbon working electrode (3 mm diameter, CH Instruments), a platinum counter electrode (3 mm diameter, CH Instruments), and a silver wire pseudo-reference (CH Instruments). The potentiostat was situated outside the glovebox, and the electrode leads were connected through a shielded electrode cable feedthrough. Glassy carbon working electrodes and the platinum counter electrode were polished manually with 0.05 μm alumina powder (CH Instruments)-Milli-Q water slurry for 2 minutes on Microcloth polishing pads, rinsed, and sonicated for 20 seconds in water from the Milli-Q system to remove residual polishing powder followed by drying in a flux of nitrogen gas. The pseudo-reference silver wire electrode was submerged in a glass tube fitted with a porous glass tip containing 0.25 M $[\text{NBu}_4][\text{PF}_6]$ in acetonitrile. Each working electrode was pre-treated with several cyclical scans in 0.25 M $[\text{NBu}_4][\text{PF}_6]$ /acetonitrile solution. In all the experiments, background voltammograms at the respective scan rate were taken. The solution was stirred between scans. A fresh, pretreated working electrode was used for each scan, and to account for the drift in

potential in non-aqueous solvents, all measured potentials were externally referenced to the ferrocene/ferrocenium couple.

2.4. Optical Methods

UV-vis experiments were carried out using a benchtop Ocean Optics UV-vis spectrometer. The light source is a DH-2000-BAL, a dual light source consisting of Deuterium and Halogen lamps. The light source is coupled to an OCEAN-FX-XRI-ES detector via optic fibers. All experiments were carried out using a 1 cm pathlength Spectrosil® quartz cuvette.

Chapter 3. Results and Discussion

3.1. Choice of Analyte and Solvent

For the determination of suitable solvent and Cr(VI) analyte, solubility experiments (Table 3.1) were carried out to determine the solubility of four Cr(VI) compounds (Bis(tetrabutylammonium) dichromate, pyridinium dichromate, ammonium dichromate, and ammonium chromate) in acetonitrile, dimethylformamide (DMF), dichloromethane, and tetrahydrofuran (THF).

Table 3.1. Solubility of Cr(VI) Compounds in Solvents.

	CH ₃ CN (5 mL)	DMF (5 mL)	CH ₂ Cl ₂ (5 mL)	THF (5 mL)
Bis (tetrabutylammonium) dichromate (25 mg)	Soluble	Soluble	Soluble	Slightly soluble
Pyridinium dichromate (25 mg)	Slightly soluble	Soluble	Sparingly soluble	Slightly soluble
Ammonium dichromate (25 mg)	Insoluble	Soluble	Insoluble	Insoluble
Ammonium chromate (25 mg)	Insoluble	Slightly soluble	Insoluble	Insoluble

As shown in Table 3.1, three out of the four compounds tested were completely soluble in dimethylformamide while only one compound was completely soluble in acetonitrile, tetrahydrofuran, and dichloromethane. Even though dimethylformamide showed the best results, acetonitrile was chosen for this research because of the availability of data on the behavior of acids in acetonitrile on glassy carbon electrodes.²⁶ Also, the pK_a values of a large number of Bronsted acids have been reported in the literature.^{27–29} Bis (tetrabutylammonium) dichromate was selected because it is the only compound that dissolved completely in acetonitrile among the compounds tested.

In this document, moving forward, Cr(VI) concentrations given refer to Bis (tetrabutylammonium) dichromate.

3.2. Cyclic Voltammetry at Glassy Carbon Electrodes in Acetonitrile

Due to the advantages of glassy carbon electrodes, such as their relative low cost, wide cathodic potential range, and chemical inertness,^{30,31} the behavior of hexavalent chromium in acetonitrile was evaluated using these electrodes. The voltammetric response of 2 mM tetrabutylammonium dichromate on a glassy carbon working electrode in acetonitrile is shown in Figure 3.1. The voltammogram shows a background trace of

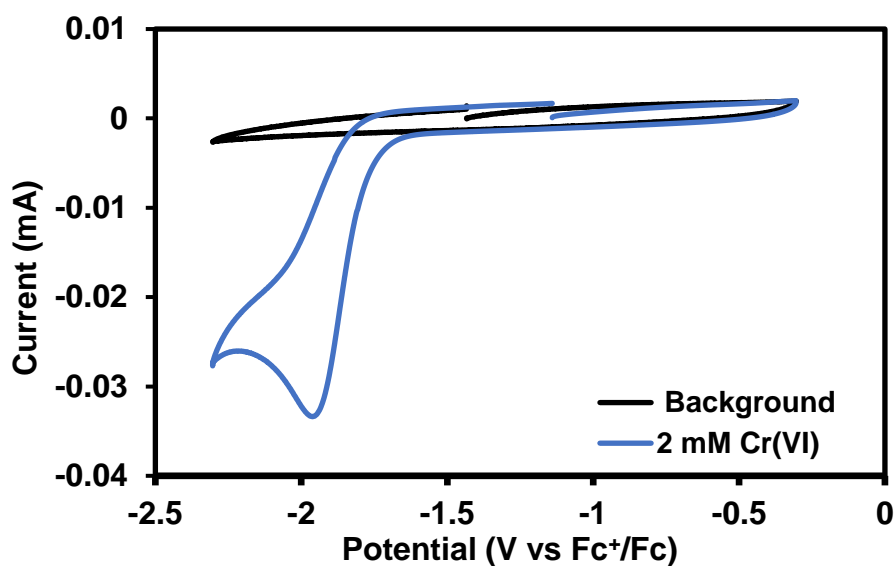


Figure 3.1. A cyclic voltammogram showing the response of a glassy carbon electrode to 2 mM Cr(VI) in 0.25 M [NBu₄][PF₆]/CH₃CN electrolyte solution. Scan rate: 50 mV/s.

the electrode (in black) and one reduction peak in the trace in the presence of hexavalent chromium (in blue). The Cr(VI) reduction current increases as scan rate increases (Figure 3.2).

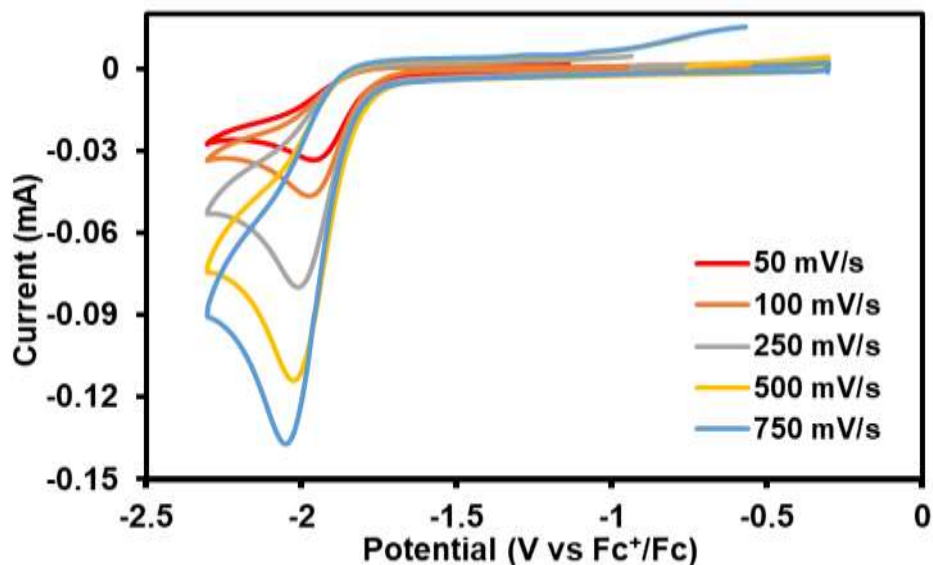


Figure 3.2. Voltammograms showing the effect of varying scan rates on the voltammetric response of glassy carbon electrodes to 2 mM Cr(VI) in 0.25 M [NBu₄][PF₆]/CH₃CN electrolyte solution.

