Title
Reaction Mechanisms and Kinetics of Reductive Transformation of Toxic Heavy Metals and Nitrate

Permalink
https://escholarship.org/uc/item/7p4490fn

Author
Chen, Gongde

Publication Date
2018

License
https://creativecommons.org/licenses/by/4.0/ 4.0

Peer reviewed|Thesis/dissertation
UNIVERSITY OF CALIFORNIA
RIVERSIDE

Reaction Mechanisms and Kinetics of Reductive Transformation of
Toxic Heavy Metals and Nitrate

A Dissertation submitted in partial satisfaction
of the requirements for the degree of

Doctor of Philosophy

in

Chemical and Environmental Engineering

by

Gongde Chen

December 2018

Dissertation Committee:
  Dr. Haizhou Liu, Chairperson
  Dr. Jinyong Liu
  Dr. Yadong Yin
The Dissertation of Gongde Chen is approved:

________________________________________

________________________________________

________________________________________

Committee Chairperson

University of California, Riverside
Acknowledgement

First and foremost, I would like to thank my adviser Dr. Haizhou Liu for his guidance, support, patience, and understanding throughout my PhD career. Without him, it would not be possible to complete my dissertation and have an interesting and productive PhD journey. Dr. Liu is wonderful adviser and a good example for me. I appreciated his trust on my academic potential and systematic training that makes me gradually become an independent and professional researcher. His hard working, active and critical thinking, strong social and networking skills, and persistence have imperceptibly influenced my growth in the past four and half years. I also would like to thank my committee members Dr. Yadong Yin and Dr. Jinyong Liu for their help and support. Without the strong support and guidance from Dr. Yin, I would not be able to complete the research in Chapter 2. Dr. Jinyong Liu is a nice professor and friend who gives me a lot of suggestions for my future academic development.

I would like to thank the entire Dr. Liu’s group: Wei Li, Michelle Chebeir, Mathew Chen, Samuel Patton, Tushar Jain, John Orta, Cheng Tan, Liang Wu, Kiran Mangalgiri, and Sumant Avasarala, for their help and support throughout my time at UCR. Your advices, understanding, and company make my PhD study and research full of joys and energy. I would like to thank Yu Shen and Priscila Coelho, the undergraduates who helped me on my research projects.

I would like to thank Wenyan Duan, Xiaobo Zhu, Quynh Tran, Chen Chen, Ji Feng, Yibo Jiang, and Changxu Ren for their friendship and help. Many thanks to Jiacheng Yang, who is wonderful friend and always happy to help me and my family.
Parts of this doctoral work have been published in, submitted to, or in preparation for the following journals, Chapter 2 (published in Water Research, 2017), Chapter 3 (published in Environmental Science and Technology, 2018), Chapter 4 (published in Environmental Science and Technology, 2017), and Chapter 5 (in preparation for submission).

This research has been funded by UC Riverside Faculty Initiation Fund, collaborative seed grants from UC Riverside Research and Economic Development Office and Center for Catalysis, U.S. National Science Foundation CAREER Program, Early-concept Grants for Exploratory Research Program, U.S. National Science Foundation GOALI Program. We also thank the support from the Los Angeles Urban Natural Resources Sustainability Science Fellowship and Corona Environmental Consulting. Any opinion, findings, and conclusions or recommendations in this material are the authors(s) and do not necessarily reflect the views of any these organizations listed above.
Dedication

This dissertation is dedicated to my great parents who are so caring, supportive and understanding in the past years. They work very hard to support me and my family even at the age when they should retire and enjoy their life. I greatly appreciate my mom to take care of my young kids during my PhD study, which makes me be able to focus on my research. Her supportiveness and dedication help me successfully complete my PhD degree.

I would like to thank my love for my whole life, my wife Junjun Tang. She sacrifices her career to support my development and take care of our family. She always stands by me and helps me get through the difficulties during my PhD journey. She is a wonderful wife to keep me persistent and motivate me move forward. Without her, I would not be able to complete so many things in the past years. I would like to thank my kids Stephen Chen and Emma Chen. Your births make me more mature and motivate me to work hard. Thank you for being with me.

Lastly, I would like to thank my sisters Hongyun Chen and Shuhua Chen and their families for the caring and supports. Many thanks to all the family members in my wife side for their understanding and support.
ABSTRACT OF THE DISSERTATION

Reaction Mechanisms and Kinetics of Reductive Transformation of Toxich Heavy Metals and Nitrate

by

Gongde Chen

Doctor of Philosophy, Graduate Program in Chemical and Environmental Engineering University of California, Riverside, December 2018
Dr. Haizhou Liu, Chairperson

Contamination of hexavalent chromium Cr(VI), pentavalent vanadium(V) and nitrate is threatening the availability of drinking water resources. Their reductive transformation into environmentally benign products is a viable and sustainable strategy. The goal of this dissertation is to investigate the reaction kinetics and mechanism of reductive transformation of Cr(VI), vanadium(V), and nitrate.

First, highly reductive TiO₂ nanocrystals were synthesized for photocatalytic Cr(VI) reduction in drinking water matrices. The synthesized catalyst with surface-bonded diethylene glycol exhibited a high electron-releasing capacity. Under UV irradiation, Cr(VI) was efficiently reduced with a fast precipitation of trivalent chromium(III) hydroxide Cr(OH)₃(s). The synthesized catalyst was reused for multiple cycles and exhibited excellent performance in Cr(VI)-contaminated groundwater.

Second, a novel denitrification process was developed for nitrate removal in drinking water matrices. Reactive radicals generated from nitrate photolysis oxidized formate into formate radical (CO₂·⁻). Kinetic modelling and principal component analyses showed that
synergistic nitrate photolysis with CO$_2$-$^\cdot$-induced reduction of nitrogen intermediates enabled synchronous removal of dissolved nitrogen and organic carbon. pH and dissolved organic matter at levels similar to those in groundwater had a negligible impact on the identification performance. The proposed process exhibited strong application potential in treating nitrate-contaminated groundwater.

Third, the redox chemistry of vanadium(V) species and their transformation products were investigated with state-of-the-art rotating ring-disk electrode techniques. VO$_2^+$ and Na$_x$H$_y$V$_{10}$O$_{28}$($^{6-x-y}$) predominantly exhibited faster intrinsic reduction kinetics than H$_x$V$_{4}$O$_{12+x}$($^{4+x}$), and HVO$_4^{2-}$. The reduction of vanadium(V) underwent a one-electron transfer process except for that of Na$_x$H$_y$V$_{10}$O$_{28}$($^{6-x-y}$) with a two-electron transfer. Ring electrode current showed that the reduction product of Na$_x$H$_y$V$_{10}$O$_{28}$($^{6-x-y}$) was stable, while the other three vanadium(V) species had half-lives from milliseconds to seconds. Phosphate complexation favored the reduction of vanadium(V) and inhibited the re-oxidation of its reduction product in water treatment.

Finally, radical-induced photochemical reduction of Cr(VI) and nitrate in the spent ion-exchange regenerant brine was investigated to increase the sustainability of ion exchange processes. CO$_2$-$^\cdot$ has been demonstrated to be more effective than alcohol-derived carbon-centered radicals to remove Cr(VI) in the spent brine. The reduction of Cr(VI) was favored at a high dosage of formate and low pHs and was not affected by ionic strength. Chloride transformed NO$_2$-$^\cdot$ into less reactive NO-$^\cdot$ and Cl$_2$-$^\cdot$ and inhibited Cr(VI) reduction. Co-removal of Cr(VI) and nitrate was achieved with an extended reaction time.
In summary, novel redox-based treatment processes have been developed to remove Cr(VI) and nitrate from drinking water and wastewater matrices. Fundamental redox chemistry of vanadium(V) species and their reduction products have been unveiled electrochemically by rotating ring-disk electrode. The developed treatment processes can be integrated into decentralized water treatment and reuse facilities to remove Cr(VI) and nitrate from local water resources. The redox chemistry of vanadium could help design effective treatment processes for vanadium(V) removal. Future work will be conducted to design treatment modules to remove Cr(VI) and nitrate in actual water matrices and extend the application of rotating ring-disk electrode for other aquatic contaminants.
# Table of Content

**Chapter 1 Introduction** ........................................................................................................... 1

1.1 Water Pollution Crisis........................................................................................................ 2

1.2 Why Toxic Heavy Metals and Nitrate ............................................................................. 3

1.3 Existing Treatment Technologies and Challenges......................................................... 8

1.4 Emerging Technologies and Sustainable Water Management .................................... 12

1.5 Motivation, Aim and Scope............................................................................................... 14

1.6 Research Hypothesis and Objectives.............................................................................. 15

**Chapter 2 Photocatalytic Removal of Hexavalent Chromium by Newly Designed and Highly Reductive TiO₂ Nanocrystals** ......................................................................................... 28

2.1 Abstract .............................................................................................................................. 29

2.2 Introduction ....................................................................................................................... 30

2.3 Materials and Methods..................................................................................................... 32

2.4 Results and Discussion .................................................................................................... 35

2.5 Conclusions ...................................................................................................................... 48

2.6 Acknowledgement ............................................................................................................ 49

**Chapter 3 Nitrate Removal via a Formate Radical-induced Photochemical Process** ......................................................................................................................................... 55

3.1 Abstract .............................................................................................................................. 56

3.2 Introduction ....................................................................................................................... 57

3.3 Materials and Methods..................................................................................................... 59

3.4 Results and Discussion .................................................................................................... 62
3.5 Environmental Implications ........................................................................................................ 76
3.6 Acknowledgement ......................................................................................................................... 78

Chapter 4 Understanding Reduction Kinetics of Aqueous Vanadium(V) and Transformation Products Using Rotating Ring-Disk Electrode ........................................ 84
4.1 Abstract ........................................................................................................................................... 85
4.2 Introduction ..................................................................................................................................... 86
4.3 Materials and Methods .................................................................................................................... 90
4.4 Results and Discussion ................................................................................................................... 92
4.5 Environmental Implications and Broader Significance ................................................................. 106
4.6 Acknowledgement .......................................................................................................................... 108

Chapter 5 Photochemical Removal of Cr(VI) and Nitrate in Spent Ion-exchange Regenerant Brine ........................................... 113
5.1 Abstract ........................................................................................................................................... 114
5.2 Introduction ..................................................................................................................................... 115
5.3 Materials and Methods .................................................................................................................... 117
5.4 Results and Discussion ................................................................................................................... 119
5.5 Environmental Implications ........................................................................................................... 131
5.6 Acknowledgement .......................................................................................................................... 132

Chapter 6 Conclusions and Broader Impacts .................................................................................... 136
6.1 Photocatalytic Removal of Hexavalent Chromium by Newly Designed and Highly Reductive TiO$_2$ Nanocrystals ................................................................. 137
6.2 Nitrate Removal via Formate Radical-induced Photochemical Process .......................... 138
6.3 Understanding Reduction Kinetics of Aqueous Vanadium(V) and Transformation Products Using Rotating Ring-Disk Electrode ............................................................. 140

6.4 Photochemical Removal of Cr(VI) and Nitrate in Spent Ion-exchange Regenerant Brine ........................................................................................................................................................................... 141

6.5 Broader Impacts and Future Studies ........................................................................................................................................................................................................... 142

Appendix A  Supporting Information for Chapter 2 ................................................................. 147

Appendix B  Supporting Information for Chapter 3 ................................................................. 169

Appendix C  Supporting Information for Chapter 4 ............................................................... 191

Appendix D  Supporting Information for Chapter 5 .............................................................. 206
List of Figures

Figure 2.1 The synthesized TiO$_2$ nanocrystals after heating TiCl$_4$ in diethylene glycol and H$_2$O for 3 hours. (A) TEM image; (B) XRD pattern; (C) FTIR spectra of diethylene glycol and TiO$_2$ nanocrystals. ................................................................................................................................. 37

Figure 2.2 The photocatalytic removal of Cr(VI) with its initial concentrations at (A) 100 µg/L and (B) 20 mg/L under UV irradiation by TiO$_2$ catalysts. pH = 7.0 with 6 mM phosphate buffer and TiO$_2$ surface area-based dosage = 7.8 m$^2$/L. ............................................ 38

Figure 2.3 Cumulative HO$^\cdot$ radical production in the presence of the synthesized TiO$_2$ nanocrystals and P25 TiO$_2$ under UV irradiation. TiO$_2$ surface area-based dosage = 7.8 m$^2$/L, TA concentration = 10 mg/L, and pH = 7 with 6 mM phosphate buffer. ......................... 40

Figure 2.4 The effect of catalyst dosage on photocatalytic reduction of Cr(VI) over the synthesized TiO$_2$ nanocrystals under UV irradiation. Initial [Cr(VI)] = 20 mg/L, pH = 7 with 6 mM phosphate buffer. ................................................................................................................................. 41

Figure 2.5 FTIR spectra of TiO$_2$ nanocrystals separated from reaction suspensions during Cr(VI) reduction process. Initial [Cr(VI)] = 20 mg/L, TiO$_2$ dosage = 50 mg/L, and pH = 7 with 6 mM phosphate buffer. ................................................................................................................................. 44

Figure 2.6 Full scan (A) and Cr 2p (B-D) XPS spectra of the synthesized TiO$_2$ nanocrystals separated from reaction suspensions during Cr(VI) reduction process. Initial [Cr(VI)] = 20 mg/L, TiO$_2$ dosage = 50 mg/L, pH = 7 with 6 mM phosphate buffer. ............................................. 46

Figure 2.7 Multiple-cycle performance of the synthesized TiO$_2$ nanocrystals for the photocatalytic reduction of Cr(VI) under UV irradiation. Initial [Cr(VI)] = 20 mg/L, TiO$_2$ dosage = 50 mg/L and pH = 2.7 with 0.2 M phosphate buffer. ................................................................. 47
Figure 3.1 Photochemical denitrification in the presence of formate. [Nitrate] = 2.0 mM, [Formate] = 6.2 mM, and pH = 7 with 20 mM phosphate buffer. Makers represent the data from experiments; Lines with shaded bands represent the predicted time profiles of average .............................................................. 63

Figure 3.2 Electron paramagnetic spectra of DMPO-radical adducts formed after 20 minutes of irradiation with medium-pressure UV lamp. [Nitrate] = 100 mM, [Formate] = 300 mM, [DMPO] = 100 mM, and pH = 7 with 200 mM phosphate buffer. .......................... 67

Figure 3.3 Model-predicted cumulative contribution of relevant species to: (A) the formation of CO$_2^{-}$; and (B) the consumption of CO$_2^{-}$. [Nitrate] = 2.0 mM, [Formate] = 6.2 mM, and pH = 7 with 20 mM phosphate buffer. .............................................................. 68

Figure 3.4 Impact of pH on photochemical denitrification in the presence formate: (A) Nitrate removal; (B) Total nitrite evolution; (C) Dissolved nitrogen removal; (D) Total formate consumption. [Nitrate] = 2.0 mM, [Formate] = 6.2 mM, and pH = 2-11 with 20 mM phosphate buffer. Total nitrite = nitrous acid + nitrite; Total formate = formic acid + formate. ........................................................................................................................................ 72

Figure 3.5 Impact of dissolved organic matter (DOM) on photochemical denitrification in the presence formate: (A) Dissolved nitrogen removal; (B) Formate consumption; [Nitrate] = 2.0 mM, [Formate] = 6.2 mM, [DOM] = 0-72 mg-C/L, and pH = 7 with 20 mM phosphate buffer. ........................................................................................................................................ 75

Figure 3.6 Photochemical denitrification in the synthetic groundwater. Chemicals added in the synthetic groundwater: [Formate] = 6.0 mM and pH = 7 with 20 mM phosphate buffer. ........................................................................................................................................ 76
**Figure 4.1** Predominance diagram of vanadium(V) species as a function of pH. Total [vanadium(V)] = 20 mM, [NaClO₄] = 0.6 M, and ionic strength = 0.6 M. V₁₀ is a combination of $\text{H}_3\text{V}_{10}\text{O}_{28}^{3-}$, $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$, $\text{NaHV}_{10}\text{O}_{28}^{4+}$, $\text{Na}_2\text{V}_{10}\text{O}_{28}^{4-}$, $\text{HV}_{10}\text{O}_{28}^{5-}$ and $\text{NaV}_{10}\text{O}_{28}^{5-}$; V₅ is $\text{V}_5\text{O}_{15}^{5-}$; V₄ is a combination of $\text{V}_4\text{O}_{12}^{4+}$ and $\text{HV}_4\text{O}_{13}^{5-}$; V₂ is a combination of $\text{H}_2\text{V}_2\text{O}_7^{2-}$ and $\text{HV}_2\text{O}_7^{3-}$; V₁ is a combination of $\text{H}_2\text{VO}_4^-$, $\text{HVO}_4^{2-}$ and $\text{VO}_4^{3-}$.

**Figure 4.2** Cyclic voltammetry of vanadium (V) species on a gold disk electrode. Total [vanadium(V)] = 20 mM, [NaClO₄] = 0.6 M, ionic strength = 0.6 M, scan rate = 50 mV/s, and dashed lines represent the voltammograms of background electrolyte at 200 mV/s. Cyclic scan on the electrode started in the cathodic direction followed by the anodic direction.

**Figure 4.3** Linear sweep voltammetry of vanadium(V) species on a rotating gold ring-disk electrode. Total [vanadium(V)] = 20 mM, [NaClO₄] = 0.6 M, ionic strength = 0.6 M, and scan rate = 50 mV/s. Ring electrode potential was fixed at 1.3, 1.0, 0.8, and 0.7 V for for $\text{VO}_2^+$, V₁₀, V₄ and $\text{HVO}_4^{2-}$, respectively. Dashed lines represent the linear sweep voltammetry of background electrolyte at 50 mV/s.

**Figure 4.4** Koutecky-Levich plots of vanadium(V) reduction on a rotating gold ring-disk electrode. Total [vanadium(V)] = 20 mM, [NaClO₄] = 0.6 M, ionic strength = 0.6 M, scan rate = 50 mV/s, and current at different rotation speeds was taken at 0.10, -0.54, -0.74, and -1.15 V for $\text{VO}_2^+$, V₁₀, V₄ and $\text{HVO}_4^{2-}$, respectively.
Figure 4.5 Impact of ring electrode potential on the collection efficient of the intermediate products produced on the gold disk electrode. Total [vanadium(V)] = 20 mM, [NaClO$_4$] = 0.6 M, ionic strength = 0.6 M, rotation speed = 2400 rpm, and scan rate = 50 mV/s. ...