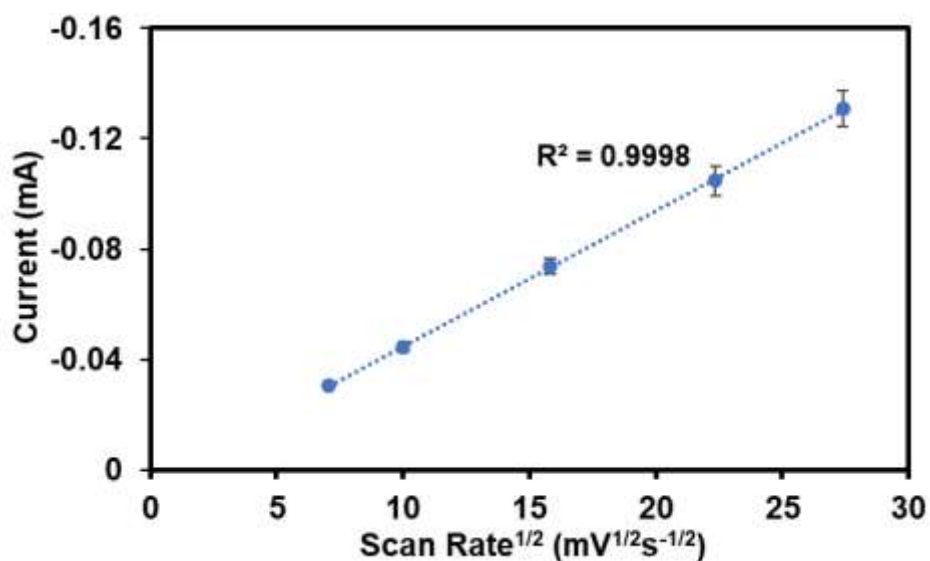


Figure 3.3. Plot of the cathodic peak current versus square root of scan rate. Cr(VI) concentration: 2 mM. Standard deviation error bars are from triplicate analyses.

concentration on the reduction process was investigated by varying the concentration from 0.2 to 6.6 mM (Figure 3.4). As shown in Figure 3.5, the peak currents showed a linear variation with Cr(VI) concentration with a R^2 value of 0.9991, indicating the linear dependence of peak current on Cr(VI) concentration. This suggests that this method

could be efficient for the determination and quantification of Cr(VI) concentration in CH₃CN.

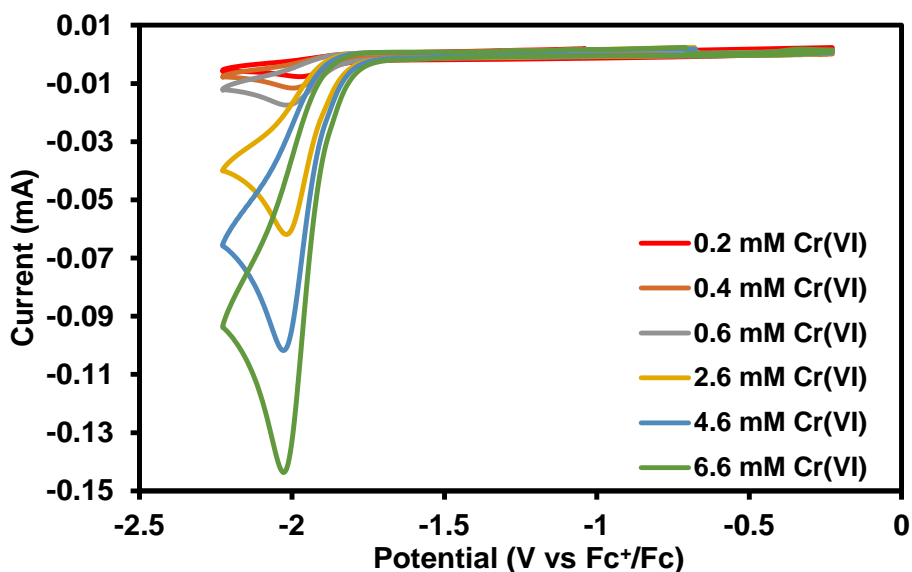


Figure 3.4. Voltammograms showing the effect of varying concentration on the voltammetric response of glassy carbon electrodes in 0.25 M [NBu₄][PF₆]/CH₃CN electrolyte solution.

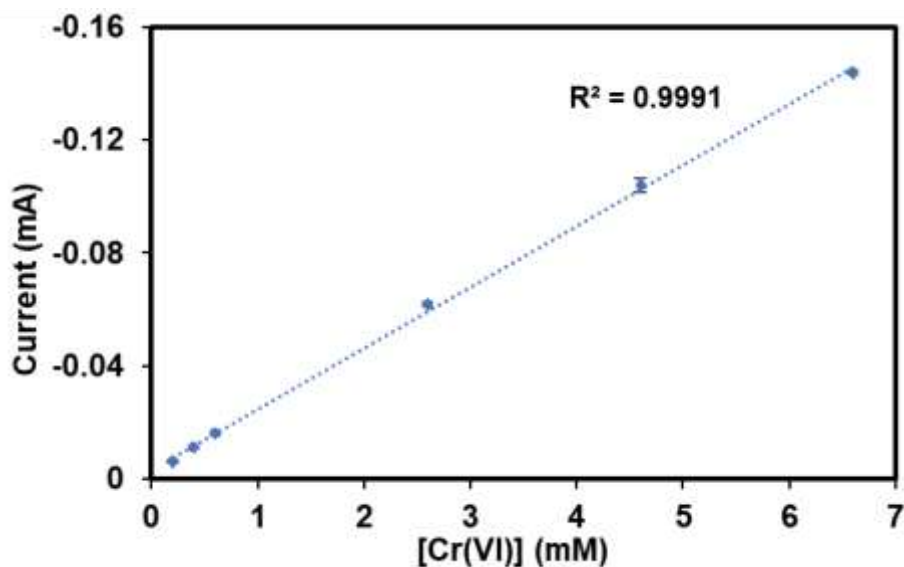


Figure 3.5. Evolution of peak current with increasing concentration of Cr(VI) in 0.25 M [NBu₄][PF₆]/CH₃CN electrolyte solution. Scan rate: 100 mV/s. Standard deviation error bars are from triplicate analyses.

3.3. Chromate-dichromate Equilibrium

The fundamental study of the electroreduction of hexavalent chromium in water is complicated by the equilibrium between chromate and dichromate (shown in Equation 1.1). This equilibrium causes hexavalent chromium to shuttle between the chromate and the dichromate form, depending on concentration and pH. At low concentrations and basic pH, chromate is the predominant species while at high concentrations and acidic pH, dichromate is the predominant species. In aprotic non-aqueous solvents, there are no "H⁺" or "H₃O⁺" equivalents. Hence the chromate-dichromate equilibrium is not expected to be a problem. As shown in Figures 3.4 and 3.5, there is a linear increase in current as the concentration of dichromate increases from 0.2 mM to 6.6 mM. The linearity of the plot suggest that dichromate is the only hexavalent chromium species at the low and high concentrations tested. To confirm this observation, reduction peak potentials from data in Figure 3.4 were plotted against log[Cr(VI)] (Figure 3.6) in a manner like Figure 1.3. The reduction peak potential shifts linearly to more negative values as the concentration of dichromate increases, which further indicates that dichromate is the only species at all concentrations. This is contrary to the loss of linearity observed at high chromate concentration by Stern *et al.*²² during the addition of increasing amount of chromate in water. The outcome of this experiment is that it is possible to investigate the reduction of dichromate at both low and high concentrations.

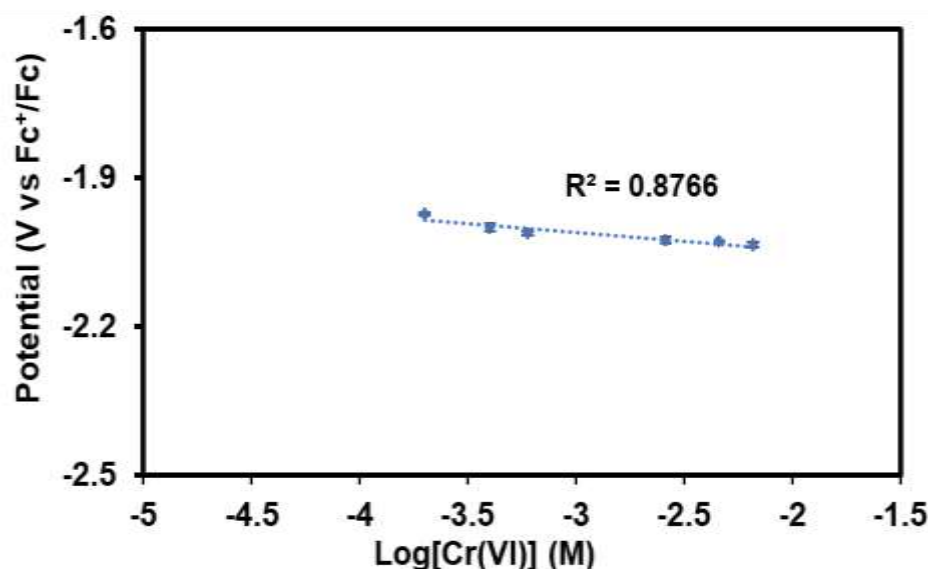


Figure 3.6. Evolution of reduction peak potential with dichromate concentration in 0.25 M [NBu₄][PF₆]/CH₃CN solution. Standard deviation error bars are from triplicate analyses.

3.4. Acid-mediated Reduction of Cr(VI)

As shown in the dichromate reduction equation:

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$, many protons and electrons are required for the reduction of hexavalent chromium. This translates to a large activation barrier, making the direct electrochemical reduction of hexavalent chromium energy demanding.³² To supply the required protons, three organic Brønsted acids (benzoic acid, phenol, and salicylic acid) were investigated as proton donors. These acids were chosen because their pK_a values, behavior and potential window in acetonitrile have been reported in the literature. Izutsu reported a pK_a value of 16.7 for salicylic acid in acetonitrile.²⁷ The pK_a of benzoic acid in acetonitrile was reported as 21.5 by Agnes Kutt *et al.*²⁸ in 2006., while that of phenol was reported as 29.14 by Agnes Kutt *et al.*²⁹ in 2008. The potential range at which these acids get reduced was reported by McCarthy *et al.*²⁶ in their study of the

behavior of Brønsted acids in acetonitrile using glassy carbon electrodes. This allows us to choose a suitable potential window for this study. Voltammograms showing the effect of phenol on the reduction of 2 mM Cr(VI) in acetonitrile are shown in Figure 3.7. The reduction peak shifts to less negative potentials as the concentration of phenol increases (Figure 3.7, black arrow). This suggests acid dependent rate determining chemical steps. Similar shifts in potentials to less negative values are observed with increasing

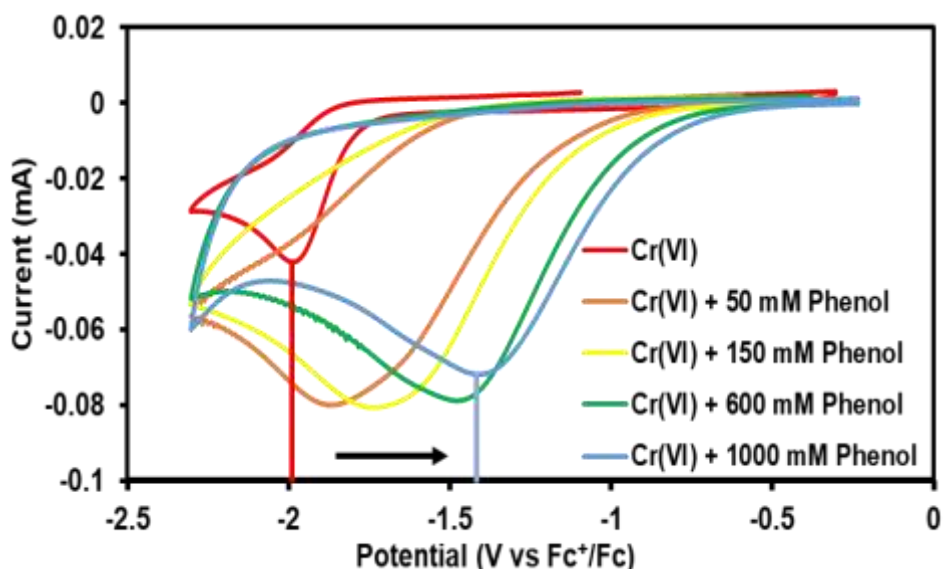


Figure 3.7. Cyclic voltammograms of 2 mM Cr(VI) with varying concentration of phenol in 0.25 M $[\text{NBu}_4][\text{PF}_6]/\text{CH}_3\text{CN}$ solution. Scan rate: 100 mV/s.

concentrations of benzoic acid (abbreviated as BA in Figure 3.8) and salicylic acid (abbreviated as SA in Figure 3.9). As shown in Figure 3.7, the reduction peak current increased with the addition of 50 mM of phenol (Figure 3.7, orange trace) while subsequent additions of phenol (Figure 3.7; yellow, green, and blue trace) yielded no significant change in peak currents. This can be attributed to the change in the rate determining step of the reduction as the number of protons available increases. The large currents observed on the addition of acid can be attributed to new species from the protonation of the dichromate ions.

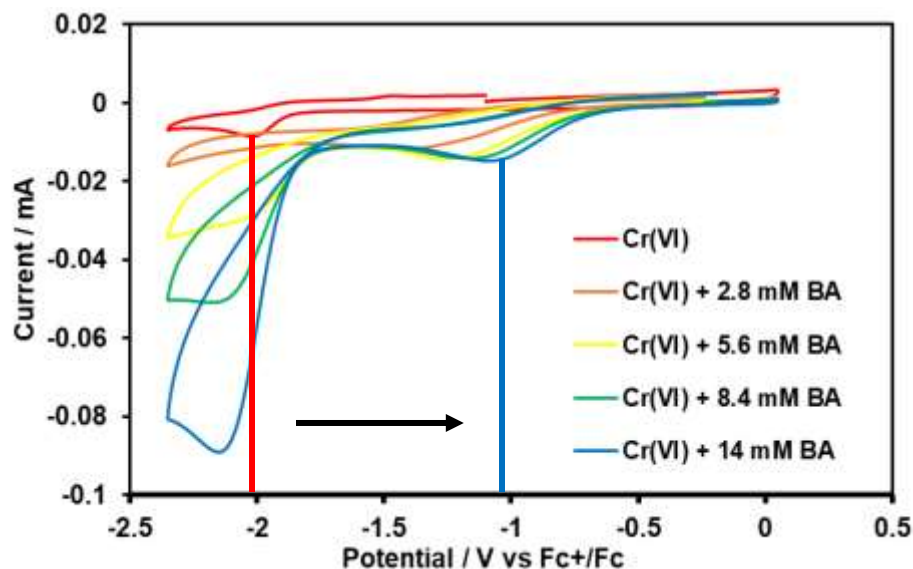


Figure 3.8. Cyclic voltammograms of 0.2 mM Cr(VI) with varying concentration of benzoic acid in 0.25 M $[\text{NBu}_4][\text{PF}_6]/\text{CH}_3\text{CN}$ electrolyte solution. Scan rate: 100 mV/s.