Figure 5.1 UV-vis absorption spectra of the spent IX regenerant brine and its major constituents. ................................................................. 121

Figure 5.2 Photochemical reduction of Cr(VI) in the spent IX regenerant brine in the presence of different organic electron donors. [Formate] = [Methanol] = [Ethanol] = [Isopropanol] = 40 mM................................................................. 122

Figure 5.3 Impact of formate dosage on photochemical reduction of Cr(VI) in the spent IX regenerant brine. [Formate] = 5-120 mM, pH = 8.4-8.7, and the sample was filtered through 0.2-µm PVDF membrane before analysis. ................................................................. 124

Figure 5.4 Impact of pH on photochemical removal of Cr(VI) in the spent IX regenerant brine. [Formate] or [Formic acid] = 40 mM. ................................................................. 124

Figure 5.5 Impact of ionic strength on photochemical reduction of Cr(VI) in the presence of nitrate and formate. [Cr(VI)] = 31.2 mg/L, [Nitrate] = 45 mM, [Formate] = 40 mM, [NaClO$_4$] = 0 - 2 M, and pH = 5.9-6.7 with 50 mM phosphate buffer ...................... 126

Figure 5.6 Impact of chloride, sulfate and bicarbonate on photochemical reduction of Cr(VI) in the presence of nitrate and formate. [Cr(VI)] = 31.2 mg/L, [NaCl] = 2 M, [Na$_2$SO$_4$] = 0.2 M, [NaHCO$_3$] = 45 mM, [NaClO$_4$] = 0 - 2 M, pH= 7.9-8.1 with 100 mM borate buffer, [ ] ................................................................. 127
Figure 5.7 Photochemical removal of chromium and nitrate from the spent IX regenerant brine in the presence of formate: (A) pH = 2.1-3.5; (B) pH = 3.4-8.6; and (C) pH = 8.6-9.1. [Formate] = 160 mM.
List of Tables

Table 3.1 Major reactions in photochemical denitrification process. [Nitrate] = 2.0 mM, [Formate] = 6.2 mM, and pH = 7 with 20 mM phosphate buffer. Entries in the eigenvector with absolute value smaller than 0.01 are not shown. .............................................................. 65

Table 3.2 Impact of formate-to-nitrate molar ratio on denitrification and reaction stoichiometry between formate and nitrate in deionized water at neutral pH. ................. 71

Table 4.1 Summary of electron transfer number, intrinsic rate constants, and diffusion coefficients of vanadium (V) species and half-lives of their reduction products on the gold ring-disk electrode. ................................................................. 99

Table 4.2 The impact of molar ratios of phosphate to vanadium(V) ([PO_4]/[V(V)]) on the kinetic parameters of vanadium(V) species on the rotating gold ring-disk electrode. k0: intrinsic rate constants; α: charge transfer coefficients; k: rate constants of VO_2^+, V_{10}, V_4 and HVO_4^{2-} at 0.45, -0.26, -0.30, and -1.10 V, respectively; [PO_4] = 0, 1, 5, 10 and 20 mM, [V(V)] = 20 mM. ................................................................. 103

Table 5.1 Composition of full-scale ion exchange spent brine and California Hazardous Soluble Threshold Limit Concentrations (STLC)................................................................. 120
List of Schemes

**Scheme 3.1** Major reaction pathways in photochemical denitrification process. [Nitrate] = 2.0 mM, [Formate] = 6.2 mM, and pH = 7 with 20 mM phosphate buffer. All referred reactions were listed in Table 3.1. ................................................................. 66

**Scheme 4.1** Principles of vanadium(V) reduction on the disk electrode and re-oxidation of its reduction products on the ring electrode under rotating conditions................................. 89
Chapter 1

Introduction
1.1 Water Pollution Crisis

Water is essential to life, socio-economic development, and healthy ecosystem. However, water pollution has become a global concern that is threatening the public health and ecological balance. The growth of world population and climate change are further aggravating the water contamination. Globally, 80% of wastewater is discharged to ecosystem without being treated or reused.\(^1\) Every day, 2 million tons of waste from sewage, agriculture, and industries are discharged into global water.\(^1\) 1.8 billion of people use water contaminated with feces as their drinking water sources. 3.1% of all deaths in the world are caused by unsafe or inadequate water sanitation and hygiene.\(^2\)

Contaminants find their way to our limited fresh water through natural processes and anthropogenic activities. According to sources, water pollution can be categorized into point source and non-point source of pollution. Point source water pollution refers to contamination caused by single and identifiable source (e.g., pipes and ditches). For instance, the discharge of inadequately treated water by wastewater treatment plants or industries is a point source of pollution that can impact the water quality of surface waters (e.g., lakes, rivers, etc.). Non-point source water pollution refers to contamination originating from leaching and diffusion rather than a single discrete source. For instance, nutrient leaching from agriculture lands and stormwater runoff are non-point source pollution that can introduce nutrients, heavy metals, and organic contaminants into groundwater and surface water. According to the locations, water pollution can be categorized into surface water and groundwater pollution. Surface water pollution refers to the water contamination in rivers, lakes, and oceans from waste water discharged from
sewerage plants and industries, surface runoff, etc. Groundwater pollution refers to water contamination in groundwater aquifer from naturally occurring, soil contaminant leaching, hydraulic fracturing, etc. The interaction between surface water and groundwater through hydrological flow can spread water pollution from one to another.

A wide spectrum of substances, including organic and inorganic contaminants and pathogens, can enter our aquatic systems and cause water contamination. Organic water contaminants include petroleum hydrocarbons, food-processing waste, industrial solvent, dyes, detergent, etc. With the advancement of analytic technologies, trace levels of emerging contaminants, including disinfection by-product, pharmaceutical and personal care products, pesticide, herbicide, and endocrine disrupting compounds, have been recognized because of their potential risk to human health and aquatic life. Inorganic water contaminants include nutrient (e.g., nitrate, ammonia, and phosphate), heavy metals (e.g., chromium, lead, arsenic, cadmium, vanadium, etc.), non-metal oxyanions (e.g., selenate, perchlorate, nitrite, etc.), inorganic acid (e.g., sulfuric acid), etc. Disease-causing pathogens include Salmonella, Legionella, Giardia lamblia, Cryptosporidium parvum, etc.

1.2 Why Toxic Heavy Metals and Nitrate

Among different types of contaminants, toxic heavy metals and nitrate have been aroused much attention because of their environmental persistence, abundance, toxicity, and ecological impact. Toxic heavy metals commonly refer to metal elements with a density greater than 5 g/cm³ and high toxicity, including chromium, vanadium, arsenic, cadmium, mercury, and lead. They are naturally found in earth crust and widely used in various industrial processes. Increasing urbanization and industrialization extracts a large
quantity of toxic heavy metals from earth crust and causes severe pollution in the aquatic systems. Toxic heavy metals are bio-accumulative and the contamination in water and soils causes their accumulation in aquatic species, plants, and animals and thus leads to global food safety issues.³

Toxic heavy metals enter aquatic system through natural weathering of mineral ores or anthropogenic activities such as mining, vehicle emission, fertilizer utilization, industrial waste discharge, and aging water infrastructures release. Even though some of them (e.g., chromium) are essential elements for human beings in small quantities, they are carcinogenic, toxic and very detrimental to human health in excess. For instance, heavy metals in living organism can combine with cellular components and interfere with their normal metabolic functions.⁴ Chronic exposure to heavy metals in a long run can cause different symptoms and diseases, including neurotic and metal disorder, bone disease, kidney damage, cancers, etc.⁴

Chromium and vanadium are the two most abundant toxic heavy metals in the earth crust.⁵ They are naturally present in various minerals and fossil fuels. In addition, chromium and vanadium are extensively used by human beings. For instance, chromium is widely used in electroplating, leather tanning, pigment production, metallurgy, and stainless steel.⁶,⁷ Vanadium is primarily used to strengthen the steel. It also widely used for pigment, dyes, pesticide, catalysts, vanadium redox flow batteries, etc.⁸ Their wide distribution in natural environment and extensive use by human beings cause worldwide water contamination.
1.2.1 Toxicity, Occurrence and Regulations of Cr(VI)

Chromium has six oxidation states (0 - VI), but only trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) are stable in aquatic environment. Cr(III), less toxic and considered as an essential element at trace levels, can be effectively immobilized as chromium hydroxide solid Cr(OH)$_3$(s) in neutral pH ranges. Cr(VI) is acutely toxic, carcinogenic and mobile and has been identified as one of high-priority contaminants by the U.S. Environmental and Protection Agency (EPA). The exposure to Cr(VI) can cause liver and kidney damage and lung cancer.

Anthropogenic activities and geological weathering are the two main sources for the occurrence of Cr(VI) in aquatic systems. Chromium is commonly found in aquifer minerals (e.g., FeCr$_2$O$_4$). Under alkaline pH and in the presence of MnO$_2$, Cr(VI) leaches into groundwater through geological weathering of chromium-containing minerals. The discharge of Cr(VI)-containing wastewaters from industries also contribute to Cr(VI) presence in water. Data mining of the UCMR3 revealed that 98% of drinking water sources in which Cr(VI) was greater than 10 µg/L originated from groundwater sources. California Department of Public Health has collected data from 2007 to 2017 and reported Cr(VI) in drinking water supplies from active and standby public wells. 3778 of 8765 wells tested were detected with Cr(VI). U.S. EPA established the maximum contaminant level for total chromium of 100 µg/L. California has more stringent drinking water regulatory standard on total chromium, i.e., 50 µg/L vs. 100 µg/L. The public health goals established by the Office of Environmental Health Hazard Assessment (OEHHA) is 0.02 µg/L for Cr(VI) in drinking water. Considering the toxicity and carcinogenicity, a new
drinking water standard for Cr(VI) is in progress. The compliance to new Cr(VI) standards expects to pose great challenges to public water utilities in future.

1.2.2 Toxicity, Occurrence and Regulations of Vanadium(V)

Vanadium has six oxidation states (-I - V) but only vanadium(IV) and vanadium(V) are relevant in aquatic systems. Vanadium is an essential element for some microorganism to properly function the enzymes and has been investigated for diabetes relief in medical treatment. The toxicity of vanadium is associated with its oxidation states. At circumneutral pHs, vanadium(IV) mainly exists as a solid phase and has a low solubility and toxicity. Vanadium(V) exists as oxyanions (e.g., HVO₄²⁻) and is highly soluble and toxic. For instance, vanadate has a similar structure and chemistry with phosphate. Its Intake by living organisms can inhibit the enzymatic activities of phosphatases and cause the toxic effects. The aqueous chemistry of vanadium(V) is quite complex. The speciation of vanadium(V) is dependent on the concentration of vanadium, solution pH, ionic strength, and the presence of organic and inorganic constituents. Vanadium(V) mainly exist as vanadate oxyanions in natural waters (e.g., H₂VO₄⁻ and HVO₄²⁻) and it tends to oligomerize into poly-vanadate anions as vanadium concentration increases.

Vanadium enters aquatic environments through natural weathering of mineral ores and anthropogenic activities including mining, industrial manufacturing, fossil fuel burnings, etc. Global anthropogenic release of vanadium into the environment is increasing because of the changing industrial practices and emerging waste streams. For instance, increased demand for high grade steel has doubled the global production of vanadium in the past 15 years because increased vanadium content is required to improve the quality of steel.
addition, vanadium redox flow batteries have been increasingly adopted for energy storage at off-grid locations.\textsuperscript{27} Total vanadium discharge into the environment has been raised through steel slag, waste incineration, and bauxite processing residue.\textsuperscript{29} The application of emerging technologies will expect to increase vanadium release. Vanadium has the fourth highest environmental enrich factor in the aquatic systems.\textsuperscript{30} Generally, vanadium(V) concentration in the aquatic environment varied from several ten micrograms per liter (0-2 µM) in groundwater to several hundred milligrams per liter (> 2 mM) in liquid waste from metallurgy plants.\textsuperscript{26} Large portions of surface water in Europe have vanadium concentrations ranging from <0.05 to 19.5 µg/L.\textsuperscript{31}

Vanadium has not been regulated in most countries of the world. In the United States, it was listed in unregulated contaminant monitoring rule 3 (UCMR 3) and has been monitored by selected public water facilities.\textsuperscript{32} The proposed notification level by OEHHA in the United States is 15 µg/L in drinking water.\textsuperscript{33} Vanadium has been added to Contaminant Candidate List 4 (CCL4) and is subject to future regulation based on further hazard and risk assessment on vanadium.\textsuperscript{34} Public water facilities will face great challenges to comply with further regulations on vanadium.

\subsection*{1.2.3 Toxicity, Occurrence and Regulations of Nitrate}

Managing the nitrogen cycle is one of 14 grand challenges in 21\textsuperscript{st} century recognized by National Academy of Engineering of the United States.\textsuperscript{35} To increase the crop production, a large quantity of nitrogen fertilizer has been produced from industrial processes. The extensive utilization of nitrogen-containing fertilizer results in excess nitrogen in the soil. However, only 30-50\% of nitrogen is utilized by crops. Excess nitrogen
fertilizer in the soil undergoes biological nitrification process and is eventually converted into nitrate.

Nitrate is one major nutrient that causes the degradation of drinking water quality and prevalent eutrophication in surface waters. It has a very high solubility and mobility and low retention capability in the soil. It can easily leach from soil into groundwater or surface water through agriculture and urban run-off. Nitrate has been ubiquitously observed in shallow and recharged groundwater in regions with intensive agricultural activities.\textsuperscript{36} For instance, agricultural drainage in Minnesota contributes to approximately 40\% of nitrate contamination in the region’s surface water.\textsuperscript{37} Approximately 10\% of groundwater in California has nitrate concentration greater than 10 mg/L.\textsuperscript{38} The study conducted by United States Environmental Protection Agency (USEPA) found that the number of public water systems violating national drinking water standard for nitrate (10 mg-N/L) has been gradually increased from 1995 to 2002. Geographically, California, Texas, and Pennsylvania have the largest number of public water systems in nitrate violation because of their extensive agriculture activities. In addition, huge loading of nitrate from agriculture run-off, animal waste and human sewage lead to serve algal blooms and expanded dead zones in the Gulf of Mexico. The elevated nitrate level in drinking water can cause infant methemoglobinemia and gastric cancer in humans.\textsuperscript{39}

1.3 Existing Treatment Technologies and Challenges

Common treatment approaches for Cr(VI) utilize chemical reduction reactions with subsequent filtration of a solid phase.\textsuperscript{40,41} Cr(VI) is reduced to Cr(III) by reducing reagents (e.g., zero-valent iron, ferrous salt and sulfur-containing chemicals) followed by
subsequent precipitation of Cr(OH)$_3$ solids at circumneutral pH.$^{42-44}$ After coagulation and filtration, Cr(VI) level in the treated water is highly reduced and the generated hazardous waste sludge required further disposal. Ion exchange has also been widely used for Cr(VI) removal given its operational simplicity, low cost and effectiveness.$^{45, 46}$ Under typical drinking water conditions, Cr(VI) mainly exists as CrO$_4^{2-}$. It can chelate with positively charged amine groups on the resin and kick out low-affinity anions (e.g., Cl$^-$) into water. The resin can be categorized into weakly and strongly basic anion exchange resins. Weakly basic resins, typically featuring primary, secondary or ternary amine groups, cannot maintain their positive charge at high pH due to deprotonation and are suitable for Cr(VI) removal at acidic pH.$^{47}$ Strongly basic resins, typically featuring quaternary amine groups, can maintain their positive charge across a wide pH range are effective to remove Cr(VI) from acidic to basic pH.$^{44}$ Ion-exchange approach can efficiently remove Cr(VI) from a continuous flow of water but require periodic regeneration of the saturated resins. Other treatment methods include electrochemical reduction and coagulation,$^{48, 49}$ adsorption,$^{50, 51}$ bioremediation,$^{52, 53}$ and reverse osmosis membrane.$^{54}$

The removal of vanadium (V) from water has been studied mainly with adsorption. The performances of different adsorbents, such as activated carbon,$^{55}$ metal hydroxide (e.g., FeOOH),$^{56}$ clay minerals (e.g., Bentonite),$^{57}$ biomass (e.g., pine sawdust, chitosan, and cellulose),$^{58-60}$ and industrial waste metal sludge,$^{61}$ have been investigated under various water chemical parameters (e.g., pH, temperature, initial vanadium concentration, etc.). Previous studies showed that the adsorption of vanadium(V) favored at moderate acidic pH under which the positively charged adsorbents adsorbed negatively charged
vanadium(V) species through electrostatic interaction. The adsorption behaviors mostly obeyed Langmuir isotherms. The maximum adsorption capacity of modified biomass-based adsorbents and ferric hydroxide was much higher than activated carbon and unmodified clay materials.\textsuperscript{55, 57, 58, 62} In addition, vanadium(V) can be removed biologically with aerobic and anaerobic microorganisms, including \textit{Shewanella oneidensis},\textsuperscript{63} \textit{Geobacter metallireducens},\textsuperscript{64} \textit{Acidithiobacillus ferrooxidans},\textsuperscript{65} etc. Recently, the removal of vanadium(V) by microbial fuel cells has attracted much attention because their capability to achieve energy production and contaminant removal simultaneously.\textsuperscript{66} Some bacteria can oxidize organic on anode and generate electrons for vanadium(V) reduction on the cathode. Other methods for V(V) removal include ion exchange,\textsuperscript{67, 68} membrane filtration,\textsuperscript{59} and chemical reduction.\textsuperscript{69, 70}

Nitrate has high solubility and stability in water, which makes it unfeasible to be treated by traditional coagulation and precipitation method. Ion exchange has been widely used for nitrate removal especially in groundwater. In this process, nitrate exchanges with chloride or bicarbonate ions until the resin is exhausted. Concentrated sodium chloride or sodium bicarbonate is used to regenerate the exhausted resins, which produces a large quantity of brine waste required additional disposal.\textsuperscript{39} Biological denitrification has been commonly used to remove nitrate from wastewater.\textsuperscript{71, 72} Under anaerobic condition, denitrifies can utilize the organics as electron donors to transform nitrate into nitrogen gas. Other treatment methods include zero-valent iron reduction,\textsuperscript{73, 74} catalytic hydrogenation,\textsuperscript{75, 76} and electrochemical reduction,\textsuperscript{77, 78}
In recent years, TiO$_2$ has been widely used as the photocatalysts to remove contaminants in water because of its high stability, low toxicity, and good optical properties. TiO$_2$ can be excited by photons with energy equal or greater than its bandgap and generated holes and electrons to induce redox reactions on TiO$_2$ surface. Holes can directly oxidize surface-adsorbed contaminants or indirectly decompose them through hydroxyl radicals (HO·).$^{79,80}$ Electrons can be utilized to reduce contaminants in the water. But this process is much less efficient than hole- / HO· - induced oxidation because of the slow interfacial electron transfer and fast electron-holes recombination.$^{81}$ To increase the availability of electrons and make TiO$_2$ more photo-reductive, prior studies utilize hole scavengers (e.g., oxalic acid, formic acid, methanol, etc) to inhibit the recombination rate of holes and electrons.$^{82-84}$ Scavengers sacrificially react with the holes and highly extend the longevity of electrons on TiO$_2$ surface under UV irradiation. This principle has been applied to photocatalytic reduction of Cr(VI), nitrate, Se(VI), and vanadium (V).$^{82-85}$ The addition of excess hole scavengers is usually required to achieve an satisfactory reduction efficiency given that interfacial hole transfer is slower than hole-electron recombination.$^{81}$

The existing treatment methods for Cr(VI), vanadium(V), and nitrate can be categorized into nondestructive physical removal and redox-based transformation. Although functional, they suffer from some drawbacks. Physical removal transfers contaminants from one phase to another. The media with accumulated contaminants (e.g., spent adsorbents and exhausted resins) and the concentrated waste streams require additional handling and disposal. Reduction-based transformation via chemical, electrochemical, photochemical, and biological approaches is a viable and more
sustainable strategy than physical removal because toxic contaminants are destructively reduced to low toxic and environmental benign products. Even so, this strategy confronts various challenges. For instance, chemical reduction of Cr(VI) and vanadium(V) generates a large quantity of hazardous waste sludge. Catalytic hydrogenation reduction of nitrate requires expensive bimetallic catalysts and flammable hydrogen gas as electron donor. Electrochemical reduction suffers from limited process capacity because of the geometry of the electrode and mass transfer. Photocatalytic reduction requires the addition of excess organic chemicals to scavenge the holes, which can cause secondary pollution. Biological reduction is susceptible to water chemical conditions and suffers from slow removal kinetics. Given these limitations, the development of innovative redox-based treatment processes with high efficiency, robustness, and sustainability are urgent to address the increasing water pollution associated with Cr(VI), vanadium(V), and nitrate.

1.4 Emerging Technologies and Sustainable Water Management

Increasing water pollution, deficiency of the existing technologies, and regulatory mandates stimulate technological innovation and sustainable water management to provide human beings with reliable and inexpensive access to clean water. Advanced materials and innovative physiochemical processes offer new opportunities and emerging solutions to enhance water security, extend water availability, reduce the footprint of treatment processes, and secure a healthy ecological system. Nanotechnology has been recognized with promising potentials to enhance the existing and next-generation of water treatment processes. Engineered nanomaterials have been demonstrated with exceptional catalytic, optical, adsorptive, electrical, antimicrobial, and quantum properties. For instance,
engineered nano-photocatalysts can increase the utilization efficiency of reactive intermediates (e.g., \(\text{HO}^\cdot\)) for contaminants removal and pathogen deactivation by selectively adsorbing them on catalytic sites.\(^{88-90}\) Carbon-nanotube layers deposited on membrane surface with applied electrical energy can effectively prevent membrane fouling and transform organic and inorganic contaminants.\(^{91-93}\) Nanostructured adsorbents can selectively adsorb target contaminants and possess in-situ regeneration capability without the aid of external chemicals.\(^{94,95}\) In addition, innovative physiochemical processes with a fit-for-purpose feature have great application potentials for contaminant removal, desalination, resource and energy recovery.\(^{96-99}\) For instance, a system with cathodic generation of \(\text{H}_2\text{O}_2\) with subsequent UV photolysis is capable to remove trace organic contaminants from local water resources.\(^{96}\) Electrochemical stripping with ion-selective and gas-diffusion membranes can recover nitrogen from source-separated urine.\(^{97}\)

Centralized urban water infrastructures are confronting great challenges to meet increasing water demand and quality requirements given climate change, population growth, socio-economic development, etc.\(^{100}\) To enhance water security, decentralized water treatment and reuse paradigms haven been proposed to increase the infrastructure resilience by integrating with centralized systems or operating independently.\(^{94}\) They can treat and reuse local water resources at locations closer to user, which reduces the energy consumption to long-distance water transportation. Nanotechnology and innovative physiochemical processes can be integrated into decentralized water treatment and reuse facilities to remove prioritized contaminants from diverse water matrices. Technological innovation with sustainable water management can ensure safe and resilient water supply.
1.5 Motivation, Aim and Scope

The motivation of this doctoral research originates from the increasing water contamination associate with Cr(VI), vanadium(V), and nitrate, challenges confronted by the existing treatment technologies, and more stringent regulatory standards promulgated in future. The overarching goal of this research is to design novel redox-based treatment processes for Cr(VI) and nitrate and fundamentally understand the redox chemistry of vanadium(V) under different water chemical conditions.