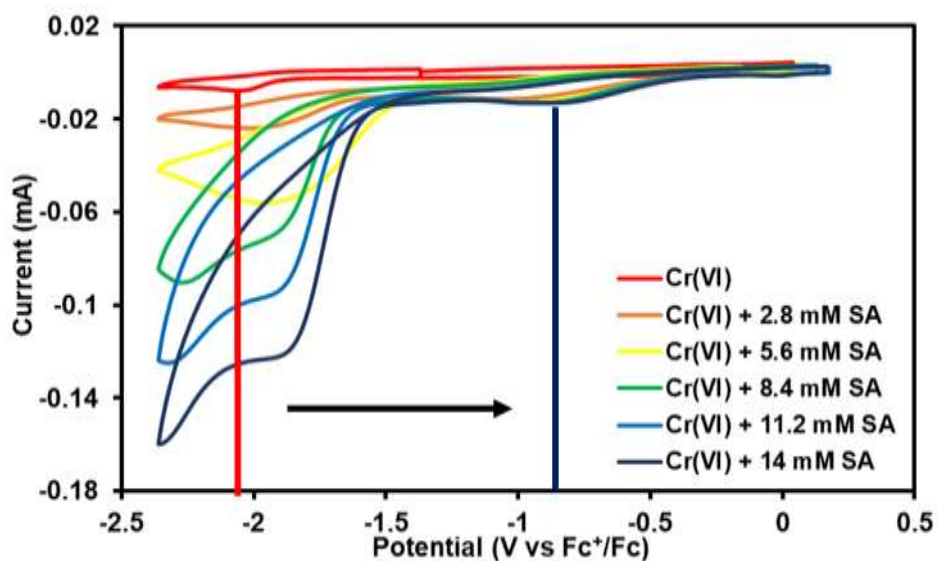


Figure 3.9. Cyclic voltammograms of 0.2 mM Cr(VI) with varying concentration of salicylic acid in 0.25 M $[\text{NBu}_4][\text{PF}_6]/\text{CH}_3\text{CN}$ electrolyte solution. Scan rate: 100 mV/s.

To compare the effect of the acids on Cr(VI) reduction and to correlate acid behavior to their strength, plots of peak potential against log of acid concentration (Figure 3.10) were made and a correlation between potential and acid strength was observed, with salicylic acid and benzoic acid shifting the potentials to more positive values.

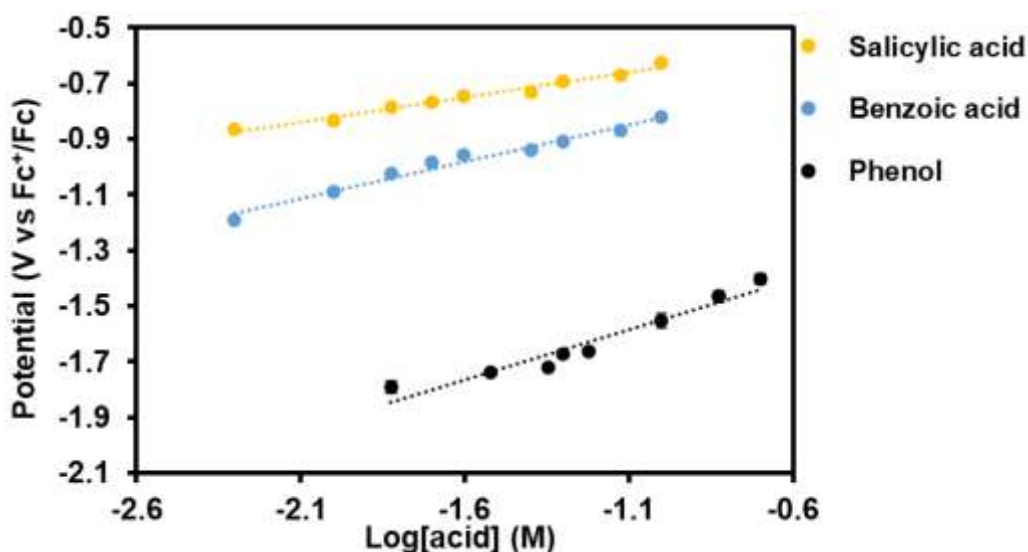


Figure 3.10. Plot of peak potential of 0.2 mM Cr(VI) in 0.25 M $[\text{NBu}_4][\text{PF}_6]/\text{CH}_3\text{CN}$ solution against the log of acid concentration. Scan rate: 100 mV/s; acid concentration range: 5 mM to 200 mM. Standard deviation error bars are from triplicate analyses.

3.5. Homogenous Electron Transfer to Cr(VI)

Due to the large number of protons and electrons required for the reduction of Cr(VI), there is an energy barrier that must be surmounted to achieve efficient reduction. While Bronsted acids have been identified as proton donors for Cr(VI) reduction, there is still a need to make the reduction process less energy demanding. A way to combat this is through catalysis using suitable catalysts that can facilitate the transfer of electrons to Cr(VI) ions. In selecting a catalyst for the reduction of hexavalent chromium, small molecules that can be oxidized by Cr(VI) and reduced back are desirable. Ferrocene is an electron donor and is capable of mediating electron transfer by switching between its oxidized state (ferrocenium) and its reduced state (ferrocene).³³ This suggests that ferrocene could act as a catalyst for Cr(VI) reduction. To investigate this hypothesis and get a fundamental understanding of the role and reactions between the various entities

involved, electron transfer from ferrocene to dichromate ions in acetonitrile was monitored using UV-vis spectroscopy. As shown in Figure 3.11., the dichromate shows an

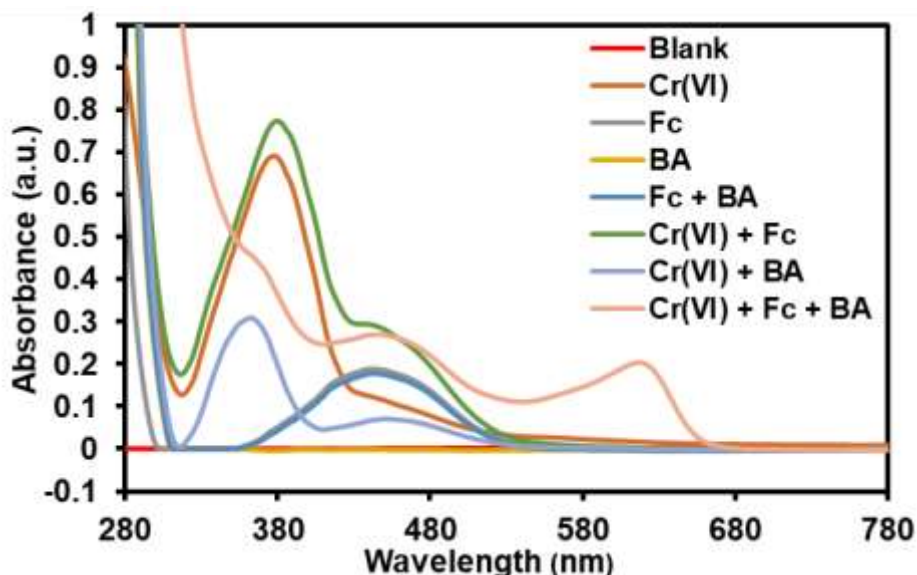


Figure 3.11. UV-vis spectra showing the interaction of different entities in the reduction of 0.2 mM Cr(VI) reduction by 2 mM ferrocene (Fc) in the presence of 200 mM benzoic acid (BA). Scan average: 100, boxcar setting: 25.