We focus on redox-based treatment approaches because they can transform Cr(VI) and nitrate into environmental benign products (i.e., Cr(OH)$_3$ and N$_2$), avoid waste accumulation, and balance the ecological cycle. With the advancement of nanotechnology, we aim to design novel photocatalysts with engineered surface chemistry to efficiently remove Cr(VI) in different water matrices. Compared with Cr(VI), nitrate has unique photochemistry. It can generate reactive radicals and induce redox reactions. Based on radical chemistry of nitrate, we aim to develop novel photochemical denitrification process to remove nitrate from water and reduce its accumulation in aquatic systems.

Vanadium(V) has been placed on Contaminant Candidate List 4 but has not been regulated in drinking water. Compared with Cr(VI) and nitrate, vanadium(V) has more complicated speciation and redox chemistry. The structure-property relationship of vanadium(V) species and their reduction products remains largely unknown under environment-relevant conditions. Given the existing knowledge gap on vanadium, we aim to utilize advanced electrochemical systems and fundamental electrochemical principles and theories to investigate the redox chemistry of vanadium(V) species and their
transformation products. The acquired knowledge aims to help public water utilities to design efficient treatment process for vanadium(V) and provide helpful insight on the transport and fate of vanadium(V) in geological system and its toxicity in biological systems.

1.6 Research Hypothesis and Objectives

To address the overall goal of this doctoral research, we proposed the following hypotheses and developed the specific research objectives in Chapters 2-4.

**Hypothesis 1: TiO$_2$ nanocrystals with covalently-bonded organic ligands on the surface are highly photo-reductive and can efficiently reduce Cr(VI) to Cr(III) under various water chemical conditions.**

Prior studies have demonstrated that polyol molecules can covalently bond with undercoordinated Ti atoms on TiO$_2$ surface via their hydroxyl oxygen atoms, induce the occupied energy state inside the TiO$_2$ band gap, and highly improve the hole trapping efficiency compared with polyol molecules that physically adsorbed on TiO$_2$ surface.$^{101}$ It is hypothesized that the synthesized TiO$_2$ nanocrystals with surface-bonded polyols can highly increase electron-releasing capacity, and effectively reduce Cr(VI) to Cr(III) under different water chemical conditions.
Objective 1: Synthesize highly reductive TiO\textsubscript{2} photocatalyst and demonstrate its superior performance for Cr(VI) reduction under different water chemical conditions.

We addressed Objective 1 in Chapter 2. Specially, we synthesized highly reductive TiO\textsubscript{2} nanocrystals through thermal hydrolysis of TiCl\textsubscript{4} in diethylene glycol (DEG). We characterized the composition, morphology, and surface properties of the synthesized TiO\textsubscript{2} photocatalyst and examined its enhanced hole-scavenging effect. In addition, we optimized synthesis parameters and examined the reaction kinetics of the synthesized TiO\textsubscript{2} photocatalyst for Cr(VI) reduction under different water chemical conditions, compared with that of standard TiO\textsubscript{2} photocatalyst (i.e., Degussa P25 TiO\textsubscript{2}). Furthermore, we monitored the surface evolution of the catalyst during the reaction and characterized the reduction products of Cr(VI). Finally, we assess the cycling performance of the synthesized TiO\textsubscript{2} photocatalyst and its application potential of in Cr(VI)-contaminated groundwater.

Hypothesis 2: Reactive radical species generated from nitrate photolysis can partially oxidize formate into high reductive radical species that drive subsequent photochemical denitrification under different water chemical conditions.

Nitrate photolysis can generate oxidative radical species (e.g., HO\textsuperscript{•}). The presence of formate during nitrate photolysis can scavenge oxidative radicals and generate highly reductive formate radicals (CO\textsubscript{2}\textsuperscript{•−}). CO\textsubscript{2}\textsuperscript{•−} is highly reductively and its potential role to drive denitrification has been suggested in TiO\textsubscript{2}-based photocatalytic nitrate reduction.\textsuperscript{102} It is
hypothesized that synergistic effect between nitrate photolysis and \( \text{CO}_2^- \)-induced reduction of nitrogen intermediates can transform nitrate into gas-nitrogen products.

**Objective 2:** Investigate the denitrification process during nitrate photolysis in the presence of formate and demonstrate its application potential for nitrate removal under different water chemical conditions.

We addressed Objective 2 in Chapter 3. Specifically, we combined the unique photochemistry of nitrate and reductive properties of formate radicals (\( \text{CO}_2^- \)) to drive denitrification process during nitrate photolysis in the presence of formate. We conducted kinetic modeling to understand the reaction mechanism and recognize the major reaction pathways that control denitrification kinetics and selectivity. In addition, we investigated the effect of water chemical parameters (e.g., pH and dissolved organic matter) on denitrification performance. Finally, we assessed the application potentials of the proposed process in nitrate-contaminated groundwater.

**Hypothesis 3:** The speciation of vanadium (V) and its complexation with phosphate impact the redox chemistry of vanadium (V) and its transformation product

Under different aquatic conditions, vanadium (V) can exist as mono, di, tetra, decavanadate, etc. It also forms aquatic complexes with phosphate. Different vanadium(V) species have quite different sizes, structures, and coordination environment for vanadium atoms. It was hypothesized that reduction kinetics of vanadium(V) and the stability of its transformation productions were associated with the speciation of vanadium (V).
Objective 3: Understand the reduction kinetics of vanadium (V) and its transformation products with electrochemical techniques.

We addressed Objective 3 in Chapter 4. Specifically, we applied fundamental electrochemical principles and rotating ring-disk electrochemical techniques to investigate the intrinsic electron-transfer kinetics of $\text{VO}_2^+$, $\text{Na}_x\text{H}_y\text{V}_{10}\text{O}_{28}^{(6-x-y)-}$, $\text{H}_x\text{V}_4\text{O}_{12+x}^{(4+x)-}$, and $\text{HVO}_4^{2-}$ and the stability of their reduction products. Furthermore, we calculated the electron-transfer numbers of different vanadium (V) species and inferred their reaction equations. In addition, we investigated the effect of phosphate complexation on the reduction kinetics of vanadium (V) species and the stability of their reduction products.

Hypothesis 4: Cr(VI) and nitrate in the spent ion-exchange regenerant brine can be removed concurrently with photochemistry of nitrate and reductive carbon-centered radical species.

Nitrate and Cr(VI) coexist in the spent ion-exchange regenerant brine. Reactive radicals produced from nitrate under UV irradiation can be utilized to generate reductive carbon-centered radicals from formate and alcohols via hydrogen abstraction. It is hypothesized that Cr(VI) and nitrate can be removed concurrently with the aid of nitrate photolysis combing with the resulted reductive carbon-centered radicals in the presence of formate and alcohols.
Objective 4: Investigate photochemical reduction of Cr(VI) and nitrate in the spent ion-exchange brine by carbon-centered radicals.

We addressed Objective 4 in Chapter 5. Specifically, we assessed the reduction performance of carbon-centered radicals derived from formate and alcohols on Cr(VI) in the spent ion-exchange brine. With the optimal radical, we further investigate the impact of organic dosage, pH, ionic strength, and the coexisting constituents on photochemical reduction of Cr(VI). In addition, we assessed the co-removal of Cr(VI) and nitrate in the spent brine.
References


34. Contaminant Candidate List (CCL) and Regulatory Determination, Chemical Contaminants - CCL 4: https://www.epa.gov/ccl/chemical-contaminants-ccl-4.


38. Quality, S. W. R. C. B. D. o. W., GROUNDWATER INFORMATION SHEET. 2010


66. Zhang, B.; Feng, C.; Ni, J.; Zhang, J.; Huang, W., Simultaneous reduction of vanadium (V) and chromium (VI) with enhanced energy recovery based on microbial fuel cell technology. J. Power Sources 2012, 204, 34-39.


Chapter 2

Photocatalytic Removal of Hexavalent Chromium by Newly Designed and Highly Reductive TiO$_2$ Nanocrystals

Previously Published in *Water Research*

2.1 Abstract

Hexavalent chromium Cr(VI), a highly toxic oxyanion, widely occurs in drinking water supplies. This study designed and synthesized a new type of highly reductive TiO$_2$ nanocrystals for photochemical Cr(VI) removal, via the thermal hydrolysis of TiCl$_4$ in the presence of diethylene glycol (DEG). Surface analyses and hydroxyl radical measurements suggested that DEG was chemically bonded on TiO$_2$ surface that resulted in an internal hole-scavenging effect and a high electron-releasing capacity, making it advantageous to conventional TiO$_2$ materials. Upon UV irradiation, the synthesized TiO$_2$ photocatalyst exhibited fast Cr(VI) reduction kinetics in diverse water chemical conditions. Fast elimination of Cr(VI) was achieved on a time scale of seconds in drinking water matrices. The removal of Cr(VI) by reductive TiO$_2$ exhibited a three-stage kinetic behavior: an initial fast-reaction phase, a lag phase resulting from surface precipitation of Cr(OH)$_3$(s), and a final reaction phase due to surface regeneration from oxidation-reduction induced ripening process. The lag phase disappeared in acidic conditions that prevented the formation of Cr(OH)$_3$(s). The catalyst exhibited extremely high electron-releasing capacity that can be reused for multiple cycles of Cr(VI) removal in drinking water treatment.
2.2 Introduction

Hexavalent chromium Cr(VI), typically existing as the oxyanion CrO$_4^{2-}$, is one emerging contaminant due to the concerns on its occurrence, toxicity and regulatory perspective 1-3. In contrast, trivalent chromium Cr(III), which exists as different Cr(III) solids (e.g., chromium hydroxide Cr(OH)$_3(s)$) in neutral pH ranges, is less toxic and considered as an essential element at trace levels 3-5. There are different treatment options to remove Cr(VI) in drinking water. Physical removal approaches including adsorption, ion exchange, or membrane separation can suffer from limited adsorption capacity, low selectivity, slow kinetics and additional waste disposal issues 6-14. Available reductive Cr(VI) treatment approaches include Fe(II)-assisted coagulation and electrochemical, biological and photocatalytic reductions, during which soluble Cr(VI) is reduced to non-toxic Cr(III) solids with subsequent particle removal 15-24. Although functional, these methods have limitations on residual handling, capacity and kinetics 25, 26.

In recent years, the application of TiO$_2$ photocatalyst for Cr(VI) removal has drew some attention 2, 3, 23. In particular, P25, a commercialized TiO$_2$ material, has been applied due to its mixed anatase and rutile phases, which facilitates the hole-electron separation and suppresses charge carrier recombination upon UV irradiation 27-30. However, the interfacial electron transfer process is several orders of magnitude slower than the electron-hole recombination in commercialized TiO$_2$ materials 31. Consequently, electrons become less available for reductive water treatment. To make TiO$_2$ more effective in releasing electrons, prior studies added organic chemicals (e.g., oxalic acid, methanol and formic acid) or inorganic ions (e.g., S$^{2-}$, I$^-$ and IO$_3^-$) as external hole scavengers to TiO$_2$ suspension
and sacrificially consumed the holes generated from the valence band of TiO$_2$. As a result of the scavenging effect, electron-hole recombination is suppressed and more electrons are freely released from TiO$_2$ to reductively remove contaminants, including nitrate, chromate, selenate, bromate and perchlorate. However, because of inefficient hole trapping by external hole scavengers, an excess amount of sacrificial organic or inorganic compounds is required to achieve a high hole-scavenging efficiency. This leads to chemical residuals in treated water and make it undesirable for drinking water applications.

To increase the hole trapping efficiency and eliminate the external addition of sacrificial hole scavengers, the design of a catalyst with an internal hole-scavenging capacity is highly advantageous for reductive Cr(VI) treatment. Internal hole scavengers that are covalently bonded or chemisorbed on TiO$_2$ surface can highly enhance the hole transfer across the interface to the trapping molecules and produce long-lived electrons. Prior studies demonstrated that scavengers with poly-hydroxyl moieties covalently bonded on TiO$_2$ surface served as efficient internal hole traps upon photo-excitation of the catalyst, and the hole-scavenging efficiency was associated with hydroxyl groups chelated on TiO$_2$ surface. This novel design of TiO$_2$ catalyst with internal hole-scavenging capacity can highly inhibit electron-hole recombination process and preferentially release a large quantity of electrons for surface reduction. However, this designing concept for the TiO$_2$ catalyst has not been reported for photocatalytic Cr(VI) removal.

The objectives of this study were to synthesize a new TiO$_2$ photocatalyst that possesses a high internal hole-scavenging capacity, and apply it for reductive Cr(VI) removal in
diverse water chemical conditions. Diethylene glycol (DEG) was chosen as the internal hole scavenger, because it has hydroxyl groups that can chelate uncoordinated Ti atoms and be chemically bonded on TiO$_2$ surface. Covalently-bonded DEG molecules serve as hole-trapping molecules and favors fast scavenging of photogenerated holes upon photoexcitation of TiO$_2$. In addition, the mechanism and kinetics of Cr(VI) removal were investigated, with emphasis on the effects of catalyst dosage, pH and the presence of background ions.

2.3 Materials and Methods

2.3.1 Synthesis and Characterizations of TiO$_2$ Nanocrystals

All chemicals were analytical grade and used as received without further purification. All solutions were prepared with deionized (DI) water (18.2 MΩ/cm) produced from Milli-Q system (Millipore). TiO$_2$ nanocrystals were synthesized via the hydrolysis of TiCl$_4$ by injection of 0.2 mL of TiCl$_4$ into 20 mL of diethylene glycol (DEG) with 0.2 mL of H$_2$O. The mixture was heated at 220 °C for duration between 1.5 and 12 hours to generate TiO$_2$ nanocrystals with different degrees of crystallinity. Subsequently, acetone was added into the solution to precipitate out the TiO$_2$ nanocrystals. The suspension was then centrifuged at 8500 rpm for 5 minutes, washed with acetone and water for five times to obtain the purified synthesized TiO$_2$. For comparison, commercialized P25 TiO$_2$ (BET surface area 52 m$^2$/g) was purchased from Acros Organics.

The nanostructure of the synthesized catalyst was investigated using a Philips Tecnai T12 transmission electron microscope (TEM) at an accelerating voltage of 120 kV. Powder
X-ray diffraction (XRD) patterns were recorded on a PANalytical Empyrean diffractometer with Cu Kα radiation $\lambda = 1.5406$ Å and a graphite monochromator (40 kV, 40 mA). The Fourier transform infrared spectroscopy (FTIR) spectra were acquired on a Nicolet 6700 FTIR spectrometer. X-ray photoelectron spectroscopy (XPS) characterization was carried out on a Kratos AXIS ULTRADLD XPS system equipped with an Al Kα monochromated X-ray source and a 165-mm mean radius electron energy hemispherical analyzer.

### 2.3.2 Photocatalytic Cr(VI) removal experiments

Batch experiments of photocatalytic Cr(VI) removal were conducted in 10-mL quartz tubes under the irradiation of a 450-W UV immersion lamp (Ace Glass, Inc.). The lamp emitted photons with wavelengths ranging between 200 and 850 nm and has a UV intensity of 42 mW/cm$^2$ (Figure S2.1). The light source wavelength and intensity were measured by thermopile (Newport 818P-010-12) and charge-coupled device (Avantes AvaSpec-EDU), respectively. The UV fluence was calculated to represent the total energy input to photocatalytic system (Text S2.1 in the Appendix A). All quartz tubes were placed in a carousel that rotated around the UV lamp. Prior to UV experiments, the synthesized TiO$_2$ suspension was sonicated for 10 min, followed by the addition to a solution with Cr(VI) concentrations varying between 0.1 and 50 mg/L prepared from a K$_2$CrO$_4$ stock solution. The dosage of the synthesized TiO$_2$ photocatalyst ranged from 5 to 500 mg/L. The specific surface area of the synthesized TiO$_2$ nanocrystals is 156 m$^2$/g (Text S2.2 in Appendix A). The pH of Cr(VI) solutions was controlled at either 7.0 or 2.7 by adding phosphate buffer.
In some experiments, synthetic groundwater and tap water from Riverside, CA were used to simulate drinking water matrices (Table S2.1)\textsuperscript{40, 41}.

To start a UV reaction, the freshly prepared TiO\textsubscript{2}/Cr(VI) suspensions in quartz tubes were sonicated for 2 minutes and immediately placed in the UV reactor. At pre-determined sampling intervals, one sacrificial quartz tube was taken out from the UV reactor. The suspension was immediately filtered through a 0.22-μm Millipore syringe filter to analyze the Cr(VI) concentration in the filtrate. To evaluate the longevity of the catalyst, experiments were conducted with multiple cycles of Cr(VI) removal using the same suspension of 50 mg/L TiO\textsubscript{2}. At the beginning of the experiment, 20 mg/L of Cr(VI) was spiked to the TiO\textsubscript{2} suspension, and a sample was withdrawn and filtered every 15 minutes. At the end of one cycle, Cr(VI) concentration in the suspension was spiked back to 20 mg/L using a K\textsubscript{2}CrO\textsubscript{4} stock solution and its removal process was monitored again. This experiment continued for a total of 10 cycles. The solution pH was controlled at 2.7 with 0.2 M phosphate buffer prepared with 0.1 M H\textsubscript{3}PO\textsubscript{4} and 0.1 M NaH\textsubscript{2}PO\textsubscript{4}.

2.3.3 Analytical methods

The concentration of Cr(VI) was measured by the standard 1,5-diphenylcarbazide (DPC) method\textsuperscript{42}. For samples with Cr(VI) concentrations higher than 100 μg/L, direct measurement with a spectrophotometer (Horiba scientific, Inc.) was conducted. For samples with Cr(VI) concentrations less than 100 μg/L, ion chromatography measurement was conducted with a Dionex IonPac AS7 column (4×250 mm) and a multi-wavelength UV detector (Dionex ICS-1000). The signal was recorded at 530 nm with eluent (250 mM (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} and 100 mM NH\textsubscript{4}OH) and post-column reagent (2 mM DPC, 10% v/v CH\textsubscript{3}OH.
and 0.5 M H$_2$SO$_4$). Total chromium concentration was analyzed by Agilent 7700 Series Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

Particle sizes of the synthesized TiO$_2$ nanocrystals during Cr(VI) reduction reaction were monitored by single-particle ICP-MS. Particle size distribution of Cr(III) solids generated from Cr(VI) reduction was estimated by sequential filtration of treated samples. Details of the particle size analysis were provided as Texts S2.3-S2.4 in the Appendix A. Surface charges of TiO$_2$ were analyzed by a zeta potential analyzer (Beckman Coulter).

To compare the hole-scavenging capacity between synthesized TiO$_2$ and P25 TiO$_2$ during the UV irradiation, the hole-driven production of hydroxyl radical (HO’) from TiO$_2$ was assessed using terephthalic acid (TA) as a probe compound. An 8-mL suspension containing 60 µM TA, 7.8 m$^2$/L TiO$_2$ (50 mg/L synthesized TiO$_2$ nanocrystals or 150 mg/L P25 TiO$_2$) and 6 mM phosphate buffer was irradiated by UV. The oxidation product of TA by HO’, i.e., 2-hydroxyterephthalic acid, was monitored using a fluorometer (Horiba scientific, Inc) with an excitation wavelength at 315 nm and emission wavelength at 425 nm.

2.4 Results and Discussion

2.4.1 Characterization and optimization of TiO$_2$ nanocrystals

The synthesized TiO$_2$ nanocrystals were irregularly shaped, with sizes of approximately 5-10 nm (Figure 2.1A). XRD peaks showed that TiO$_2$ existed as the anatase phase (Figure 2.1B). The average domain size of TiO$_2$ nanocrystals was approximately 4 nm (Calculation shown as Text S2.5 in the Appendix A), which also agreed with the TEM
observation (Figure 2.1A). FTIR spectra showed that DEG was chemically bonded on the surface of TiO$_2$ (Figure 2.1C). Specifically, the FTIR absorption peaks at wavenumbers of 889, 1052, 1124, and 1352 cm$^{-1}$ corresponded to –OC$_2$H$_4$, -C-O stretching in COH, OH in-plane bending, and -CH$_2$ bending, respectively.$^{44}$ The peak for C-O stretching in COH shifts from 1052 to 1080 cm$^{-1}$, indicating the formation of C-O-Ti bond between DEG and Ti$^{4+}$ on the surface of synthesized TiO$_2$ nanocrystals $^{45,46}$.

The synthesis parameter of TiO$_2$ nanocrystals was optimized to achieve the optimal performance for Cr(VI) removal. The hydrolysis time was a key parameter because it impacted the number of DEG molecules that were chemically bonded on TiO$_2$ surface. Details on the optimization of synthesis parameter were provided in Text S2.6, Table S2.2, and Figure S2.2 in the Appendix A. The optimal hydrolysis time was determined as 3 hours.
Figure 2.1 The synthesized TiO$_2$ nanocrystals after heating TiCl$_4$ in diethylene glycol and H$_2$O for 3 hours. (A) TEM image; (B) XRD pattern; (C) FTIR spectra of diethylene glycol and TiO$_2$ nanocrystals.
2.4.2 Photocatalytic reduction of Cr(VI) by TiO$_2$

![Graph A](image)

![Graph B](image)

**Figure 2.2** The photocatalytic removal of Cr(VI) with its initial concentrations at (A) 100 µg/L and (B) 20 mg/L under UV irradiation by TiO$_2$ catalysts. pH = 7.0 with 6 mM phosphate buffer and TiO$_2$ surface area-based dosage = 7.8 m$^2$/L.
The synthesized TiO$_2$ nanocrystals were used for photocatalytic reduction of Cr(VI) and their performance was compared with the commercial grade P25 TiO$_2$. With an Cr(VI) concentration of 100 µg/L and a surface area-based TiO$_2$ dosage of 7.8 m$^2$/L, the synthesized TiO$_2$ nanocrystals exhibited a much higher Cr(VI) removal efficiency than P25, especially at the initial stage of the reaction (Figure 2.2A). For example, within 10 seconds of UV irradiation, 60% of Cr(VI) was removed by the synthesized TiO$_2$ nanocrystals, while only 10% removal was achieved by P25 TiO$_2$. Only 10 min was required to reduce Cr(VI) concentration to below 10 µg/L with the synthesized TiO$_2$. Adsorption control showed TiO$_2$ particles had negligible effect on Cr(VI) adsorption (Figure 2.2), mainly due to the electrostatic repulsion between Cr(VI) and the catalyst surface, as evidenced by the negative zeta potential of TiO$_2$ nanoparticles at neutral pH ranges (Figure S2.3). Control experiments showed that Cr(VI) was not removed by direct photolysis (Figure 2.2). With an initial Cr(VI) concentration of 20 mg/L, a nearly complete removal was achieved after 120 minutes of UV irradiation with the synthesized TiO$_2$, while only 12% of Cr(VI) was removed with P25 TiO$_2$ (Figure 2.2B). The synthesized TiO$_2$ also exhibited a much higher treatment efficiency than P25 TiO$_2$ with 1 and 50 mg/L of initial Cr(VI) (Figure S2.4).

2.4.3 Identification of internal hole-scavenging capacity

The highly reductive nature of the synthesized TiO$_2$ resulted from its intrinsic hole-scavenging capacity. The chemically-bonded DEG on the TiO$_2$ surface can trap photogenerated holes more efficiently. DEG has two hydroxyl groups and it is connected to the synthesized TiO$_2$ surface by the Ti-O-C chemical bond. The characteristic time of
hole-scavenging (<100 fs) by chemically-bonded polyhydroxyl moieties is much shorter than that of hole-electron recombination (10-20 ps) \(^{38, 47}\). Therefore, the hole-electron recombination process is inhibited and more electrons can be released for Cr(VI) reduction. The internal hole-scavenging capacity of the synthesized TiO\(_2\) nanocrystals was confirmed using terephthalic acid (TA) to trap HO\(^-\) which was produced from hole-induced oxidation of water molecule \(^{48}\). The synthesized TiO\(_2\) produced 0.2 µM HO\(^-\) after 90 seconds of UV irradiation, while P25 TiO\(_2\) produced 2.7 µM HO\(^-\) with the same duration of reaction (Figure 2.3). This confirmed that the synthesized TiO\(_2\) possessed a much higher hole-scavenging capacity than P25 TiO\(_2\).

**Figure 2.3** Cumulative HO\(^-\) radical production in the presence of the synthesized TiO\(_2\) nanocrystals and P25 TiO\(_2\) under UV irradiation. TiO\(_2\) surface area-based dosage = 7.8 m\(^2\)/L, TA concentration = 10 mg/L, and pH = 7 with 6 mM phosphate buffer.
2.4.4 Kinetics of photocatalytic Cr(VI) removal by TiO₂

**Figure 2.4** The effect of catalyst dosage on photocatalytic reduction of Cr(VI) over the synthesized TiO₂ nanocrystals under UV irradiation. Initial [Cr(VI)] = 20 mg/L, pH = 7 with 6 mM phosphate buffer.

An increase of catalyst dosage enhanced Cr(VI) removal efficiency (Figure 2.4). With an initial Cr(VI) concentration of 20 mg/L, Cr(VI) removal kinetics exhibited three distinct phases: an initial fast-reaction phase, a lag phase and a final decay phase (Figure 2.4). For example, with 50 mg/L of TiO₂, Cr(VI) concentration decreased fast by 12% within 4 minutes of reaction, changed slowly during the next 20 minutes, and further decreased until a complete removal. When the catalyst dosage increased from 50 to 500 mg/L, the duration of the lag phase was shortened and eventually eliminated. The reaction time required to achieve 95% of Cr(VI) removal decreased from 120 to 8 minutes (Figure 2.4). Similar trends were also observed for 0.1, 1 and 50 mg/L of Cr(VI) (Figure S2.5).
A second-order kinetic model was developed to describe reductive Cr(VI) by TiO$_2$ at the early stage of reaction:

$$\frac{d[Cr(VI)]}{dt} = -k_{Cr(VI)}[TiO_2][Cr(VI)](S_{TiO_2})$$

(1)

Where $k_{Cr(VI)}$ is the surface area-normalized rate constant of Cr(VI) reduction (L·m$^{-2}$·min$^{-1}$). $[TiO_2]$ is the dosage of TiO$_2$ (g/L), $[Cr(VI)]$ is the concentration of Cr(VI) (mg/L), and $S_{TiO_2}$ is the surface area of TiO$_2$ catalyst (m$^2$/g).

The synthesized TiO$_2$ nanocrystals exhibited a much higher $k_{Cr(VI)}$ than P25 TiO$_2$ (Figure S2.6). As Cr(VI) concentration increased from 0.1 to 1 mg/L, $k_{Cr(VI)}$ of the synthesized TiO$_2$ nanocrystals increased by 220% from 0.29 to 0.93 L·m$^{-2}$·min$^{-1}$. This was caused by an increase of collision frequency between Cr(VI) and catalyst surface which increased the probability of Cr(VI) to grab electrons from the surface. However, a further increase of Cr(VI) from 1 to 50 mg/L led to a significant drop of $k_{Cr(VI)}$ from 0.93 to 0.014 L·m$^{-2}$·min$^{-1}$ which was caused by fast surface passivation from Cr(OH)$_3$(s). It has been discussed in details in section 3.5.

2.4.5 Identification of Cr(VI)/TiO$_2$ Surface Reduction Mechanism

The three-phase kinetic behavior resulted from the deposition of Cr(OH)$_3$(s) solids on the TiO$_2$ surface. At the neutral pH, the predominant species of Cr(III) solids formed on the catalyst surface was Cr(OH)$_3$(s), according to Cr(III) speciation at different pHs (Figure S2.7). The green solids generated during the reaction (Figure S2.8) was also consistent with the visual appearance of Cr(OH)$_3$(s) $^{49}$. At a low catalyst dosage, the precipitated
Cr(OH)$_3(s)$ quickly blocked the active sites of the catalyst surface that would otherwise be available for Cr(VI) reduction. As a result, an extended lag phase was observed after the initial rapid reduction (Figure 2.2B and Figure 2.4). During the lag phase, Cr(OH)$_3(s)$ was oxidized to Cr(VI) by photogenerated holes, but the formed Cr(VI) was quickly converted back to Cr(OH)$_3(s)$ again by photogenerated electrons. This reaction sequence induced a ripening process on TiO$_2$ surface, in which smaller Cr(OH)$_3(s)$ particles were oxidatively dissolved followed by a reductive re-deposition onto larger Cr(OH)$_3(s)$, leading to the regeneration of some reactive TiO$_2$ surface and the subsequent recovery of its reactivity. Consequently, a final decay phase took place. When the TiO$_2$ dosage was considerably high, the active surface sites were not completely blocked by Cr(OH)$_3(s)$ precipitation, and the lag phase was shortened or eliminated (Figure 2.2B and Figure 2.4).

The growth of Cr(OH)$_3(s)$ in the surface ripening process was further confirmed by the changes of particle sizes over time. The fraction of Cr(OH)$_3(s)$ with larger particle sizes increased gradually with reaction time (Figures S2.9-S2.10). At the initial reaction stage (0.2 minutes of reaction), 46% of the Cr(OH)$_3(s)$ had particle sizes less than 25 nm. This fraction decreased to 10% after 30 minutes of reaction. In contrast, the fraction of Cr(OH)$_3(s)$ solid with sizes between 25 and 220 nm increased from 37% to 64% from 0.2 to 30 minutes. Particles with sizes larger than 220 nm increased from 18% to 25% with the same duration of reaction. Therefore, Cr(OH)$_3(s)$ particles grew with the reaction time. To further confirm the effect of Cr(OH)$_3(s)$ passivation on the reactivity of TiO$_2$ nanocrystals, additional experiments were performed at the acidic pH of 2.7, at which Cr(III) existed as
the dissolved ion Cr$^{3+}$. Cr(VI) removal kinetics was much faster at pH of 2.7 than that at 7.0, and the lag phase completely disappeared at pH 2.7 (Figures S2.11- S2.12).

Figure 2.5 FTIR spectra of TiO$_2$ nanocrystals separated from reaction suspensions during Cr(VI) reduction process. Initial [Cr(VI)] = 20 mg/L, TiO$_2$ dosage = 50 mg/L, and pH = 7 with 6 mM phosphate buffer.

FTIR spectra of TiO$_2$ at different reaction times exhibited dramatic changes that were indicative of surface phenomena (Figure 2.5). At time zero, the absorption peaks at 889, 1124 and 1352 cm$^{-1}$ corresponded to –OC$_2$H$_4$ stretching, –C-O stretching and –CH$_2$ bending, which were characteristic of DEG molecules. The peak at 1080 cm$^{-1}$ corresponded to the –C-O-Ti stretching, characteristic of the chemical bonding between DEG and Ti atoms. As the reaction time increased to 120 minutes, the characteristic peaks of DEG and its bonding with TiO$_2$ were still persistent, indicating that DEG was strongly bonded on the catalyst surface as an internal hole scavenger. The broad absorption band between 1700 and 1900 cm$^{-1}$ increasing with reaction time suggested the generation of –C=O groups that
resulted from the oxidation of hydroxyl groups in DEG by photo-generated holes. In addition, the intensity increase of the broad bands at 950-1050 cm\(^{-1}\) with reaction time corresponded to Cr-OH stretching, suggesting the formation of Cr species on the TiO\(_2\) surfaces.\(^{50}\)

XPS spectra identified the oxidation states of Cr species generated on catalyst surface over time (Figure 2.6). At time zero, characteristic peaks from O 1s, Ti 2s, Ti 2p and C 1s orbits were observed. They agreed with the composition of the synthesized TiO\(_2\) nanocrystals. Meanwhile, typical peaks of Cr from its 2p orbit appeared with increasing reaction time, indicating the formation of Cr species on the catalyst surface (Figure 2.6A). After 2 minutes of reaction, the doublet peaks at ~577 and ~586 eV attributed to Cr(III) 2p\(_{1/2}\) and Cr 2p\(_{3/2}\) levels resulted from Cr 2p spin-orbit splitting (Figure 2.6B). The peaks centered at ~580 and ~589 eV corresponded to the binding energies of Cr(VI) 2p\(_{3/2}\) and Cr(VI) 2p\(_{1/2}\), respectively.\(^{51}\) Weak signals from Cr(VI) at 2 minutes probably resulted from Cr(VI) adsorbed on TiO\(_2\) surfaces. After 20 minutes of reaction, peaks from surface-adsorbed Cr(VI) disappeared and only doublet from Cr(III) 2p\(_{3/2}\) and Cr(III) 2p\(_{1/2}\) was present (Figure 2.6C). After 120 minutes of reaction, the doublet peaks from Cr(III) 2p\(_{3/2}\) and Cr(III) 2p\(_{1/2}\) became stronger, indicating more Cr(III) deposited on the surface (Figure 2.6D). The Cr(III)-to-Ti molar ratio on TiO\(_2\) surfaces, estimated on the basis of XPS spectra, showed a dramatic increase from 0 to 0.23 during the fast-reaction phase (0 to 2 minutes), then slightly increased to 0.25 during the lag phase (2 to 20 minutes), and finally increased to 0.46 at the end of the decay phase (120 minutes). The evolution of XPS
spectra from 2 to 120 minutes indicated the consumption of Cr(VI) and generation of Cr(III) on the catalyst surface.

**Figure 2.6** Full scan (A) and Cr 2p (B-D) XPS spectra of the synthesized TiO$_2$ nanocrystals separated from reaction suspensions during Cr(VI) reduction process. Initial [Cr(VI)] = 20 mg/L, TiO$_2$ dosage = 50 mg/L, pH = 7 with 6 mM phosphate buffer.
Furthermore, the surface charges of TiO$_2$ nanocrystals became increasingly negative during the initial fast-reaction stage because of the precipitation of negatively charged Cr(OH)$_3$(s) on TiO$_2$ surface (Figures S2.13-S2.14). Following that, it became less negative due to the decrease of surface coverage of Cr(OH)$_3$(s) impacted by the ripening process. The zeta potential of TiO$_2$ nanocrystals eventually stabilized at approximately -50 mV because of the combined effect from Cr(OH)$_3$(s) precipitation and surface regeneration through ripening process. Single particle ICP-MS analysis also showed that the particles size of TiO$_2$ nanocrystals during the UV reaction was constantly between 10 and 20 nm, suggesting no strong aggregation of TiO$_2$ nanocrystals in the Cr(VI) solution (Figure S2.15).

2.4.6 Assessment of application potentials

![Graph](image.png)

**Figure 2.7** Multiple-cycle performance of the synthesized TiO2 nanocrystals for the photocatalytic reduction of Cr(VI) under UV irradiation. Initial [Cr(VI)] = 20 mg/L, TiO$_2$ dosage = 50 mg/L and pH = 2.7 with 0.2 M phosphate buffer.
Longevity and reductive performance in actual water matrices are assessed for the application potentials of TiO₂ nanocrystals. To examine the longevity and stability, the synthesized TiO₂ nanocrystals were evaluated for multiple cycles of Cr(VI) treatment. Cr(VI) removal efficiency was higher than 95% during the first three cycles, and remained at nearly 80% in subsequent cycles (Figure 2.7). To quantify electron released from the synthesized TiO₂, the electron capacity (mole e⁻/g TiO₂) in each cycle was calculated (Text S2.7 and Figure S2.16). The total electron capacity for 10 cycles was 0.187 mol/g, indicating that the synthesized TiO₂ nanocrystals have a large electron-releasing capacity for Cr(VI) reduction. The modest decrease of electron capacity after 3 cycles was likely associated with the consumption of surface-bonded DEG on TiO₂ nanocrystals in the hole scavenging process.

The solution chemical conditions could affect the Cr(VI) removal efficiency by synthesized TiO₂. Cr(VI) removal kinetics was faster in synthetic groundwater or tap water matrice than in DI water (Figure S2.17). It is likely that the presence of anions, cations or natural organic matter in both groundwater and tap water acted as additional hole-scavengers, which improved electron releasing capacity of TiO₂ for reductive Cr(VI) removal. Assessment of longevity and water matrice impact demonstrated that the synthesized TiO₂ was robust to treat Cr(VI) in diverse water matrices.

2.5 Conclusions

The newly synthesized TiO₂ catalyst was advantageous to traditional TiO₂ materials, because it possessed a strong internal hole-scavenging capacity achieved by chemically-bonded DEG with a cost-effective and low-temperature thermal hydrolysis synthesis. The
synthesized catalyst worked efficiently in diverse water chemical matrices and possessed a good longevity for multiple use. Surface-deposited Cr(OH)$_{3(s)}$ caused multi-phasic Cr(VI) reduction kinetics. High catalyst dosage or acid pH highly improved Cr(VI) reduction efficiency. To design a photocatalytic Cr(VI) treatment unit, the synthesized TiO$_2$ can be immobilized on a surface under UV irradiation in a flow-through photochemical reactor, or suspended in a completely-mixed reactor. Future work will examine the separation of TiO$_2$, *e.g.*, by making the synthesized TiO$_2$ catalyst magnetic and separating it by a magnetic field.

### 2.6 Acknowledgement

The study was supported by UC Riverside Faculty Initiation Fund, and collaborative seed grants from UC Riverside Research and Economic Development Office and Center for Catalysis. We thank our undergraduate group member Priscila Coelho for her participation in this project.
References


Chapter 3

Nitrate Removal via a Formate Radical-induced Photochemical Process

Previously Published in Environmental Science and Technology

3.1 Abstract

Removal of excess nitrate is critical to balance the nitrogen cycle in aquatic systems. This study investigated a novel denitrification process by tailoring photochemistry of nitrate with formate. Under UV light irradiation, short-lived radicals (i.e., HO·, NO2· and CO3·-) generated from nitrate photolysis partially oxidized formate to highly reductive formate radical (CO2·). CO2· further reduced nitrogen intermediates generated during photochemical denitrification (mainly NO·, HNO, and N2O) to gas-phase nitrogen (i.e., N2O and N2). The degradation kinetics of total dissolved nitrogen was mainly controlled by the photolysis rates of nitrate and nitrite. The distribution of final products was controlled by the reaction between CO2·- and N2O. To achieve a simultaneous and complete removal of dissolved nitrogen (i.e., nitrate, nitrite, and ammonia) and organic carbon, the formate-to-nitrate stoichiometry was determined as 3.1 ± 0.2 at neutral pH in deionized water. Solution pH impacted the removal rates of nitrate and nitrite, but not that of total dissolved nitrogen or formate. The presence of dissolved organic matter at levels similar to groundwater had a negligible impact on the photochemical denitrification process. A high denitrification efficiency was also achieved in a synthetic groundwater matrix. Outcome from this study provides a potential denitrification technology for decentralized water treatment and reuse facilities to abate nitrate in local water resources.
3.2 Introduction

Managing the global nitrogen cycle is one grand challenge in the 21st century identified by the U.S. National Academy of Engineering.1 Extensive utilization of nitrogen fertilizers elevates nitrate (NO$_3^-$) levels in natural waters, causing eutrophication and posing great public health risks.2-4 U.S. EPA established a maximum contaminant level (MCL) of nitrate in drinking water at 10 mg-N/L. Approximately 95% of public water systems that violate nitrate MCL use groundwater as the drinking water source.4 Nitrate concentrations in national groundwater and drinking wells increased across the United States from 1988 to 2012, indicating a persistent nitrate contamination issue in groundwater.5, 6

Ion exchange is commonly used to remove nitrate from groundwater, however, resin regeneration produces concentrated brine waste that requires costly disposal. Reductive transformation nitrate to nitrogen gas (N$_2$), also known as denitrification, is another approach to remove nitrate from groundwater. For example, biological denitrification, catalytic hydrogenation, photocatalytic and electrochemical reduction can convert nitrate to gas-phase nitrogen.7-12 Biological processes rely on specific enzymes in microbes to facilitate sequential electron-transfer.13 Catalytic hydrogenation, photocatalytic and electrochemical reduction require active sites on catalysts to effectively bind and selectively transform nitrate to gas-phase nitrogen.10-12 Although functional, these technologies have not been widely used in drinking water treatment because of high operational complexity, additional handling for biomass and dissolve organics, inadequate selectivity toward nitrogen gas, strong inhibition effects from competitive species, and mass-transfer limitation from bulk to the electrode surface.14-16
Photochemical denitrification provides a promising alternative for nitrate removal. The unique photochemistry of nitrate – formation of short-lived reactive radicals upon UV irradiation – can be harnessed to drive homogeneous denitrification\textsuperscript{17, 18}. However, prior studies on the photochemistry of nitrate largely emphasized on its photosensitizing role in the degradation of organic contaminants.\textsuperscript{19, 20} Recent efforts on denitrification mainly focus on the design of new catalysts processing unique catalytic properties or mimicking natural enzymatic processes.\textsuperscript{21-23} In contrast, homogeneous denitrification process based on the photochemistry of nitrate has not been explored. Furthermore, direct photolysis of nitrate generates more toxic nitrite as the end product, making it infeasible as a standalone treatment option\textsuperscript{17, 18} Therefore, additional reducing reagents that can be in-situ generated during nitrate photolysis are desired to convert nitrate to $\text{N}_2$.