absorption maximum at 377 nm (orange trace), while the absorption maximum of ferrocene can be seen at 440 nm (grey trace). Benzoic acid showed no signal in the wavelength range studied. Also, there was no change in the ferrocene signal on the addition of benzoic acid. Similarly, there was no change in the UV-vis signal of either Cr(VI) or ferrocene when they were added together. This implies the lack of reaction between ferrocene and benzoic acid, or between Cr(VI) and ferrocene. However, the dichromate absorption peak at 377 nm disappears and two new peaks at 365 nm and 450 nm appear on the addition of benzoic acid. These peaks can be attributed to the products of the protonation of the dichromate ions; however, further study is required to determine their speciation. On the addition of ferrocene and benzoic acid to Cr(VI) (Figure 3.11, pink trace), the ferrocene peak at 440 nm, the Cr(VI) peak at 377 nm, and

the peaks at 365 nm and 450 nm are not observed. Instead, two new peaks appear. The first one at 460 nm can be attributed to the reduction of the products formed from the protonation of dichromate ions, while the more prominent peak at 620 nm can be attributed to ferrocenium formed by the oxidation of ferrocene by Cr(VI). These new peaks show that ferrocene can donate the electrons needed to reduce Cr(VI), albeit in the presence of protons, and could act as a small molecule catalyst for the reduction of Cr(VI). Overall, the UV-vis experiments reinforce our observations from electrochemical studies which suggest that the reduction of Cr(VI) proceeds via proton-coupled electron transfer (PCET).

3.6. Reproducibility Studies

In this study, different factors affecting the collection of reproducible data were discovered. First, the cathodic peak potentials for Cr(VI) in acetonitrile were found to be affected by the presence of trace amount of water. As shown in Figure 3.12, the

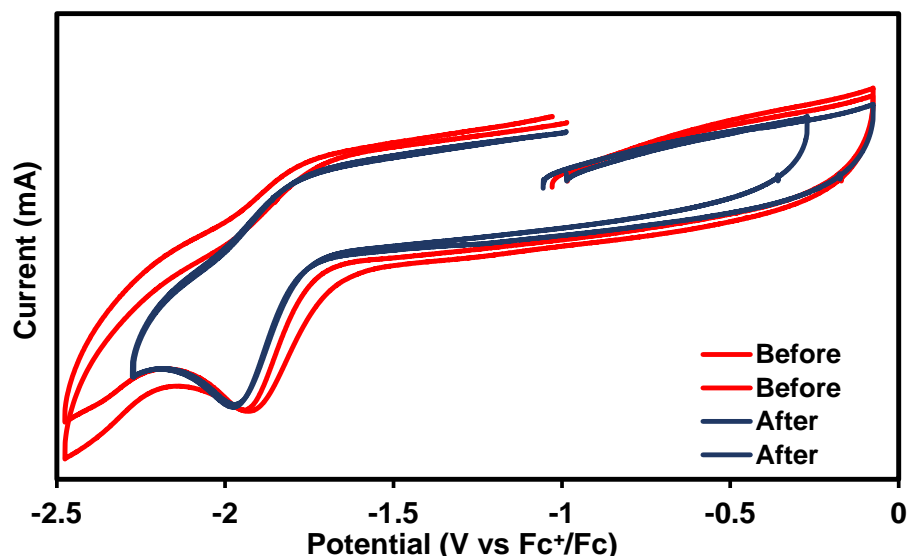


Figure 3.12. Voltammograms obtained for 0.2 mM Cr(VI) in 0.25 M [NBu₄][PF₆]/CH₃CN solution showing peak potentials before and after changing the molecular sieves in the solvent. Scan rate: 100 mV/s.

reduction of Cr(VI) occurred at a less negative potentials when a solvent which was suspected to contain trace of water was used. The peak potential shifted to more negative values after replacing the molecular sieves in the solvent, suggesting that water is acting as a proton donor. This could be helpful in making the reduction of hexavalent chromium less energy demanding, however, it is difficult to account for the number of protons supplied by H₂O compared to externally added acids, making the mechanism of the reduction process difficult to understand. Therefore, to have a better understanding of the behavior of hexavalent chromium in nonaqueous media and obtain reproducible data, the effect of water must be minimized. This was done by carrying out all experiments in a nitrogen-filled glove box with solvent that had been degassed and dried with activated molecular sieves. Another reproducibility parameter is the residence time of electrodes in solution during experiments. This was discovered during time dependency experiments. As shown in Figure 3.13, results from 15 seconds and 30 seconds residence time were compared and it was found that reproducible data are obtained at 30 seconds residence

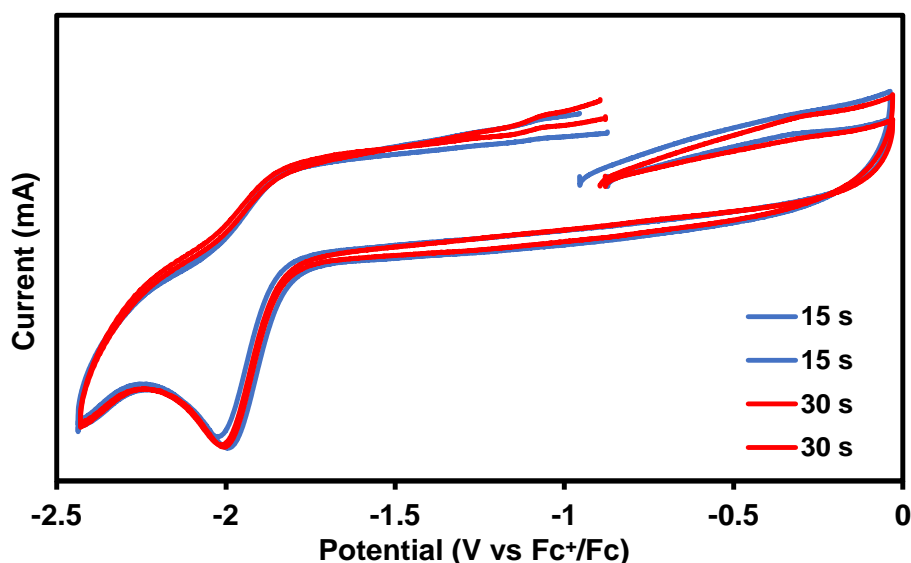


Figure 3.13. Voltammograms obtained at 15- and 30-seconds electrode residence time for 0.2 mM Cr(VI) in 0.25 M [NBu₄][PF₆]/CH₃CN solution. Scan rate: 100 mV/s.

time. As shown in Figure 3.14, by applying the new method of data collection, data were obtained for the reduction of 0.2 mM Cr(VI) in three consecutive experiments with some degree of reproducibility. Statistical analysis of the peak potentials for the three experiments was carried out and a mean \pm standard deviation value of -1.972 ± 0.005 V was obtained with a low relative standard deviation value of 0.26%. This study shows that reproducible Cr(VI) data in acetonitrile can be obtained at glassy carbon electrodes.