Formate radical ($\text{CO}_2\cdot$) can be a promising reducing reagent. It is highly reductive ($E^0(\text{CO}_2/\text{CO}_2\cdot) = -1.9$ V) and thermodynamically feasible to convert nitrate to $\text{N}_2$ ($E^0(\text{NO}_3^-/\text{N}_2) = 1.24$ V).\textsuperscript{24} Prior studies have applied $\text{CO}_2\cdot$ to reductive removal of chlorinated chemicals and toxic heavy metals.\textsuperscript{25, 26} $\text{CO}_2\cdot$ can be generated via formate reacting with oxidative radicals (e.g., HO·) that are intermediates of nitrate photolysis. In addition, the formation of $\text{CO}_2\cdot$ and its potential role in contaminant destruction have been reported in heterogeneous photocatalysis, where formate was used as a hole scavenger.\textsuperscript{27} Despite that, the feasibility and mechanism of utilizing $\text{CO}_2\cdot$ for homogeneous denitrification induced by nitrate photolysis remain largely unknown.\textsuperscript{15, 27} Furthermore, there lacks a mechanistic understanding of photochemical denitrification processes and
quantitative determination of major reaction pathways because of the complexity of denitrification processes.

In this study, we aimed to develop a CO$_2$-induced denitrification process utilizing the photochemistry of nitrate. The key is to harness transiently in-situ produced radicals (e.g., HO·, NO$_2^·$, and CO$_3^·$) from nitrate photolysis to partially oxidize formate to highly reductive CO$_2^·$. A new kinetic model with principal component analysis was established to interpret the denitrification mechanism. Furthermore, we determined the formate-to-nitrate stoichiometry at which a complete removal of both dissolved nitrogen and organic carbon was achieved simultaneously. The impact of solution pH and dissolved organic matter on photochemical denitrification was investigated. The applicability of this new denitrification process was evaluated with the synthetic groundwater.

3.3 Materials and Methods

3.3.1 Photochemical experiments and sample analysis

Batch experiments of photochemical denitrification were performed in 10-mL quartz tubes rotating around a 450-W medium pressure UV immersion lamp (Ace Glass, Inc.). The light intensity of the lamp is 42 mW/cm$^2$ measured by thermopile (Newport 818P-010-12). Its spectrum with wavelengths ranging between 200 and 850 nm measured by charge-coupled device (Avantes AvaSpec-EDU) was provided in Figure S3.1 of Supporting Information (SI) section. To start an experiment, solutions containing 2 mM nitrate and 0-20 mM formate were transferred to quartz tubes followed by UV exposure. Suwannee River natural organic matter (SRNOM) as dissolve organic matter between 0 and 72 mg/L
was also added to the solution. The solution pH was controlled at a targeted level between 2 and 11 using 20 mM phosphate buffer. Synthetic groundwater was used in some experiments (chemical matrix listed in Table S3.1 of Appendix B).

At pre-determined time intervals, one sacrificial quartz tube was taken out of the UV reactor for chemical analysis. Concentrations of nitrate, nitrite and formate were analyzed by ion chromatography (DX-120, Thermo Fisher Scientific) with an anion column (Dionex Ion Pac AS22) and a conductivity detector. The eluent was 4.5 mM Na₂CO₃ and 1.4 mM NaHCO₃, and the flow rate was set at 0.86 mL/min. Ammonia was analyzed by a UV/vis spectrophotometer (Horiba scientific, Inc.) using phenate method. Total organic carbon and dissolved nitrogen were analyzed by a TOC analyzer with a total nitrogen module (Aurora 1030C).

To determine the composition of nitrogen products in the gas phase during the photochemical denitrification, 40 mL of reaction solution containing nitrate (2.0 mM), formate (6.1 mM), and phosphate buffer (20 mM, pH = 7) was irradiated in a homemade gas-tight cylindrical reactor with headspace pre-vacuumed and filled with helium gas. Gas samples taken from the headspace of the reactor were analyzed by gas chromatography (GC). N₂ gas was analyzed using GC with packed column (Molecular Sieve 13X, 2.1 mm × 6 feet), thermal conductivity detector (operation temperature: 110 °C), and helium as the carrier gas. Details on gas-phase nitrogen analysis were provided in Text S3.1 (Appendix B).

Furthermore, to quantify the generation of short-lived radicals during the photochemical reaction, a solution containing nitrate (100 mM), formate (300 mM), 5,5-
dimethyl-1-pyrroline N-oxide (DMPO, 100 mM), and phosphate buffer (200 mM, pH=7) was irradiated by medium-pressure UV lamp. Control experiments were carried out in the absence of formate or both nitrate and formate, respectively. Samples taken at 20 minutes of irradiation were transferred to quartz vials for electron paramagnetic resonance (EPR) analysis using X-Band EPR Spectrometer (Bruker EMX spectrometer, Germany). Typical instrumental conditions were as follows: center field: 3325 G; sweep width: 1000 G; microwave power: 20 mW; microwave frequency: 9.33 GHZ; receiver gain: 7.1×10³; modulation amplitude: 2.0 G; modulation frequency: 100 kHz; time constant: 10.24 ms; sweep time: 20.97 ms.

3.3.2 Kinetic modeling and principal component analysis

To simulate photochemical denitrification process, kinetic modeling with uncertainty analysis was performed on a total of 139 reactions using Kintecus V6.01 program. Uncertainty analyses were performed by introducing 20% relative standard deviation to the fitted rate constants. 95% confidence interval was specified to calculate confidence band. Time profiles of average concentrations of nitrogen species and formate with 95% confidence intervals were generated using the kinetic model. To determine the major reactions that controlled the reaction kinetics and product distribution, principal component analyses were performed with Kintecus V6.01 and Atropos V1.00 programs. Normalized sensitivity coefficients (NSC) of each reaction in the kinetic model at predetermined time intervals were calculated by Kintecus program. Subsequently, principal component analyses were conducted by Atropos program through eigenvalue-eigenvector analysis of the matrix composed of NSCs of each reaction at all time
intervals. The reactions with significant entries in the eigenvector (i.e., principal component) that has the largest eigenvalues are the most important. Entries with absolute values in the eigenvector smaller than 0.01 are not reported. Details on kinetic modeling and principal component analyses were provided in Texts S3.2-S3.3 of SI.

3.4 Results and Discussion

3.4.1 Photochemical denitrification in the presence of formate

Photochemical denitrification of nitrate was investigated in the presence of formate. The optimal formate-to-nitrate molar ratio was determined as 3.1 at which a nearly complete removal of dissolved nitrogen and formate was achieved at pH 7 after 180 minutes of UV irradiation (Figure 3.1). As nitrate was removed, nitrite was initially generated but subsequently decayed to a negligible level (Figure 3.1). Ammonia was not observed throughout the reaction. The removal of total dissolved nitrogen indicated the conversion of nitrate to gas-phase nitrogen. A control experiment conducted in the absence of formate showed that nitrate was only partially converted to nitrite with no change in total dissolved nitrogen (Figure S3.2). Because denitrification was not observed in the control, it indicated the importance of formate in driving photochemical denitrification.

When the formate-to-nitrate molar ratio was less than 3.1 (i.e., 1.1 and 1.7), nitrate was partially reduced to nitrite and less than 20% of dissolved nitrogen was removed (Figure S3.3A and S3.3B). As the ratio increased beyond 3.1 (i.e., 5.8 and 11.3), nitrate was completed removed, but excess formate remained in the system (Figure S3.3C and S3.3D). Therefore, the optimal formate-to-nitrate molar ratio was 3.1 for photochemical denitrification process in deionized water at neutral pH.
3.4.2 Mechanism of photochemical denitrification

To understand the mechanism of photochemical denitrification in the presence of formate, a comprehensive kinetic model that includes all possible reactions was established to simulate and quantify the denitrification process. The complete list of reactions in the model is provided in Table S3.2. The model prediction with 95% confidence intervals well fits the experimental data at different formate-to-nitrate molar ratios (Figure 3.1 and Figures S3.2-S3.3). Following that, principal component analyses were conducted and 18 major reactions that controlled the denitrification process at an optimal formate-to-nitrate molar ratio (i.e., 3.1) at pH 7 were identified (Table 3.1). The analyses showed that all major reactions had significant entries in the eigenvectors (i.e., principal components) with the largest four eigenvalues (Table 3.1), which indicated that they were the major reaction pathways in the denitrification process. For example, nitrate photolysis is important in
denitrification process because it generates reactive radical species and initializes subsequent reactions. Photolysis reactions of nitrate (i.e., R1 and R2) have much more significant entries in the eigenvectors (e.g., 0.64 and -0.73) than the threshold value (i.e., 0.01), indicating that these two reactions are very important.

Based on the major reactions identified from the model (Table 3.1), the mechanism of photochemical denitrification at a formate-to-nitrate molar ratio of 3.1 and pH 7 was illustrated (Scheme 3.1). Nitrate has a strong $\pi \rightarrow \pi^*$ absorption band peaked at 200 nm and a weak $n \rightarrow \pi^*$ absorption band peaked at 302 nm (Figure S3.1 in Appendix B). Under the irradiation of polychromatic light, nitrate dissociated into NO$_2^\cdot$ and HO$^\cdot$ (R1 in Scheme 3.1; all reactions henceforth refer to Table 3.1) or isomerized into peroxynitrite (ONOO$^-$) (R2). ONOO$^-$ reacted with dissolved CO$_2$ from air and formate oxidation (R3). The formed ONOOCO$_2^-$ subsequently decomposed into NO$_3^-$ and CO$_2$ (R4), or NO$_2^\cdot$ and CO$_3^-$ (R5). The presence of formate converted CO$_3^-$, HO$^\cdot$ and NO$_2^\cdot$ to CO$_2^-$ (R6-R8). Once formed, CO$_2^-$ underwent self-recombination (R9) or reacted with dissolved oxygen to generate O$_2^-$ (R10). As an intermediate, NO$_2^-$ was mainly generated from the reaction between NO$_2^\cdot$ and HCOO$^-$ (R8) and subsequently photolyzed to NO$^-$ and HO$^\cdot$ (R11). In the presence of CO$_2^-$, NO$^-$ was eventually reduced to HNO through a three-step reaction pathway (R12-14). The formed HNO either self-combined into N$_2$O (R15) or reduced to H$_2$NO$^\cdot$ by CO$_2^-$ (R16). Both H$_2$NO$^\cdot$ and N$_2$O served as the source of N$_2$ by self-recombination (R17) and CO$_2^-$-induced reduction (R18), respectively.
Table 3.1 Major reactions in photochemical denitrification process. [Nitrate] = 2.0 mM, [Formate] = 6.2 mM, and pH = 7 with 20 mM phosphate buffer. Entries in the eigenvector with absolute value smaller than 0.01 are not shown.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reactions</th>
<th>Rate constants</th>
<th>References</th>
<th>Eigenvector</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$NO_2^+$ $\rightarrow$ $ONO_2^-$</td>
<td>$4.6 \times 10^4$ s$^{-1}$</td>
<td>This study</td>
<td>0.64</td>
</tr>
<tr>
<td>2</td>
<td>$NO_2^+$ $\rightarrow$ $NO_2^- + O^-$ (o$^{-}$ + H$^+$ $\rightarrow$ OH)</td>
<td>$1.3 \times 10^4$ s$^{-1}$</td>
<td>This study</td>
<td>0.73</td>
</tr>
<tr>
<td>3</td>
<td>$ONO_2^- + CO_2 \rightarrow$ $ONOOCO_2^-$</td>
<td>$3.0 \times 10^8$ M$^{-1}$ s$^{-1}$</td>
<td>48</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>$ONOOCO_2^- \rightarrow$ $NO_2^- + CO_2$</td>
<td>$6.7 \times 10^5$ s$^{-1}$</td>
<td>49</td>
<td>-0.75</td>
</tr>
<tr>
<td>5</td>
<td>$ONOOCO_2^- \rightarrow$ $NO_2^- + CO_3$</td>
<td>$3.3 \times 10^5$ s$^{-1}$</td>
<td>49</td>
<td>0.65</td>
</tr>
<tr>
<td>6</td>
<td>$CO_2^- + HCOO^- \rightarrow$ $CO_2^- + HCO_3^-$</td>
<td>$1.1 \times 10^8$ M$^{-1}$ s$^{-1}$</td>
<td>50</td>
<td>-0.05</td>
</tr>
<tr>
<td>7</td>
<td>$OH + HCOO^- \rightarrow$ $CO_2^- + H_2O$</td>
<td>$3.2 \times 10^8$ M$^{-1}$ s$^{-1}$</td>
<td>42</td>
<td>0.12</td>
</tr>
<tr>
<td>8</td>
<td>$NO_2 + HCOO^- \rightarrow$ $NO_2^- + CO_2^- + H^+$</td>
<td>$5.0 \times 10^5$ s$^{-1}$</td>
<td>This study</td>
<td>0.05</td>
</tr>
<tr>
<td>9</td>
<td>$CO_2^- + CO_2^- \rightarrow$ $C_2O_4^-$</td>
<td>$6.5 \times 10^8$ M$^{-1}$ s$^{-1}$</td>
<td>51</td>
<td>-0.29</td>
</tr>
<tr>
<td>10</td>
<td>$CO_2^- + O_2 \rightarrow$ $CO_2 + O_2^-$</td>
<td>$2.4 \times 10^8$ M$^{-1}$ s$^{-1}$</td>
<td>52</td>
<td>0.07</td>
</tr>
<tr>
<td>11</td>
<td>$NO_2^+$ $\rightarrow$ $NO^- + O^-$ (o$^{-}$ + H$^+$ $\rightarrow$ OH)</td>
<td>$7.9 \times 10^4$ s$^{-1}$</td>
<td>This study</td>
<td>0.14</td>
</tr>
<tr>
<td>12</td>
<td>$NO^- + CO_2^- \rightarrow$ $NOCO_2^-$</td>
<td>$2.9 \times 10^7$ M$^{-1}$ s$^{-1}$</td>
<td>53</td>
<td>-0.15</td>
</tr>
<tr>
<td>13</td>
<td>$NO^- + NOCO_2^- \rightarrow$ $N_2O_2^- + CO_2$</td>
<td>$6.8 \times 10^5$ M$^{-1}$ s$^{-1}$</td>
<td>53</td>
<td>-0.04</td>
</tr>
<tr>
<td>14</td>
<td>$N_2O_2^- \rightarrow$ $NO^- + NO^- (NO^- + H^+ \rightarrow$ HNO)</td>
<td>$6.6 \times 10^8$ s$^{-1}$</td>
<td>54</td>
<td>-0.09</td>
</tr>
<tr>
<td>15</td>
<td>$HNO + HNO \rightarrow$ $N_2O + H_2O$</td>
<td>$8.0 \times 10^8$ M$^{-1}$ s$^{-1}$</td>
<td>54</td>
<td>0.03</td>
</tr>
<tr>
<td>16</td>
<td>$HNO + CO_2^- + H_2O \rightarrow$ $N_2O NO^- + OH^- + CO_2$</td>
<td>$1.3 \times 10^8$ M$^{-1}$ s$^{-1}$</td>
<td>55</td>
<td>-0.08</td>
</tr>
<tr>
<td>17</td>
<td>$H_2NO^- + H_2NO \rightarrow$ $N_2 + 2H_2O$</td>
<td>$2.8 \times 10^8$ M$^{-1}$ s$^{-1}$</td>
<td>55</td>
<td>0.09</td>
</tr>
<tr>
<td>18</td>
<td>$N_2O + CO_2^- + H_2O \rightarrow$ $N_2 + OH^- + CO_2$</td>
<td>$1.6 \times 10^8$ M$^{-1}$ s$^{-1}$</td>
<td>56</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Scheme 3.1 Major reaction pathways in photochemical denitrification process. [Nitrate] = 2.0 mM, [Formate] = 6.2 mM, and pH = 7 with 20 mM phosphate buffer. All referred reactions were listed in Table 3.1.
The addition of formate in the photochemical system is critical to denitrification. Formate prevented the re-oxidation NO$_2^-$ to nitrate by scavenging oxidative radicals (e.g., HO· and CO$_3^-$). In addition, the reaction between NO$_2^-$ and HCOO$^-$ (R8) was critical to the denitrification process but has not been reported previously. Vibronically-excited NO$_2^-$ generated during nitrate photolysis abstracted hydrogen from HCOO$^-$ to generate CO$_2^-$.

Model-predicted rate constant between NO$_2^-$ and formate (R8) is $5.0 \times 10^5$ M$^{-1}$ s$^{-1}$. Therefore, the addition of formate during nitrate photolysis converted NO$_2^-$ to NO$_2^-$ and generated reductive CO$_2^-$ for subsequent denitrification.

![Figure 3.2](image)

**Figure 3.2** Electron paramagnetic spectra of DMPO-radical adducts formed after 20 minutes of irradiation with medium-pressure UV lamp. [Nitrate] = 100 mM, [Formate] = 300 mM, [DMPO]= 100 mM, and pH = 7 with 200 mM phosphate buffer.

The formation of CO$_2^-$ in the photochemical system was confirmed by EPR using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as the trapping reagent (**Figure 3.2**). EPR spectrum of nitrate photolysis in the presence of formate showed six equal-height spectral lines with
g value of 2.0054 and hyperfine splitting constants $a_N=15.7$ G and $a_{\beta-H}=19.0$ G. The spectral characteristic was consistent with that of DMPO-CO$_2^-$ adduct (Figure 3.2). As a control, nitrate photolysis in the absence of formate generated a quartet EPR spectrum ($g=2.0051$ and $a_N=a_{\beta-H}=15.0$ G) with peak intensity ratios of 1:2:2:1, which was attributed to DMPO-HO$^-$ adduct (Figure 3.2). EPR spectrum of DMPO alone showed no appreciable signal (Figure 3.2). The contrasting EPR spectra confirmed the formation of CO$_2^-$ during photolysis of nitrate in the presence of formate.

![Graph](image.png)

**Figure 3.3** Model-predicted cumulative contribution of relevant species to: (A) the formation of CO$_2^-$; and (B) the consumption of CO$_2^-$. [Nitrate] = 2.0 mM, [Formate] = 6.2 mM, and pH = 7 with 20 mM phosphate buffer.
The respective contribution of HO·, NO2· and CO3· to the yield of CO2· depends on the steady-state concentration of each radical species and its respective rate constant with formate. Model-predicted concentrations of NO2· and CO3· were four orders of magnitude higher than that of HO· (10^{-10} vs. 10^{-14} M) (Figure S3.4), mainly because NO2· and CO3· were less reactive with HCOO· than HO· (10^5 vs. 10^9 M^{-1}s^{-1}). Calculation based on kinetic modeling showed that NO2· contributed most to CO2· formation (49%) followed by HO· (39%) and CO3· (12%), i.e., R8, R7, and R6 in Scheme 3.1, respectively (Figure 3.3A and Text S3.4).