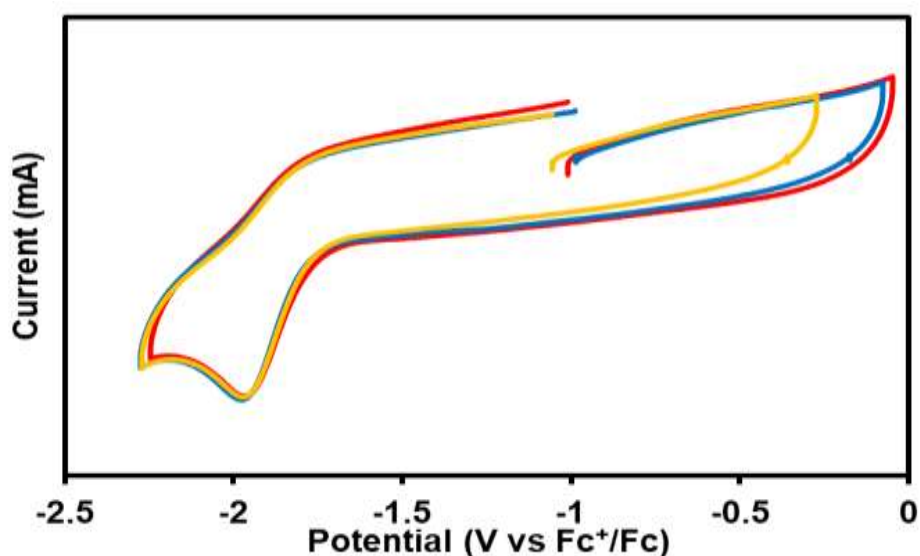


Figure 3.14. Voltammograms for the reduction of 0.2 mM Cr(VI) in three different experiments. Scan rate: 100 mV/s.

Chapter 4. Conclusions

This work has shown that Cr(VI) in acetonitrile can be reduced at glassy carbon electrodes under certain conditions. The reduction of Cr(VI) at glassy carbon electrodes was found to be irreversible and diffusion controlled. The reduction potential for the electroreduction of Cr(VI) was also found to be energy demanding as indicated by the high potential value. This can be attributed to the kinetic barrier caused by the huge numbers of protons and electrons required for the reduction process. However, this study has shown that this kinetic barrier can be overcome using Bronsted-Lowry acids as proton mediators. Electrochemical and UV-Vis studies suggest that the reduction of Cr(VI) proceeds via a proton-coupled electron transfer process.

Outstanding challenges include understanding the mechanism of the reduction process, nature of the products formed and identifying suitable electrocatalysts that can efficiently mediate the transfer of protons and electrons between Cr(VI) and the electrodes. Finding solutions to these challenges will boost Cr(VI) remediation efforts in non-aqueous sources.

Appendix A. Reuse Permission Request for Figure 1.1

Reuse Permission

Temitope O Jegede <tjged1@lsu.edu>

Mon 5/24/2021 10:21 PM

To: support@services.acs.org <support@services.acs.org>

Dear Publisher,

I am completing a master's thesis at Louisiana State University titled "Electrochemical Reduction of Hexavalent Chromium in Acetonitrile using Glassy Carbon Electrodes"

I would like your permission to reprint an image in my thesis, as part of preparation toward my graduation in August 2021.

Original Article: <https://doi.org/10.1021/tx700198a>

Image Title: Figure 4. Major steps in uptake, metabolism, and formation of DNA damage by Cr(VI).

Size of reproduction: One-third of page

Planned placement: Interior

Please contact me if you have any questions or need additional information.

Sincerely,

Temitope Jegede

Department of Chemistry,

Louisiana State University,

United States.

+12252882847

tjged1@lsu.edu

Appendix B. Reuse Permission for Figure 1.1

Regarding Incident 4371880 Reuse Permission

support@services.acs.org <support@services.acs.org>

Mon 5/24/2021 10:32 PM

To: Temitope O Jegede <tjeged1@lsu.edu>



Dear Temitope,

Thank you for contacting ACS Publications Support.

Your permission requested is granted and there is no fee for this reuse. In your planned reuse, you must cite the ACS article as the source, add this direct link <https://pubs.acs.org/doi/10.1021/tx700198a>, and include a notice to readers that further permissions related to the material excerpted should be directed to the ACS.

If you need further assistance, please let me know.

Sincerely,

Keith Pearl

ACS Publications Support

Customer Services & Information

Website: <https://help.acs.org/>

Incident Information:

Incident #: 4371880

Date Created: 2021-05-25T08:52:01

Priority: 3

Customer: Temitope O Jegede

Title: Reuse Permission

Description: Dear Publisher,

I am completing a master's thesis at Louisiana State University titled "Electrochemical Reduction of Hexavalent Chromium in Acetonitrile using Glassy Carbon Electrodes"

I would like your permission to reprint an image in my thesis, as part of preparation toward my graduation in August 2021.

Original Article: <https://doi.org/10.1021/tx700198a>

Image Title: Figure 4. Major steps in uptake, metabolism, and formation of DNA damage by Cr(VI).

Size of reproduction: One-third of page

Planned placement: Interior

Please contact me if you have any questions or need additional information.

Sincerely,

Appendix C. Reuse Permission Request and Permission for Figure 1.2

ELSEVIER LICENSE TERMS AND CONDITIONS

May 26, 2021

This Agreement between Mr. Temitope Jegede ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	5074640204057
License date	May 23, 2021
Licensed Content Publisher	Elsevier
Licensed Content Publication	Talanta
Licensed Content Title	Reduction of hexavalent chromium at solid electrodes in acidic media: reaction mechanism and analytical applications
Licensed Content Author	Christine M. Welch, Olga Nekrassova, Richard G. Compton
Licensed Content Date	Jan 15, 2005
Licensed Content Volume	65
Licensed Content Issue	1
Licensed Content Pages	7
Start Page	74
End Page	80
Type of Use	reuse in a thesis/dissertation
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No
Title	Electrochemical Reduction of Hexavalent Chromium in Acetonitrile using Glassy Carbon Electrodes
Institution name	Louisiana State University
Expected presentation date	Aug 2021
Portions	Figure 1
Requestor Location	Mr. Temitope Jegede 1132 W Lee Dr, Apt B Apt B BATON ROUGE, LA 70820 United States Attn: Mr. Temitope Jegede
Publisher Tax ID	98-0397604
Total	0.00 USD

Appendix D. Reuse Permission Request for Figure 1.3

Reuse permission request

Temitope O Jegede <tjeged1@lsu.edu>

Thu 5/27/2021 12:16 PM

To: Noemie Elgrishi <noemie@lsu.edu>

5/27/2021

Department of Chemistry,
Louisiana State University,
Baton Rouge, Louisiana,
United States.

Dear Dr Elgrishi,

I am completing a master's thesis at Louisiana State University titled "Electrochemical Reduction of Hexavalent Chromium in Acetonitrile using Glassy Carbon Electrodes"

I would like your permission to reprint the following material in my thesis, as part of preparation toward my graduation in August 2021:

Original Article: Carbon Electrodes are Effective for the Detection and Reduction of Hexavalent Chromium in Water.

DOI: <https://doi.org/10.1039/D0EW00146E>

Figure: Figure S7.

Size of reproduction: ¼ page

Planned placement: Interior

My thesis will be viewable on LSU Digital Commons. Please contact me if you have any questions or need additional information.

Sincerely,

Temitope Jegede

Appendix E. Reuse Permission for Figure 1.3

Re: Reuse permission request

Noemie Elgrishi <noemie@lsu.edu>

Thu 5/27/2021 12:26 PM

To: Temitope O Jegede <tjeged1@lsu.edu>

Dear Temitope Jegede,

Following the applicable RSC guidelines, I authorize you to re-print Figure S7 from the SI of this paper in your LSU master's thesis with the proper citation to the original open access work.