The contribution of CO2· to denitrification mainly resulted from its reactions with NO· (R12, Scheme 3.1). Kinetic modeling showed that NO· accounted for 42% of cumulative consumption of CO2· and served as the major sink of CO2· (Figure 3.3B). Besides that, dissolved oxygen and self-recombination were two additional sinks for CO2·. In the first five minutes, 99% of CO2· was scavenged by O2 (Figure 3.3B and Text S3.4), because O2 is present in air-saturated solution (0.25 mM) and it has a high reactivity with CO2· (2.4×10^9 M^{-1}s^{-1}, Table 3.1). As O2 was depleted, the concentration of CO2· increased rapidly from 10^{-12} to 10^{-8} M (Figure S3.5). As a result, self-scavenging became prominent for CO2· (R9, Scheme 3.1), which accounted for ca. 30% of integrated consumption of CO2· (Figure 3.3B). HNO was an important intermediate associated with final product distribution (i.e., N2O and N2). Calculation based on the kinetic modeling (Figure S3.6) showed that 83% of HNO self-combined into N2O (R15, Scheme 3.1) and the remaining 17% was reduced to H2NO· by CO2· (R16). N2O was the main product of HNO. Despite that the self-recombination of H2NO· to N2 was fast (R17), the subsequent
reaction between CO$_2$·$^-$ and N$_2$O was kinetically unfavorable (1600 M$^{-1}$s$^{-1}$, R18), which limited the overall formation of N$_2$. Product analyses by gas chromatography showed that N$_2$ gas accounted for 30% of gaseous products (Figure S3.7). N$_2$O gas was predicted as another major product by kinetic modeling (Figure S3.8). It accounted for the remaining 70% of gas-phase nitrogen based on mass balance.

### 3.4.3 Denitrification stoichiometry

Photochemical denitrification is a multi-step electron transfer process. Experimental data showed that the formate-to-nitrate molar ratio affects the availability of electrons for denitrification and consequently the final product distribution (Table 3.2). In the absence of formate, nitrate only photolyzed into nitrite (Table 3.2), because transient species generated during nitrate photolysis (e.g., HO·, ONOO$^-$, NO$_2$·, NO$-$, N$_2$O$_4$, and N$_2$O$_3$) underwent simultaneous oxidation, hydrolysis and combination reactions that prohibited the transformation of nitrate into gas-phase products.$^{17}$ As formate-to-nitrate molar ratio increased, additional electrons from formate converted oxidative radicals (e.g., HO· and NO$^-$) to CO$_2$·$^-$, promoted the reduction of nitrate, and inhibited the accumulation of nitrite (Table 3.2). High formate-to-nitrate molar ratio favored denitrification but increased residual organics in the system (Table 3.2). The stoichiometry between formate and nitrate to achieve a complete removal of dissolved nitrogen and organic carbon was determined as 3.1 ± 0.2, which was consistent with the model prediction (3.2 ± 0.1, Table 3.2). Based on the observed product distribution of gas-phase nitrogen (70% of N$_2$O and 30% of N$_2$) and electron-transfer numbers with respect to nitrate, the theoretical stoichiometry of formate to nitrate was calculated as 2.2 (Text S3.5). The actual formate-use efficiency
during denitrification process was determined as 74%, based on the ratio of theoretical to measured stoichiometry. The lower-than-ideal stoichiometry mainly resulted from the scavenging of CO$_2$· by itself (R9, Scheme 3.1) and dissolved O$_2$ (R10, Scheme 3.1).

Table 3.2 Impact of formate-to-nitrate molar ratio on denitrification and reaction stoichiometry between formate and nitrate in deionized water at neutral pH.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>53.6</td>
<td>52.0</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.1</td>
<td>54.9</td>
<td>52.6</td>
<td>0</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.7</td>
<td>69.6</td>
<td>51.8</td>
<td>17.4</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.1</td>
<td>97.9</td>
<td>0.53</td>
<td>97.1</td>
<td>93.5</td>
<td>3.1</td>
<td>3.1</td>
</tr>
<tr>
<td>5.8</td>
<td>100</td>
<td>0</td>
<td>99.0</td>
<td>50.9</td>
<td>3.0</td>
<td>3.2</td>
</tr>
<tr>
<td>11.3</td>
<td>100</td>
<td>0</td>
<td>99.6</td>
<td>29.2</td>
<td>3.3</td>
<td>3.2</td>
</tr>
<tr>
<td>Average Stoichiometry of Formate to Nitrate</td>
<td>3.1 ± 0.2</td>
<td>3.2 ± 0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.4.4 Effects of solution pH

Photochemical denitrification was closely associated with the speciation of nitrogen intermediates (e.g., ONOO$^-$ and NO$_2^-$) and other species (e.g., CO$_2$(aq) and HCOO$^-$). Solution pH impacts their speciation (ONOOH/ONOO$^-$, pK=6.5-6.8; HNO$_2$/NO$_2^-$, pK=3.3; CO$_2$/HCO$_3^-$/CO$_3^{2-}$, pK$_1$= 6.3 and pK$_2$=10.3; HCOOH/HCOO$^-$, pK=3.8.$^{37}$), as well as their molar extinction coefficients, quantum yields and reactivities. The data showed that pH moderately affected the removal of nitrate and nitrite, but insignificantly affected the removal of dissolved nitrogen and formate (Figure 3.4). Nitrate removal was slightly enhanced at pH 11 in comparison with that at pH 2 and 7, respectively (Figure 3.4A). The initial accumulation of nitrite was largely avoided at pH 2 compared to other pHs (Figure 3.4B). The formation of ammonia was negligible regardless of pHs (data not shown). Combining effects of nitrate and nitrite slightly enhanced the removal of dissolved...
nitrogen at pH 2 and 11, compared with that at pH 7 (Figure 3.4C), indicating that the solution pH has no significant impact on photochemical denitrification.

![Figure 3.4](image_url)

**Figure 3.4** Impact of pH on photochemical denitrification in the presence formate: (A) Nitrate removal; (B) Total nitrite evolution; (C) Dissolved nitrogen removal; (D) Total formate consumption. [Nitrate] = 2.0 mM, [Formate] = 6.2 mM, and pH = 2-11 with 20 mM phosphate buffer. Total nitrite = nitrous acid + nitrite; Total formate = formic acid + formate.

Model prediction of photochemical denitrification process at different pHs well matched with the experimental observations (Figure 3.4). The enhanced nitrate removal at alkaline pH was associated with the speciation of inorganic carbon that was generated from formate oxidation. At pH 11, OH\(^-\) catalyzed the hydration of CO\(_2\)\((aq)\) into HCO\(_3^-\), which suppressed the formation of NO\(_3^-\) from ONOO\(^-\) (R3 and R4, Scheme 3.1) and subsequently
enhanced the removal of nitrate. Model-predicted concentration of CO$_2$$_{(aq)}$ (ca. $10^{-8}$ M) at pH 11 was much lower than that at pH 2 and 7 (ca. $10^{-5}$-$10^{-3}$ M).

The pH-induced drastic difference in nitrite evolution was associated with its speciation. At pH 2, nitrite became protonated to nitrous acid (i.e., HNO$_2$). HNO$_2$ has a larger molar extinction coefficient and higher photolysis quantum yield than NO$_2^-$.$^{38}$ Model-predicted photolysis of HNO$_2$ at pH 2 ($2.5\times10^{-3}$ s$^{-1}$, R66, Table S3.2) was 3 times faster than that of NO$_2^-$ at pH 7 ($7.9\times10^{-4}$ s$^{-1}$, R49, Table S3.2). Fast photolysis of HNO$_2$ prevented its build-up at pH 2. In contrast, at pH 11, photolysis of nitrite slowed down in comparison to that at pH 7. This is likely because of light attenuation by the accumulated ONOO$^-$ that has a strong UV absorption between 250 and 400 nm (e.g., $\varepsilon_{(ONOO^-)302nm}=1670$ M$^{-1}$cm$^{-1}$).$^{39}$ Model-predicted concentration of ONOO$^-$ at pH 11 (ca. $10^{-6}$ M) was two orders of magnitude higher than that at pH 7 (ca.$10^{-8}$ M). Consequently, the predicted photolysis rate of NO$_2^-$ at pH 11 ($3.9\times10^{-4}$ s$^{-1}$, R49, Table S3.2) was 2 times smaller than that at pH 7, which resulted in more initial accumulation of nitrite at pH 11.

3.4.5 Effects of dissolved organic matters

Dissolved organic matter (DOM) is commonly present in natural waters. It can absorb light, produce reactive intermediates (e.g., $^3$DOM*, $^1$O$_2$, O$_2^-$, $\text{e}_{\text{aq}}^-$, etc.), scavenge radical species (e.g., ·OH), and potentially impact the photochemical denitrification process.$^{40,41}$ SRNOM was used as the model compound to investigate the impact of DOM. At a low DOM concentration (i.e., 5 mg-C/L) that simulates its level in groundwater, denitrification efficiency was comparable to that in the absence of DOM (Figure 3.5A). At high DOM
concentrations (i.e., 24 and 72 mg-C/L) that simulated its levels in eutrophic surface water and wastewater, denitrification efficiency was partially suppressed (Figure 3.5A). The decay of nitrate was also inhibited, indicating that reactive species generated from DOM made insignificant contribution to nitrate removal. Despite that, 68% and 43% of total dissolved nitrogen was removed at DOM concentrations of 24 and 72 mg-C/L, respectively. In addition, DOM exhibited a similar impact on formate removal (Figure 3.5B).

DOM impacted the denitrification process mainly because of its light-shading and electron-donating effects. To simulate the impact of DOM on denitrification process, light-shading and ·OH-scavenging effects of DOM were considered in the kinetic model. Other unknown effects of DOM that could not be quantitively considered in the model were assessed by comparing the difference between model predication and experimental data. High concentrations of DOM shielded light from nitrate and nitrite. For instance, in the range of 200-240 nm where nitrate has strong absorption, 72 mg-C/L of DOM absorbed 22% to 100% of total irradiance at the initial stage (Figure S3.9). The light-shading effect of DOM also suppressed the decay of nitrate and increased the accumulation of nitrite when the DOM levels reached 24 and 72 mg-C/L (Figure S3.10 and S3.11). With photolysis rates of nitrate and nitrite optimized in the model to account for light shading effect of DOM, the model well predicted the removal of total dissolved nitrogen (Figure 3.5A). Kinetic modeling showed that 72 mg-C/L of DOM decreased the photolysis rates of nitrate and nitrite by 55% and 90%, respectively, compared with those in the absence of DOM.
Figure 3.5 Impact of dissolved organic matter (DOM) on photochemical denitrification in the presence formate: (A) Dissolved nitrogen removal; (B) Formate consumption; [Nitrate] = 2.0 mM, [Formate] = 6.2 mM, [DOM] = 0-72 mg-C/L, and pH = 7 with 20 mM phosphate buffer.

The scavenging effect of DOM on ·OH was included in the model but the effect was insignificant, because DOM reacted with ·OH much more slowly than it with formate ($k_{\text{SRNOM-HO}^-} = 1.4 - 4.5 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ vs. $k_{\text{HCOO}^--\text{HO}^-} = 3.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$). Additional effect of DOM were indicated by the over-predicted decay of formate at high DOM concentrations by the model (i.e., 72 mg-C/L, Figure 3.5B). The deviation indicated that additional
electron-releasing capacity from DOM benefited the denitrification process. For instance, electron-rich moieties in DOM and its degradation products could serve as electron donors for denitrification process, which reduced the overall consumption of formate.\textsuperscript{43}

### 3.5 Environmental Implications

![Figure 3.6](image)

**Figure 3.6** Photochemical denitrification in the synthetic groundwater. Chemicals added in the synthetic groundwater: [Formate] = 6.0 mM and pH = 7 with 20 mM phosphate buffer.

This study demonstrates a promising denitrification technology to transformation of nitrate into gas-phase nitrogen. Application potentials of this technology were further assessed in the synthetic groundwater chemical matrix, and the denitrification efficiency was comparable with that in DI water (**Figure 3.6**). Kinetic modeling showed that the model predication well fitted the experimental data and indicated that major groundwater constituents (e.g., Cl\(^-\), SO\(_4^{2-}\), HCO\(_3^-\), DOM, etc.) did not significantly interfere with photochemical denitrification process. The result showed that this process can be highly effective to treat authentic nitrate-contaminated groundwater.
The proposed denitrification mechanism is based on kinetic modeling, qualitative analyses of major radicals (i.e., HO· and CO₂·⁻) and quantitative analyses of the reactants and products. To further validate the proposed reaction pathways, quantitative analyses of unstable intermediates are required. The study showed that gas-phase product distribution of photochemical denitrification was mainly controlled by low reactivity between CO₂·⁻ and N₂O. Future studies can strive to minimize the formation of N₂O through introducing hydrated electrons because of their high reactivity to transform N₂O to N₂ (9.1×10⁹ M⁻¹ s⁻¹). The kinetics of photochemical denitrification was governed by photolysis of nitrate and nitrite. Prior studies demonstrated that photolysis of nitrate and nitrite under the irradiation of polychromatic light predominantly resulted from photons less than 280 nm. Based on that, effective electric energy per order of dissolved nitrogen removal was determined as 17 KWh/m³/order for bench-scale photochemical denitrification. Even though it is more energy intensive than conventional UV processes (e.g., UV/H₂O₂ and UV/O₃: 0.1-1KW KWh/m³/order), the energy efficiency can be substantially improved via further optimization on operational and reaction parameters. For instance, nitrate has a strong absorption and high photolysis quantum yield below 240 nm. Utilization of UV lamps with a photon flux below 240 nm can highly enhance the photon-use efficiency, accelerate the reaction kinetics, and reduce the energy consumption. Further optimization on reactor configuration and process capacity can significantly decrease the energy demand of the full-scale treatment compared with bench-scale test.

The proposed denitrification technology has a high adaptability to different water chemical conditions. The operational flexibility and simplicity enable it as fit-for-purpose
technology for water treatment and reuse. It can be implemented as a treatment module that helps urban areas treat local water resources to supplement conventional water supplies. In addition, it can be integrated in a decentralized water treatment unit to help remote communities remove nitrate from local water supplies. Prior to full implementation, pilot-scale test and process optimization should be performed.

Formate has already been used in treatment process for in situ groundwater denitrification and TiO$_2$-based photocatalytic denitrification.\textsuperscript{14, 27, 47} As the simplest carboxylate, formate can be readily mineralized into carbon dioxide. The optimal formate-to-nitrate molar ratio should be utilized to prevent secondary contamination from formate. Our work shows that the optimal formate-to-nitrate ratio has little dependency on pH and major water constituents (e.g. DOM and inorganic constituents) at levels similar to those in groundwater (Table S3.3). For source waters with chemical constituents that strongly impact the formate-use efficiency and denitrification performance, pretreatment (e.g., membrane filtration) can be conducted to minimize their potential adverse effect on the treatment efficiency.

### 3.6 Acknowledgement

The study was supported by U.S. National Science Foundation GOALI Program (CBET-1611306). We also thank the support to G.C. from the Los Angeles Urban Natural Resources Sustainability Science Fellowship, and the assistance from Yibo Jiang and Kun Li for gas-phase nitrogen analysis.
References


Chapter 4

Understanding Reduction Kinetics of Aqueous Vanadium(V) and Transformation Products Using Rotating Ring-Disk Electrode

Previously Published in *Environmental Science and Technology*

4.1 Abstract

Vanadium(V) is an emerging contaminant in the most recent EPA’s candidate contaminant list (CCL4). The redox chemistry of vanadium controls its occurrence in the aquatic environment, but the impact of vanadium(V) speciation on the redox properties remains largely unknown. This study utilized rotating ring-disk electrode technique to examine the reduction kinetics of four pH- and concentration-dependent vanadium(V) species in the presence and absence of phosphate. Results showed that the reduction of $\text{VO}_2^+$, $\text{H}_x\text{V}_4\text{O}_{12+x}^{(4+x)^-}$ ($V_4$) and $\text{HVO}_4^{2\text{-}}$ proceeded via a one-electron transfer, while that of $\text{Na}_x\text{H}_y\text{V}_{10}\text{O}_{28}^{(6-x-y)^-}$ ($V_{10}$) underwent a two-electron transfer. Koutecky-Levich and Tafel analyses showed that the intrinsic reduction rate constants followed the order of $V_{10} > \text{VO}_2^+ > V_4 > \text{HVO}_4^{2\text{-}}$. Ring electrode collection efficiency indicated that the reduction product of $V_{10}$ was stable, while those of $\text{VO}_2^+$, $\text{HVO}_4^{2\text{-}}$ and $V_4$ had short half-lives from milliseconds to seconds. With molar ratios of phosphate to vanadium(V) varying from 0 to 1, phosphate accelerated the reduction kinetics of $V_{10}$ and $V_4$, and enhanced the stability of the reduction products of $\text{VO}_2^+$, $V_4$ and $\text{HVO}_4^{2\text{-}}$. This study suggests that phosphate complexation could enhance the reductive removal of vanadium(V) and inhibit the re-oxidation of its reduction product in water treatment.
4.2 Introduction

Vanadium is widely present in the earth crust, with vanadium(IV) and vanadium(V) as the most common species in the aquatic environment.\textsuperscript{1, 2} Vanadium(V) is toxic and highly soluble, while vanadium(IV) is less toxic and exists in solid phases at neutral pH.\textsuperscript{3, 4} Ingestion of vanadium(V) can lead to adverse health effects including pulmonary tumors.\textsuperscript{1} Considering the public health risks, U.S. Environmental Protection Agency included vanadium in its fourth round of contaminate candidate list (CCL4), and proposed a minimum reporting level of 0.2 µg/L during the third Unregulated Contaminant Monitoring Rule (UCMR3) program.\textsuperscript{5, 6} A notification level of 15 µg/L in drinking water was recommended in California.\textsuperscript{1}

Geological weathering of vanadium-containing minerals (\textit{e.g.}, mafic and andesitic rock) naturally releases vanadium into groundwater under oxic and alkaline conditions.\textsuperscript{7} Data collected in California from 1996 to 2007 showed that 18% of public drinking water systems had vanadium levels higher than 21 µg/L.\textsuperscript{8} Up to 220 µg/L of vanadium has been detected in watersheds containing vanadium-associated ores.\textsuperscript{9} The anthropogenic release of vanadium is mainly from the combustion of vanadium-rich fossil fuels, wastewater discharge from mining, steel and phosphorus chemical industry.\textsuperscript{2, 10} In addition, vanadium-containing minerals, \textit{e.g.}, vanadinite Pb\textsubscript{5}(VO\textsubscript{4})\textsubscript{3}Cl\textsubscript{(s)}, was found to cumulate in the corrosion solids of lead-containing drinking water distribution systems, where mass concentrations of vanadium were several orders of magnitude higher than that in the treated drinking water.\textsuperscript{11,12} Destabilization of vanadium-containing corrosion solids potentially leaches vanadium and elevates its concentration in treated drinking water.
Aqueous vanadium(V) exists as monomeric and polymeric oxo-vanadate species depending on pH, vanadium(V) concentration and ionic strength. Monomeric vanadium(V) species (e.g., H$_2$VO$_4^-$ and HVO$_4^{2-}$) are preferentially present in oxic natural waters. Increasing vanadium concentration promotes their oligomerization into dimers (e.g., H$_2$V$_2$O$_7^{2-}$), tetramers (e.g., V$_4$O$_{12}^{4-}$) and decamers (e.g., HV$_{10}$O$_{28}^{5-}$). Increasing acidity favors the formation of decamers and VO$_2^+$ in water matrix. Considering the wide occurrence and regulatory perspective, vanadium removal from drinking water especially reductive transformation of vanadium(V) to vanadium(IV) using chemicals, photocatalysts and microbes with subsequent particle separation is needed in the future.