Sincerely,

Noémie Elgrishi, PhD

Assistant Professor, Department of Chemistry
Louisiana State University
office: 225-578-6917 | CMB 301A
noemie@lsu.edu

From: Temitope O Jegede <tjeged1@lsu.edu>

Sent: Thursday, May 27, 2021 12:16

To: Noemie Elgrishi <noemie@lsu.edu>

Subject: Reuse permission request

Appendix F. Reuse Permission Request for Figure 3.1

Reuse Permission

Temitope O Jegede <tjged1@lsu.edu>

Sat 5/22/2021 3:56 PM

To: support@services.acs.org <support@services.acs.org>

Dear Publisher,

I am completing a master's thesis at Louisiana State University titled "Electrochemical Reduction of Hexavalent Chromium in Acetonitrile using Glassy Carbon Electrodes"

I would like your permission to reprint an image in my thesis, as part of preparation toward my graduation in August 2021:

Original Article: <https://doi.org/10.1021/acs.jchemed.7b00361>

Image Title: Figure 4. Schematic representation of an electrochemical cell for CV experiments.

Size of reproduction: ¼ page

Planned placement: Interior

Please contact me if you have any questions or need additional information.

Sincerely,

Temitope Jegede

Department of Chemistry,

Louisiana State University,

United States.

+12252882847

tjged1@lsu.edu

Appendix G. Reuse Permission for Figure 3.1

Regarding Incident 4367888 Reuse Permission

support@services.acs.org <support@services.acs.org>

Sun 5/23/2021 8:59 PM

To: Temitope O Jegede <tjged1@ku.edu>



Dear Temitope O Jegede,

Your permission requested is granted and there is no fee for this reuse. In your planned reuse, you must cite the ACS article as the source, add this direct link <https://pubs.acs.org/doi/10.1021/acs.jchemed.7b00361> and include a notice to readers that further permissions related to the material excerpted should be directed to the ACS.

If you need further assistance, please let me know.

Sincerely,
Simran Mehra
ACS Publications Support
Customer Services & Information
Website: <https://help.acs.org/>

Incident Information:

Incident #: 4367888

Date Created: 2021-05-23T02:27:27

Priority: 3

Customer: Temitope O Jegede

Title: Reuse Permission

Description: Dear Publisher,

I am completing a master's thesis at Louisiana State University titled "Electrochemical Reduction of Hexavalent Chromium in Acetonitrile using Glassy Carbon Electrodes"

I would like your permission to reprint an image in my thesis, as part of preparation toward my graduation in August 2021:

Original Article: <https://doi.org/10.1021/acs.jchemed.7b00361>

Image Title: Figure 4, Schematic representation of an electrochemical cell for CV experiments.

Size of reproduction: 1/4 page

Planned placement: Interior

Please contact me if you have any questions or need additional information.

Sincerely,

References

1. Barnhart, J. Occurrences, Uses, and Properties of Chromium. *Regul. Toxicol. Pharmacol.* **1997**, 26 (1 I), S3–S7. <https://doi.org/10.1006/rtph.1997.1132>.
2. Sedman, R. M.; Beaumont, J.; McDonald, T. A.; Reynolds, S.; Krowech, G.; Howd, R. Review of the Evidence Regarding the Carcinogenicity of Hexavalent Chromium in Drinking Water. *J. Environ. Sci. Heal. Part C* **2006**, 24 (1), 155–182. <https://doi.org/10.1080/10590500600614337>.
3. Tripathi, R. M.; Rao, R. P.; Tsuzuki, T. Green Synthesis of Sulfur Nanoparticles and Evaluation of Their Catalytic Detoxification of Hexavalent Chromium in Water. *RSC Adv.* **2018**, 8 (63), 36345–36352. <https://doi.org/10.1039/c8ra07845a>.
4. Salnikow, K.; Zhitkovich, A. Genetic and Epigenetic Mechanisms in Metal Carcinogenesis and Cocarcinogenesis: Nickel, Arsenic, and Chromium. *Chemical Research in Toxicology*. American Chemical Society January **2008**, pp 28–44. <https://doi.org/10.1021/tx700198a>.
5. Yaman, B. Health Effects of Chromium and Its Concentrations in Cereal Foods Together with Sulfur. *Expo. Heal.* **2020**, 12 (2), 153–161. <https://doi.org/10.1007/s12403-019-00298-9>.
6. Welch, C. M.; Nekrassova, O.; Compton, R. G. Reduction of Hexavalent Chromium at Solid Electrodes in Acidic Media: Reaction Mechanism and Analytical Applications. *Talanta* **2005**, 65 (1), 74–80. <https://doi.org/10.1016/j.talanta.2004.05.017>.
7. Chaudhary, A. J.; Goswami, N. C.; Grimes, S. M. Electrolytic Removal of Hexavalent Chromium from Aqueous Solutions. *J. Chem. Technol. Biotechnol.* **2003**, 78 (8), 877–883. <https://doi.org/10.1002/jctb.871>.
8. Mohan, D.; Singh, K. P.; Singh, V. K. Removal of Hexavalent Chromium from Aqueous Solution Using Low-Cost Activated Carbons Derived from Agricultural Waste Materials and Activated Carbon Fabric Cloth. *Ind. Eng. Chem. Res.* **2005**, 44 (4), 1027–1042. <https://doi.org/10.1021/ie0400898>.
9. Mohan, D.; Pittman, C. U. Activated Carbons and Low-Cost Adsorbents for Remediation of Tri- and Hexavalent Chromium from Water. *Journal of Hazardous Materials*. Elsevier September 21, **2006**, pp 762–811. <https://doi.org/10.1016/j.jhazmat.2006.06.060>.
10. Swaroop, A.; Bagchi, M.; Preuss, H. G.; Zafra-Stone, S.; Ahmad, T.; Bagchi, D. Benefits of Chromium(III) Complexes in Animal and Human Health. In *The Nutritional Biochemistry of Chromium (III)*; Elsevier, **2019**; pp 251–278. <https://doi.org/10.1016/b978-0-444-64121-2.00008-8>.
11. Zhou, L.; Liu, D.; Li, S.; Yin, X.; Zhang, C.; Li, X.; Zhang, C.; Zhang, W.; Cao, X.; Wang, J.; Wang, Z. L. Effective Removing of Hexavalent Chromium from Wasted Water by

Triboelectric Nanogenerator Driven Self-Powered Electrochemical System – Why Pulsed DC Is Better than Continuous DC? *Nano Energy* **2019**, 64, 103915. <https://doi.org/10.1016/j.nanoen.2019.103915>.