Prior studies on vanadium(V) chemistry have mostly focused on its application in medical insulin mimetics, flow batteries and petroleum refining. Although the redox behaviors of VO$_2^+/VO^{2+}$ and V$^{3+}$/V$^{2+}$ pairs at extremely acidic conditions have been previously examined for redox flow batteries, the experimental conditions highly deviated from environmentally relevant conditions. Vanadium(V) speciation also impacted its reactivity in aquatic environment. Prior study showed that VO$_2^+$ cation was reactive towards humic substances and the reduction of decavanadate by humic substances required its decomposition into VO$_2^+$. Decavanadate was also reported to be more prone to reduction than metavanadate (monomer, dimer, tetramer, etc.), and its cage-like structure remained unchanged after its partial reduction. However, the structure-redox property relationship, underlying electron-transfer mechanism and properties of reduction products remained largely unknown for aquatic vanadium(V) species. In addition, complexation of
organic and inorganic ligands with vanadium(V) affects its redox behavior.\textsuperscript{13, 32} In particular, vanadium(V) forms stronger complexes with phosphate than other inorganic ligands.\textsuperscript{33} Phosphate was ubiquitously present in aquatic system mainly because of extensive utilization of phosphorous-containing fertilizers with subsequent agriculture run-off.\textsuperscript{34} In addition, geological weathering of vanadium-bearing phosphorous mineral ores simultaneously leaches vanadium and phosphate into water matrixes.\textsuperscript{35, 36} Their co-occurrence in aquatic system makes the complexation of vanadium with phosphate environmentally relevant. However, there lacks a fundamental understanding of phosphate impact on reduction kinetics of vanadium(V) species and the stability of their reduction products.

Electrochemical techniques (EC) are robust means to examine the nature of redox-active metal(loid) species and the \textit{in-situ} formation of intermediate products.\textsuperscript{37-40} In particular, rotating ring disk electrode (RRDE) provides insightful information on the electron-transfer kinetics and reaction mechanism. RRDE is an advanced hydrodynamic EC method, in which the substrate is convectively transported to a disk electrode with a potential sweep, and the products generated on the disk is conveyed to the ring with a fixed potential (Scheme 4.1). However, prior research using RRDE technique to understand physical and redox properties of environment-relevant species and their transformation products is limited. RRDE technique revealed the generation mechanism of Pb(III) intermediate in Pb(II)/PbO\textsubscript{2} system and the role of Pb(III) in Pb(II) oxidation in the drinking water conditions.\textsuperscript{37} Its application in electrochemical reduction of monoiodoacetic acid and iodoform in the presence of natural organic matter provided insight on their
diffusion properties and unveiled their different reduction pathway from Cl- and Br-containing disinfection byproducts.\textsuperscript{39} For vanadium with multiple valence states and complex speciation, RRDE technique can effectively characterize physical properties and redox behaviors of electrochemically active species, unveil their electron-transfer mechanism, and probe their transformation products.

\textbf{Scheme 4.1} Principles of vanadium(V) reduction on the disk electrode and re-oxidation of its reduction products on the ring electrode under rotating conditions.
The objective of this study was to investigate the mechanisms and kinetics of the reduction of pH- and concentration-dependent vanadium(V) species and characterize the formation of intermediate products during the reduction pathway using RRDE techniques combined with conventional cyclic voltammetry (CV). The impact of phosphate on the redox properties of vanadium(V) species was also examined for the aquatic environment with molar ratios of phosphate to vanadium(V) ranging from 0 to 1.

4.3 Materials and Methods

4.3.1 Electrochemical system

EC experiments were carried out in a 150-mL five-port cell with a gold RRDE working electrode (AFE7R8AUAU), a platinum counter electrode (AFCTR5), and a Ag/AgCl reference electrode. The disk and ring electrode were controlled by a Pine AFCBP2 bipotentiostat (Pine Research Instrumentation, Durham, NC). The outer diameters of disk and ring electrode was 4.57 and 5.38 mm, respectively, with a gap of 0.18 mm between them. The disk electrode surface area was 0.1642 cm². The theoretical collection efficiency of intermediates by RRDE was determined as 24% based on the reduction of ferricyanide. The counter electrode was separated from the testing solution using a fritted glass tube. EC potentials was measured and quoted vs. Ag/AgCl reference electrode (+0.197 V vs. standard hydrogen electrode, SHE).

4.3.2 Electrochemical measurements

All solutions were prepared with chemicals (analytical grade) and deionized (DI) water (18.2 MΩ/cm). A 20-mM vanadium(V) solution prepared from NaVO₃ was purged
with N₂ gas for 30 minutes to maintain a negligible level of dissolved O₂. A continuous N₂ gas flow was positioned above the solution to prevent the ingress of O₂ into the solution during EC experiments. pH was fixed at a targeted value of 1, 4, 7 or 11 by adding HClO₄ or NaOH. The predominance diagrams of vanadium(V) (Figure 4.1 and Figure S4.1 in Appendix C) and vanadium(IV) (Figure S4.2) were prepared using Visual Minteq software based on the equilibrium reactions and constants (Text S4.1 in Appendix C). In some experiments, 1-20 mM of phosphate was added. EC experiments were conducted using 0.6 M NaClO₄ as the background electrolyte at 22±2 °C. Changes of pH during EC experiments were negligible. Prior to each experiment, the gold RRDE was polished with alumina slurry and subsequently rinsed with methanol, 0.5 M H₂SO₄ and deionized (DI) water for 30 seconds each. The reproducibility of RRDE surface was confirmed by CV scans with the background electrolyte.

In CV experiments, the disk electrode potential was scanned between -1.35 and 1.30 V, with a scan rate ranging from 25 to 200 mV/s. In RRDE experiments, the electrode rotating speed varied from 400 to 2700 rpm with a constant scan rate of 50 mV/s. When rotating, the potential of disk electrode was scanned within a targeted range, while the ring electrode potential was fixed at a particular value. EC currents on both electrodes were recorded. The collection efficiency of the reduction products was calculated from the ratio of ring electrode current to disk electrode current.
4.4 Results and Discussion

4.4.1 Speciation of concentration- and pH-dependent aqueous vanadium(V)

At a fixed ionic strength (0.6 M), the speciation of vanadium(V) is both concentration- and pH-dependent. At low concentration of 2 µM (102 µg-V/L), only monomeric oxo-vanadate species (\(\text{VO}_2^+, \text{H}_2\text{VO}_4^{2-}, \text{HVO}_4^{2-}\), and \(\text{VO}_4^{3-}\)) were present (Figure S4.1A). As concentration increased from 2 to 20 µM (102 to 1020 µg-V/L), a small portion of \(\text{H}_2\text{VO}_4^-\) dimerized into \(\text{H}_2\text{V}_2\text{O}_7^{2-}\) in the pH range from 3 to 9 (Figure S4.1B). A further increase of the concentration to 0.2 and 2 mM promoted the oligomerization of monomeric species into dimers (\(\text{V}_2\)), tetraters (\(\text{V}_4\)), pentamers (\(\text{V}_5\)), and decamers (\(\text{V}_{10}\)) (Figure S4.1C and Figure S4.1D). Vanadium(V) at near neutral pHs existed as a mixture of \(\text{H}_2\text{VO}_4^-, \text{V}_2, \text{V}_4, \text{V}_5, \text{V}_{10}\) in equilibrium. To create a regime where only one species predominated at a targeted pH, we further increased vanadium(V) concentration to 20 mM, at which the predominant vanadium(V) species was \(\text{VO}_2^+, \text{V}_{10}, \text{V}_4, \text{HVO}_4^{2-}\) at pH 1, 4, 7 and 11, respectively (Figure S4.1E).

As pH and vanadium concentration change, monomeric vanadate \(\text{V}_1\) can undergo condensation reactions to form dimers \(\text{V}_2\), tetraters \(\text{V}_4\), pentamers \(\text{V}_5\) and decamers \(\text{V}_{10}\). With an ionic strength of 0.6 M and total vanadium concentration of 20 mM, the predominant vanadium(V) species was cationic \(\text{VO}_2^+\) at pH less than 2 (Figure 4.1 and Figure S4.1E). As pH raised from 2 to 6, \(\text{V}_{10}\) species became predominant. \(\text{V}_{10}\) had a cage-like molecular structure, with two vanadium atoms located in the center, four in the middle, and the remaining four at the edge. As pH increased from 6 to 9, small oligomers of \(\text{V}_4\) species with a cyclic-structure predominated. When pH was higher than 9, \(\text{V}_1\) as \(\text{HVO}_4^{2-}\)
became the major species (Figure 4.1 and Figure S4.1E). The presence of V_2 and V_5 species were insignificant. Therefore, the redox behaviors of VO_2^+, V_{10}, V_4 and HVO_4^{2-} at pHs of 1, 4, 7 and 11 were subsequently examined using EC tools.

**Figure 4.1** Predominance diagram of vanadium(V) species as a function of pH. Total [vanadium(V)] = 20 mM, [NaClO_4] = 0.6 M, and ionic strength = 0.6 M. V_{10} is a combination of H_3V_{10}O_{28}^{3-}, H_2V_{10}O_{28}^{4-}, NaHV_{10}O_{28}^{4-}, Na_2V_{10}O_{28}^{4-}, HV_{10}O_{28}^{5-} and NaV_{10}O_{28}^{5-}; V_5 is V_5O_{15}^{5-}; V_4 is a combination of V_4O_{12}^{4-} and HV_4O_{13}^{5-}; V_2 is a combination of H_2V_2O_7^{2-} and HV_2O_7^{3-}; V_{1} is a combination of H_2VO_4^-, HVO_4^{2-} and VO_4^{3-}.

**4.4.2 Electrochemical reduction of vanadium(V) species**

To examine the redox properties of four vanadium(V) species and their reduction products, CV at different scan rates was first conducted with a static gold disk electrode. Compared to the background electrolyte, both the cathodic reduction current from vanadium(V) species and the anodic oxidation current from their reduction products increased with the scan rates in vanadium(V)-containing solutions (Figure 4.2). A well-defined peak was observed at 0.40, -0.53, -0.76 and -1.15 V, corresponding to the EC reduction of VO_2^+, V_{10}, V_4 and HVO_4^{2-}, respectively (Figure 4.2). As the solution pH
increased, the onset reduction potential shifted negatively from 0.65 to -0.67 V, suggesting that the thermodynamic feasibility to reduce vanadium(V) followed the order of $\text{VO}_2^+ > \text{V}_{10} > \text{V}_4 > \text{HVO}_4^{2-}$. Increasing the scan rates caused negative and positive shifts of cathodic and anodic peaks, respectively, because faster scan rates shortened the time for electron transfer between vanadium species and the electrode surface. Consequently, a higher overpotential was required to accelerate the reaction kinetics to observe a current response, which caused the shift of both cathodic and anodic peaks. The reduction peak current was linearly correlated with the square root of the scan rate at the static disk electrode (Figure S4.3). This suggested that electrochemical reduction of vanadium(V) was diffusion-controlled in the static condition.\textsuperscript{41}

As the disk electrode started to rotate with a rate from 400 to 2700 rpm, the cathodic current on disk electrode increased (Figure 4.3). This suggested that mass transfer limitation was involved in vanadium(V) EC reduction on the disk electrode. Specifically, disk currents corresponding to the reduction of $\text{VO}_2^+$ started to increase at 0.60 V and plateaued at 0.25 V. With an increase of rotation speed, the disk current in the plateau region increased by 157%, and the ring electrode current exhibited a similar trend (Figure 4.3A). For $\text{V}_{10}$ species, disk and ring electrode currents gradually increased from a disk potential of 0.21 V and reached the maximum value at -0.54 V, followed by a drop at a more negative potential. An increase of rotation speed enhanced the EC current by 113% (Figure 4.3B). The current drop was likely due to a strong interaction between the $\text{V}_{10}$ reduction products and the gold electrode. As the electrode potential became increasingly
negative, fast reduction kinetics led to an accumulation of vanadium products on the electrode, and consequently, less electrode surface was available for electron transfer.

**Figure 4.2** Cyclic voltammetry of vanadium (V) species on a gold disk electrode. Total [vanadium(V)] = 20 mM, [NaClO₄] = 0.6 M, ionic strength = 0.6 M, scan rate = 50 mV/s, and dashed lines represent the voltammograms of background electrolyte at 200 mV/s. Cyclic scan on the electrode started in the cathodic direction followed by the anodic direction.

Disk electrode current of V₄ reduction increased from a disk potential of -0.21 V and reached a limiting current at -0.74 V (**Figure 4.3C**). The reduction current of V₄ increased by 17%, while the ring current remained nearly constant with varying rotation speed. For HVO₄²⁻, it exhibited a disk peak centered at -1.15 V which increased by 54% as the rotation speed increased (**Figure 4.3D**). The ultimate reduction product of HVO₄²⁻ was VO(OH)₃⁻ (Figure S4.2). At potentials more negative than -1.15V, a fast reduction of HVO₄²⁻ could
accumulate adsorbed VO(OH)$_3^-$ on the electrode surface, which inhibited the further reduction of HVO$_4^{2-}$ and reduced the disk current (Figure 4.3D). Furthermore, the maximum disk current of $V_4$ was more than one order of magnitude smaller than that of other species (Figure 4.3C), indicating that $V_4$ was the least electrochemically active.

**Figure 4.3** Linear sweep voltammetry of vanadium(V) species on a rotating gold ring-disk electrode. Total [vanadium(V)] = 20 mM, [NaClO$_4$] = 0.6 M, ionic strength = 0.6 M, and scan rate = 50 mV/s. Ring electrode potential was fixed at 1.3, 1.0, 0.8, and 0.7 V for VO$_2^+$, V$_{10}$, $V_4$ and HVO$_4^{2-}$, respectively. Dashed lines represent the linear sweep voltammetry of background electrolyte at 50 mV/s.

4.4.3 Reduction kinetics and electron transfer of vanadium(V) species

The kinetics and electron-transfer mechanism of vanadium(V) reduction reactions were investigated based on the CV and RRDE results. The mixed kinetic-diffusion regime
for vanadium redox reactions on the rotating disk electrode were analyzed based on the Koutecky-Levich method (Equation 1):

\[
\frac{1}{i} = \frac{1}{i_K} + \frac{1}{i_D} = \frac{1}{i_K} + \frac{1}{0.62nFA(D)^{2/3}(\omega)^{1/2}(\nu)^{-1/6}C_0}
\]  

(1)

where \( i \) is the current measured on the disk electrode (A), \( i_K \) represents the kinetic current in the absence of diffusion limitation (A), \( i_D \) is the diffusion current (A), \( n \) is electron-transfer number of vanadium(V) reduction, \( F \) is Faradic constant (C/mol), \( A \) is the electrode surface area (cm\(^2\)), \( D \) is the diffusion coefficient (cm\(^2\)/s), \( \omega \) is angular frequency of the rotation (s\(^{-1}\)), \( \nu \) is the kinematic viscosity (cm\(^2\)/s), and \( C_0 \) is the bulk concentration (mol/cm\(^3\)).

Koutecky-Levich plots of RRDE data showed that the reciprocal current (\(1/i\)) was linearly correlated with \((\omega)^{-1/2}\), indicating that vanadium(V) reduction was diffusion limited (Figure 4.4). The slope of the plots was \(1/(0.62nFA(D)^{2/3}(\omega)^{1/2}(\nu)^{-1/6}C_0)\), and the intercept corresponded to the kinetic current in the absence of diffusion limitation. Electron-transfer number of each vanadium(V) species was calculated based on Koutecky-Levich plots and the correlation of reduction peak current vs. square root of scan rates from CV curves (Text S4.2).

Calculation showed that the first step of EC reduction of \( \text{VO}_2^+ \), \( \text{V}_4 \), and \( \text{HVO}_4^{2-} \) was approximately one-electron transfer process, while \( \text{V}_{10} \) reduction was approximately two-electron transfer process (Table 4.1). Prior studies showed that \( \text{V}_{10} \) was partially reduced by ascorbate and Fe(II) via a two-electron transfer process and maintained its cage-like original structure.\(^{29,30,42}\) The EC-calculated electron-transfer number of \( \text{V}_{10} \) reduction was
smaller than two \((n=1.5)\), because the reduction current was likely impacted by strong interaction between vanadium reduction products and electrode surface. This was supported by a decrease of reduction current at high overpotentials, \(i.e.,\) the difference between applied potential and onset reduction potential (Figure 4.3B).

**Figure 4.4** Koutecky-Levich plots of vanadium(V) reduction on a rotating gold ring-disk electrode. Total [vanadium(V)] = 20 mM, \([\text{NaClO}_4]\) = 0.6 M, ionic strength = 0.6 M, scan rate = 50 mV/s, and current at different rotation speeds was taken at 0.10, -0.54, -0.74, and -1.15 V for \(\text{VO}_2^+\), \(\text{V}_{10}\), \(\text{V}_4\) and \(\text{HVO}_4^{2-}\), respectively.

Based on the calculated electron-transfer number (Table 4.1) and predicted vanadium(IV) speciation (Figure S4.2), the EC reduction reactions of four vanadium(V) species are described as follows:

\[
\text{VO}_2^+ + e^- + 2H^+ \leftrightarrow \text{VO}^{2+} + H_2O \quad \quad \text{(2)}
\]

\[
\text{HV}_{10}^{V} \text{O}_{28}^{5-} + 2e^- \leftrightarrow \text{HV}_{9}^{W} \text{V}_{2}^{IV} \text{O}_{28}^{7-} \quad \quad \text{(3)}
\]

\[
\text{V}_{4}^{4} \text{O}_{12}^{4-} + e^- + 4H_2O \leftrightarrow \text{VO(OH)}_3^3^- + H_2\text{V}_2\text{O}_7^{2-} + H_2\text{VO}_4^- + OH^- \quad \quad \text{(4)}
\]
\[ \text{HVO}_4^{2-} + e^- + 2H_2O \leftrightarrow \text{VO(OH)}_3^- + 2OH^- \] (5)

The diffusion coefficient of vanadium(V) species was further calculated using Levich equation (Text S4.2), and it followed the order of \( V_{\text{III}} > \text{VO}_2^+ > V_4 > \text{HVO}_4^{2-} \) (Table 4.1). This difference was associated with the limiting ionic equivalent conductivity and ionic charge of vanadium(V) in the solution.\(^{43}\)

**Table 4.1** Summary of electron transfer number, intrinsic rate constants, and diffusion coefficients of vanadium (V) species and half-lives of their reduction products on the gold ring-disk electrode.

<table>
<thead>
<tr>
<th>pH</th>
<th>Vanadium(V) Species</th>
<th>Electron-transfer Number</th>
<th>Diffusion coefficient (cm(^2)/s)</th>
<th>Intrinsic rate constant (cm/s)</th>
<th>Half-life of reduction products (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>VO(_2^+)</td>
<td>1.0</td>
<td>5.8 \times 10^{-6}</td>
<td>3.6 \times 10^{-5}</td>
<td>3.5</td>
</tr>
<tr>
<td>4</td>
<td>V(_{\text{III}})</td>
<td>1.5</td>
<td>5.8 \times 10^{-5}</td>
<td>2.6 \times 10^{-3}</td>
<td>213</td>
</tr>
<tr>
<td>7</td>
<td>V(_4)</td>
<td>0.9</td>
<td>1.5 \times 10^{-6}</td>
<td>2.5 \times 10^{-5}</td>
<td>0.08</td>
</tr>
<tr>
<td>11</td>
<td>HVO(_4^{2-})</td>
<td>1.1</td>
<td>4.7 \times 10^{-7}</td>
<td>3.1 \times 10^{-6}</td>
<td>1.4</td>
</tr>
</tbody>
</table>

To gain insight into electron-transfer process involving vanadium(V) reduction at the gold electrode, the intrinsic rate constants \( k_0 \) were calculated based on Butler-Volmer electrode kinetics. \( k_0 \) represents the reduction kinetics of vanadium(V) species in the absence of an overpotential and indicates electron-transfer feasibility between vanadium(V) species and electrode. \( k_0 \) is associated with the rate constant at a targeted overpotential \( k \) and charge transfer coefficient \( \alpha \):\(^{41}\)

\[
k_0 = k / \exp \left( -\frac{\alpha F \eta}{RT} \right)
\] (6)
η is the overpotential applied on the electrode, R is the ideal gas constant, and T is the temperature. k was calculated through Koutecky-Levich plots of RRDE data at targeted overpotentials (Text S4.3 and Figures S4.4-S4.5). α was obtained through Tafel analysis of RRDE data at high rotation speeds (Text S4.3 and Figures S4.6-S4.7). α represents the fraction of the total energy change on the electrode that applied to lower the reduction barrier of vanadium(V) species.\textsuperscript{41} Calculations showed that V\textsubscript{10} had the highest intrinsic rate constant, which was two orders of magnitude larger than those of VO\textsubscript{2}\textsuperscript{+} and V\textsubscript{4}, and three orders of magnitude larger than that of HVO\textsubscript{4}\textsuperscript{2-} (Table 4.1).