12. Panizza, M.; Bocca, C.; Cerisola, G. Electrochemical Treatment of Wastewater Containing Polyaromatic Organic Pollutants. *Water Res.* **2000**, 34 (9), 2601–2605. [https://doi.org/10.1016/S0043-1354\(00\)00145-7](https://doi.org/10.1016/S0043-1354(00)00145-7).
13. Rajkumar, D.; Palanivelu, K. Electrochemical Treatment of Industrial Wastewater. *J. Hazard. Mater.* **2004**, 113 (1–3), 123–129. <https://doi.org/10.1016/j.jhazmat.2004.05.039>.
14. Ahmed Basha, C.; Bhadrinarayana, N. S.; Anantharaman, N.; Meera Sheriffa Begum, K. M. Heavy Metal Removal from Copper Smelting Effluent Using Electrochemical Cylindrical Flow Reactor. *J. Hazard. Mater.* **2008**, 152 (1), 71–78. <https://doi.org/10.1016/j.jhazmat.2007.06.069>.
15. Rosa, M. A.; Egido, J. A.; Márquez, M. C. Enhanced Electrochemical Removal of Arsenic and Heavy Metals from Mine Tailings. *J. Taiwan Inst. Chem. Eng.* **2017**, 78, 409–415. <https://doi.org/10.1016/j.jtice.2017.06.046>.
16. Ya, V.; Martin, N.; Chou, Y. H.; Chen, Y. M.; Choo, K. H.; Chen, S. S.; Li, C. W. Electrochemical Treatment for Simultaneous Removal of Heavy Metals and Organics from Surface Finishing Wastewater Using Sacrificial Iron Anode. *J. Taiwan Inst. Chem. Eng.* **2018**, 83, 107–114. <https://doi.org/10.1016/j.jtice.2017.12.004>.
17. Dianat, S.; Hatefi-Mehrjardi, A.; Mahmoodzadeh, K.; Kakhki, S. Electrocatalytic Determination of Cd²⁺ and Pb²⁺ Using an L-Cysteine Tungstophosphate Self-Assembled Monolayer on a Polycrystalline Gold Electrode. *New J. Chem.* **2019**, 43 (36), 14417–14425. <https://doi.org/10.1039/c9nj03459e>.
18. Fu, F.; Wang, Q. Removal of Heavy Metal Ions from Wastewaters: A Review. *Journal of Environmental Management*. Academic Press March 1, **2011**, pp 407–418. <https://doi.org/10.1016/j.jenvman.2010.11.011>.
19. Abda, M.; Gavra, Z.; Oren, Y. Removal of Chromium from Aqueous Solutions by Treatment with Fibrous Carbon Electrodes: Column Effects. *J. Appl. Electrochem.* **1991**, 21 (8), 734–739. <https://doi.org/10.1007/BF01034054>.
20. Walsh, F. C. Electrochemical Technology for Environmental Treatment and Clean Energy Conversion. In *Pure and Applied Chemistry*; Walter de Gruyter GmbH, **2001**; Vol. 73, pp 1819–1837. <https://doi.org/10.1351/pac200173121819>.
21. Faldini, S. B.; Agostinho, S. M. L.; Chagas, H. C. The Effect of Chloride Ions on the Electrochemical Reduction of Cr(VI) to Cr(III) at a Rotating Disk Electrode. *J. Electroanal. Chem.* **1990**, 284 (1), 173–183. [https://doi.org/10.1016/0022-0728\(90\)87070-Z](https://doi.org/10.1016/0022-0728(90)87070-Z).
22. Stern, C. M.; Hayes, D. W.; Kgoadi, L. O.; Elgrishi, N. Emerging Investigator Series: Carbon Electrodes Are Effective for the Detection and Reduction of Hexavalent

Chromium in Water. *Environ. Sci. Water Res. Technol.* **2020**, 6 (5), 1256–1261. <https://doi.org/10.1039/d0ew00146e>.

23. Kissinger, P. T.; Heineman, W. R. Cyclic Voltammetry. *Journal of Chemical Education*. Division of Chemical Education 1983, pp 702–706. <https://doi.org/10.1021/ed060p702>.
24. Elgrishi, N.; Rountree, K. J.; McCarthy, B. D.; Rountree, E. S.; Eisenhart, T. T.; Dempsey, J. L. A Practical Beginner's Guide to Cyclic Voltammetry. *J. Chem. Educ.* **2018**, 95 (2), 197–206. <https://doi.org/10.1021/acs.jchemed.7b00361>.
25. Chen, Z.; Deutsch, T. G.; Dinh, H. N.; Domen, K.; Emery, K.; Forman, A. J.; Gaillard, N.; Garland, R.; Heske, C.; Jaramillo, T. F.; Kleiman-Shwarsstein, A.; Miller, E.; Takanabe, K.; Turner, J. UV-Vis Spectroscopy; Springer, New York, NY, 2013; pp 49–62. https://doi.org/10.1007/978-1-4614-8298-7_5.
26. McCarthy, B. D.; Martin, D. J.; Rountree, E. S.; Ullman, A. C.; Dempsey, J. L. Electrochemical Reduction of Brønsted Acids by Glassy Carbon in Acetonitrile-Implications for Electrocatalytic Hydrogen Evolution. *Inorg. Chem.* **2014**, 53 (16), 8350–8361. <https://doi.org/10.1021/ic500770k>.
27. Izutsu, K. Acid-Base Dissociation Constants in Dipolar Aprotic Solvents; IUPAC Chemical Data Series. *Blackwell Sci. Oxford, U.K.*, **1990**, 166 pp.
28. Kütt, A.; Leito, I.; Kaljurand, I.; Sooväli, L.; Vlasov, V. M.; Yagupolskii, L. M.; Koppel, I. A. A Comprehensive Self-Consistent Spectrophotometric Acidity Scale of Neutral Brønsted Acids in Acetonitrile. *J. Org. Chem.* **2006**, 71 (7), 2829–2838. <https://doi.org/10.1021/jo060031y>.
29. Kütt, A.; Movchun, V.; Rodima, T.; Dansauer, T.; Rusanov, E. B.; Leito, I.; Kaljurand, I.; Koppel, J.; Pihl, V.; Koppel, I.; Ovsjannikov, G.; Toom, L.; Mishima, M.; Medebielle, M.; Lork, E.; Rösenthaller, G. V.; Koppel, I. A.; Kolomeitsev, A. A. Pentakis(Trifluoromethyl)Phenyl, a Sterically Crowded and Electron-Withdrawing Group: Synthesis and Acidity of Pentakis(Trifluoromethyl) Benzene, -Toluene, -Phenol, and -Aniline. *J. Org. Chem.* **2008**, 73 (7), 2607–2620. <https://doi.org/10.1021/jo702513w>.
30. Zittel, H. E.; Miller, F. J. A Glassy-Carbon Electrode for Voltammetry. *Anal. Chem.* **1965**, 37 (2), 200–203. <https://doi.org/10.1021/ac60221a006>.
31. Van der Linden, W. E.; Dieker, J. W. Glassy Carbon as Electrode Material in Electro-Analytical Chemistry. *Analytica Chimica Acta*. Elsevier September 1, 1980, pp 1–24. [https://doi.org/10.1016/S0003-2670\(00\)00025-8](https://doi.org/10.1016/S0003-2670(00)00025-8).
32. Stern, C. M.; Jegede, T. O.; Hulse, V. A.; Elgrishi, N. Electrochemical Reduction of Cr(vi) in Water: Lessons Learned from Fundamental Studies and Applications. *Chem. Soc. Rev.* **2021**, 50 (3), 1642–1667. <https://doi.org/10.1039/d0cs01165g>.
33. Astruc, D. Why Is Ferrocene So Exceptional? *European Journal of Inorganic Chemistry*. Wiley-VCH Verlag January 3, 2017, pp 6–29. <https://doi.org/10.1002/ejic.201600983>.

Vita

Temitope Oluwaseyi Jegede, born in Ilesa, Nigeria, obtained his bachelor's degree from Ladoke Akintola University of Technology, Nigeria. He later got a Master of Science degree from Obafemi Awolowo University during which he focused on geochemistry. Having witnessed the devastation of the environment due to poor exploration practices, he developed an interest in environmental remediation and clean energy studies. He joined the Department of Chemistry at Louisiana State University where he investigated the remediation of toxic hexavalent chromium in acetonitrile. He plans to receive his master's degree in august 2021.