According to Marcus Theory, the intrinsic rate constant is associated with the interaction of vanadium(V) with electrode surface and the reorganization of vanadium molecules during the reduction reaction.\textsuperscript{41} V\textsubscript{10} had cage-like superstructure with interactive vanadium atoms linked through oxygen atoms, which favored the electron transfer. This structure was not available in VO\textsubscript{2}\textsuperscript{+}, V\textsubscript{4} and HVO\textsubscript{4}\textsuperscript{2-}.\textsuperscript{44} In addition, V\textsubscript{10} underwent much smaller configuration change than the other three species, during the reduction process which also contributed to its largest intrinsic rate constants (Reaction 2-5).\textsuperscript{28, 30, 42} Prior study also showed that decavanadate was more active to stimulate NADH oxidation than metavanadate (V\textsubscript{4} dominated) because of fast electron-transfer kinetics in cage-like superstructure.\textsuperscript{31} The di-oxo ligands in VO\textsubscript{2}\textsuperscript{+} and the cyclic structure of V\textsubscript{4} likely made vanadium atoms more intrinsically reducible than that in HVO\textsubscript{4}\textsuperscript{2-}. Consequently, both species had larger intrinsic rate constants than HVO\textsubscript{4}\textsuperscript{2-} (Table 4.1).
4.4.4 Re-oxidation and stability of vanadium(IV) products

The nature of vanadium(IV) intermediate products from the reduction of VO$_2^+$, V$_{10}$, V$_4$ and HVO$_4^{2-}$ was further examined by their collection efficiency on the ring electrode. The vanadium(IV) products was convectively transported from the disk to the ring electrode and re-oxidized. The collection efficiency was calculated as the ratio of oxidation current of vanadium(IV) products on the ring electrode and reduction current of vanadium (V) on the disk electrode (Scheme 4.1). Results showed that the collection efficiency increased with the ring electrode potential until it reached a plateau, beyond which the oxidation of vanadium(IV) products on the ring electrode was not limited by kinetics (Figure 4.5). The onset ring electrode potential in response to a discernible collection efficiency represents the thermodynamic oxidation potential of vanadium(IV) products, i.e., a smaller onset ring electrode potential corresponded to a lower thermodynamic barrier. Based on the correlation of collection efficiency with ring electrode potential, the reduction product of HVO$_4^{2-}$ was thermodynamically more easily to be re-oxidized than that of V$_{10}$, followed by V$_4$ and VO$_2^+$. Furthermore, the maximal collection efficiency correlated with the stability of vanadium(IV) intermediate products, and their half-lives were subsequently calculated (Text S4.4). The maximum collection efficiency of vanadium(IV) products of VO$_2^+$, V$_{10}$, V$_4$ and HVO$_4^{2-}$ was 22.4%, 23.3%, 4.3% and 17.1%, respectively (Figure S4.8). The half-life of their reduction products was 3.5, 213, 0.08, and 1.4 seconds, respectively (Table 4.1). Partially reduced V$_{10}$ had a half-life of minutes for re-oxidation. V$_4$ had the most redox active and unstable reduction product, which quickly decayed within milliseconds.
Figure 4.5 Impact of ring electrode potential on the collection efficient of the intermediate products produced on the gold disk electrode. Total [vanadium(V)] = 20 mM, [NaClO₄] = 0.6 M, ionic strength = 0.6 M, rotation speed = 2400 rpm, and scan rate = 50 mV/s.

4.4.5 Impact of phosphate on the reduction of vanadium(V) species

The formation constant between vanadium(V) and phosphate is sufficiently high that the impact of phosphate present in water matrices on the redox properties of vanadium should be considered. To quantify the impact of phosphate on the reduction kinetics of vanadium(V) species, EC reduction rate constants of four vanadium(V) species \((k)\) were calculated from the RRDE data at different phosphate concentrations (Text S4.3). The results showed that the presence of phosphate accelerated the reduction kinetics of \(V_{10}\) and \(V_4\), but had a minimal impact on that of \(VO_2^+\) and \(HVO_2\) \(^2^-\) (rate constant \(k\) in Table 4.2). As molar ratios of phosphate to vanadium(V) increased from 0 to 1, the EC reduction rate constants of \(V_{10}\) and \(V_4\) increased by 53\% and 150\%, respectively, whereas those of \(VO_2^+\) and \(HVO_2\) \(^2^-\) remained relatively constant (rate constant \(k\) in Table 4.2).
Table 4.2 The impact of molar ratios of phosphate to vanadium(V) ([PO₄]/[V(V)]) on the kinetic parameters of vanadium(V) species on the rotating gold ring-disk electrode. *k₀*: intrinsic rate constants; *α*: charge transfer coefficients; *k*: rate constants of VO₂⁺, V₁₀, V₄ and HVO₄²⁻ at 0.45, -0.26, -0.30, and -1.10 V, respectively; [PO₄] = 0, 1, 5, 10 and 20 mM, [V(V)] = 20 mM.

<table>
<thead>
<tr>
<th>[PO₄]/[V(V)]</th>
<th>VO₂⁺</th>
<th></th>
<th></th>
<th>V₁₀</th>
<th></th>
<th></th>
<th></th>
<th>V₄</th>
<th></th>
<th></th>
<th>HVO₄²⁻</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><em>k₀</em> (cm/s)</td>
<td><em>α</em></td>
<td><em>k</em> (cm/s)</td>
<td><em>k₀</em> (cm/s)</td>
<td><em>α</em></td>
<td><em>k</em> (cm/s)</td>
<td><em>k₀</em> (cm/s)</td>
<td><em>α</em></td>
<td><em>k</em> (cm/s)</td>
<td><em>k₀</em> (cm/s)</td>
<td><em>α</em></td>
<td><em>k</em> (cm/s)</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>3.6×10⁻⁵</td>
<td>0.59</td>
<td>3.9×10⁻¹</td>
<td>2.6×10⁻³</td>
<td>0.08</td>
<td>1.4×10⁻²</td>
<td>2.5×10⁻⁵</td>
<td>0.23</td>
<td>9.8×10⁻⁵</td>
<td>3.1×10⁻⁶</td>
<td>0.30</td>
<td>4.8×10⁺⁴</td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>4.1×10⁻⁵</td>
<td>0.59</td>
<td>4.3×10⁻¹</td>
<td>2.3×10⁻³</td>
<td>0.10</td>
<td>1.9×10⁻²</td>
<td>3.6×10⁻⁵</td>
<td>0.21</td>
<td>1.2×10⁻⁴</td>
<td>1.2×10⁻⁶</td>
<td>0.36</td>
<td>5.1×10⁻⁴</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>5.2×10⁻⁵</td>
<td>0.58</td>
<td>4.8×10⁻¹</td>
<td>6.9×10⁻⁴</td>
<td>0.16</td>
<td>1.9×10⁻²</td>
<td>3.4×10⁻⁵</td>
<td>0.18</td>
<td>1.0×10⁻⁴</td>
<td>1.1×10⁻⁶</td>
<td>0.36</td>
<td>4.8×10⁻⁴</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>4.2×10⁻⁵</td>
<td>0.59</td>
<td>4.4×10⁻¹</td>
<td>5.5×10⁻⁴</td>
<td>0.18</td>
<td>2.2×10⁻²</td>
<td>6.6×10⁻⁵</td>
<td>0.19</td>
<td>2.1×10⁻⁴</td>
<td>1.0×10⁻⁶</td>
<td>0.36</td>
<td>4.3×10⁻⁴</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3.5×10⁻⁵</td>
<td>0.60</td>
<td>3.7×10⁻¹</td>
<td>5.6×10⁻⁴</td>
<td>0.18</td>
<td>2.2×10⁻²</td>
<td>9.8×10⁻⁵</td>
<td>0.18</td>
<td>2.8×10⁻⁴</td>
<td>1.6×10⁻⁶</td>
<td>0.33</td>
<td>4.8×10⁻⁴</td>
<td></td>
</tr>
</tbody>
</table>
To gain insight into phosphate impact on the rate constants \( (k) \) of vanadium(V) species, the intrinsic rate constant \( (k_0) \) and charge transfer coefficient \( (\alpha) \) were further calculated. Based on Bulter-Volmer electrode kinetics, \( k \) at targeted potentials is associated with \( k_0 \) and \( \alpha \) (Equation 6). Increasing \( k_0 \) and \( \alpha \) can promote the electron transfer between vanadium(V) and electrode, lower the reduction barrier, and consequently accelerate the reduction kinetics of vanadium(V) species.\(^{41}\) Calculation showed that the increase of molar ratios of phosphate to vanadium(V) from 0 to 1 had a negligible impact on \( k_0 \) and \( \alpha \) of \( \text{VO}_2^+ \), and thus its reduction rate constants \( k \) was nearly unchanged (Table 4.2 and Figure S4.9A). On the contrary, varying molar ratios of phosphate to vanadium(V) from 0 to 1 increased \( \alpha \) of \( \text{V}_{10} \) by 125%, which was consistent with the observed enhancement in \( \text{V}_{10} \) reduction kinetics at \(-0.26\) V (Table 4.2 and Figure S4.9B). Phosphate prominently increased \( k_0 \) of \( \text{V}_4 \) by 4 times, which accounted for the enhanced reduction kinetics of \( \text{V}_4 \) at \(-0.30\) V (Table 4.2 and Figure S4.9C). The presence of phosphate decreased \( k_0 \) but increased \( \alpha \) of \( \text{HVO}_4^{2-} \). Consequently, the overall effects of \( k_0 \) and \( \alpha \) exerted no impact on the reduction rate constants of \( \text{HVO}_4^{2-} \) (Table 4.2 and Figure S4.9D).

The observed phosphate-induced changes on reduction activities of vanadium(V) species were likely associated with vanadium(V)-phosphate complexation. At pH 1, \( \text{H}_3\text{PO}_4 \) (predominant phosphate species, Figure S4.10) was less likely to form complex with \( \text{VO}_2^+ \) via ligand exchange, considering its steric hindrance and reluctance to share electron with vanadium. Therefore, phosphate had a negligible impact on the reduction activity of \( \text{VO}_2^+ \) (rate constant \( k \) in Table 4.2). At pH 4, \( \text{VO}_2^+ \) was polymerized to decavanadate \( \text{V}_{10} \), and \( \text{H}_3\text{PO}_4 \) deprotonated into \( \text{H}_2\text{PO}_4^- \) (Figure 4.1 and Figure S4.10). Prior study reported that
Phosphate was readily incorporated into polyvanadate ions.\textsuperscript{45} $\text{H}_2\text{PO}_4^-$ likely complexed with the decavanadate $\text{V}_{10}$ ions to form anhydrides.\textsuperscript{46} The added phosphate group in the structure tended to pull the electrons away from vanadium atoms, lower their electron density and reduction barrier, and consequently facilitate their electron transfer with electrode surface. Increasing molar ratios of phosphate to vanadium from 0 to 1 promoted phosphate complexation with $\text{V}_{10}$. This led to the formation of more reducible vanadium, and thus increased reduction kinetics of $\text{V}_{10}$ at low overpotentials (rate constant $k$ in Table 4.2).

As pH further increased to 7, $\text{V}_4$ was the main species (Figure 4.1) and in fast exchange with mono- and di-vanadate species at a timescale of milli-seconds.\textsuperscript{47} Previous study indicated that $\text{H}_2\text{PO}_4^-$ and $\text{HPO}_4^-$ promoted the decomposition of $\text{V}_4$ to $\text{H}_2\text{VO}_4^-$ and induced complexation of $\text{H}_2\text{VO}_4^-$ to form anhydrides ($\text{H}_2\text{VPO}_7^{2-}$ and $\text{HVPO}_7^{3-}$).\textsuperscript{45} Phosphate-induced changes on $\text{V}_4$ made vanadium more reducible, and consequently accelerated the reduction kinetics of vanadium(V) as molar ratios of phosphate to vanadate increased from 0 to 1 (rate constant $k$ in Table 4.2).\textsuperscript{45} Phosphate-enhanced reduction kinetics of $\text{V}_{10}$ and $\text{V}_4$ was consistent with prior observation that phosphate catalyzed the oxidation of NADH by polyvanadate in biological systems.\textsuperscript{31} A further increase of pH to 11 induced the hydrolysis of $\text{V}_4$ to $\text{HVO}_4^{2-}$. $\text{HVO}_4^{2-}$ rapidly complexed with $\text{HPO}_4^-$ (the dominant phosphate species, Figure S4.10) to form unstable anhydride.\textsuperscript{45} The weak interaction of phosphate with $\text{HVO}_4^{2-}$ exhibited little impact on the reduction kinetics of $\text{HVO}_4^{2-}$ (rate constant $k$ in Table 4.2).
Furthermore, phosphate affected the stability of vanadium(V) EC reduction products, \( i.e. \), vanadium(IV). As the molar ratio of phosphate to vanadium increased from 0 to 1, ring electrode collection efficiency increased for the reduction products of \( \text{VO}_2^+ \), \( \text{V}_4 \) and \( \text{HVO}_4^{2-} \) but had minimal change for that of \( \text{V}_{10} \) (Figure S4.11). That indicated that phosphate likely stabilized the reduction products of \( \text{VO}_2^+ \), \( \text{V}_4 \), and \( \text{HVO}_4^{2-} \) but had little impact on that of \( \text{V}_{10} \). The reduction products of \( \text{VO}_2^+ \), \( \text{V}_4 \), and \( \text{HVO}_4^{2-} \) were \( \text{VO}^{2+} \), \( \text{VO(OH)}_3^- \), and \( \text{VO(OH)}_3^- \), respectively (Equations 2, 4 and 5). For \( \text{V}_{10} \), partially reduced product with the original cage-like structure (\( \text{HV}_8^\text{V}_{12}^\text{IV}_2^\text{O}_{28}^7^- \)) was generated (Equation 3). Prior study demonstrated that \( \text{VO}^{2+} \) unit could complex with phosphate to form vanadyl-phosphate complexes.\(^{47}\) The strong interaction of \( \text{VO}^{2+} \) with phosphate group in adenosine triphosphate (ATP) inhibited the oxidation of \( \text{VO}^{2+} \). Phosphate also likely coordinated with \( \text{VO}^{2+} \) and \( \text{VO(OH)}_3^- \) to form thermodynamically stable complexes. For partially reduced \( \text{V}_{10} \) (\( \text{HV}_8^\text{V}_{12}^\text{IV}_2^\text{O}_{28}^7^- \)), its intrinsic cage-like structure highly stabilized the reduced vanadium. The data suggested that phosphate had minimal impact on the stability of vanadium(IV) in partially reduced \( \text{V}_{10} \) (\( \text{HV}_8^\text{V}_{12}^\text{IV}_2^\text{O}_{28}^7^- \)).

### 4.5 Environmental Implications and Broader Significance

EC data from this study suggest that the change of vanadium(V) speciation with pH and the presence of phosphate in source water can significantly impact the reactivity of vanadium(V) during the reductive water treatment. Vanadium(V) in acidic wastewater, \( e.g. \), wastewater discharged during the extraction of phosphoric acid from vanadium-enriched phosphorus ores and manufacturing of vanadium pentoxide, is expected to have higher reactivity than wastewater in neutral or alkaline conditions.\(^{48}\) In the aquatic
environment with molar ratios of phosphate to vanadium(V) from 0 to 1, e.g., watersheds with remarkably geological weathering of vanadium-bearing minerals and water bodies contaminated by point discharge of concentrated vanadium wastewater, phosphate can promote the reduction of vanadium(V), and stabilize vanadium(IV) under oxic environment, and consequently inhibit the inadvertently re-occurrence of vanadium(V). Even though the impact of bicarbonate, carbonate, sulfate and natural organic matters (e.g., humic acid) are not examined in this study, they can potentially affect the reduction kinetics and half-lives of the intermediate products due to complexation reactions. These effects will be examined in future work. Considering the biological effect of vanadium(V) and sensitive response from enzymatic activities, interactions of trace-level vanadium(V) and vanadium(IV) species with environment-relevant ligands can also be investigated by a simple and fast enzyme kinetic method in future.\textsuperscript{28}

The EC techniques unveiled the redox nature and stability of vanadium species. Current-potential responses on static and rotating electrode combined with classical EC theories allowed for the study of diffusivity, electron-transfer kinetics, and product stability of aquatic contaminants. Even though the concentration of vanadium(V) employed in this study is much higher than that in drinking water, the fundamental redox behaviors are the same. Furthermore, the EC techniques developed from this study have broader applications that can be extended to examine other toxic and redox-active contaminants, e.g., chromate, selenate and halogenated organics. The intrinsic kinetic and thermodynamic nature of electron transfer processes involving these contaminants obtained from EC tools can guide the design of efficient treatment units to minimize their presence in drinking water.
4.6 Acknowledgement

The study was supported by U.S. National Science Foundation CAREER Program (CBET- 1653931) and Early-concept Grants for Exploratory Research Program (CBET-1619915). We thank Dr. Juchen Guo at UC Riverside for suggestions on the data analysis.
References


46. Williams, R. J., Metal ions in biological systems. *Biological Reviews* 1953, 28 (4), 381-412.


48. Zhang, B.; Feng, C.; Ni, J.; Zhang, J.; Huang, W., Simultaneous reduction of vanadium (V) and chromium (VI) with enhanced energy recovery based on microbial fuel cell technology. *J. Power Sources* 2012, 204, 34-39.
Chapter 5

Photochemical Removal of Cr(VI) and Nitrate in Spent Ion-exchange Regenerant Brine

In preparation for Submission

Chen, G. & Liu, H.
5.1 Abstract

The accumulation of Cr(VI) and nitrate renders the spent ion-exchange (IX) regenerant brine as hazardous waste and challenging for disposal. This study investigated photochemical reduction of Cr(VI) and nitrate in the spent brine by utilizing the photochemistry of nitrate and reductive carbon-centered radicals. Under UV irradiation, nitrate in spent brine generated highly reactive intermediates (e.g., HO· and NO₂⁻) that oxidized formate or alcohols into carbon-centered radicals (e.g., CO₂⁺, ·CH₂OH, CH₃·CHOH, and (CH₃)₃·COH). CO₂⁺ had the most negative standard reduction potential and exhibited the highest reduction efficiency for Cr(VI). Increasing the dosage of formate promoted the formation of CO₂⁺ and accelerated the reduction kinetics of Cr(VI). Despite that the post pH adjustment is required to induce the precipitation of Cr(OH)₃ solids, acidic pH favored photochemical reduction of Cr(VI) mainly because of the enhanced production of CO₂⁺, reduced scavenging effects from CO₃²⁻, and the formation of more reducible HCrO₄⁻. Ionic strength exhibited no adverse effect on Cr(VI) reduction because of homogenous reaction mechanism. Chloride prominently inhibited the reduction of Cr(VI) via transforming NO₂⁻ into less reactive NO⁻ and Cl₂⁻. Co-removal of Cr(VI) and nitrate was achieved at acidic pHs with an extended reaction time. Outcome of this study provided IX process an alternative treatment technology for the disposal and reuse of hazardous brine waste.
5.2 Introduction

Hexavalent chromium (Cr(VI)) and nitrate are widely occurred in groundwater because of natural occurring and anthropogenic activities.\textsuperscript{1, 2} Statistics on oxyanions in drinking water wells shows strong positive correlation between Cr(VI) and nitrate, indicating their cooccurrence in groundwater.\textsuperscript{1} The toxicity and ecological impacts require their removal from water. Ion exchange has been demonstrated as a promising process to remove toxic oxyanions from groundwater given its effectiveness, operational simplicity, and large processing capacity.\textsuperscript{3-5} Prior studies have shown that strong-base anion exchange (SBA-IX) can effectively remove Cr(VI) and nitrate from groundwater because quaternary amine groups on the resin remain positively charged in wide pH ranges and have great affinity and capacity to bind negatively charged oxyanions.\textsuperscript{4, 6} Even though the concentration of Cr(VI) is usually much lower than that of nitrate in groundwater, regenerable anion exchange resins has much higher affinity toward Cr(VI) than nitrate.\textsuperscript{7} The combing effect causes the co-removal of Cr(VI) and nitrate from groundwater in IX processes. Frequent regeneration of exhausted resins produces a large quantity of Cr(VI)- and nitrate-laden brine. The accumulation of Cr(VI) greater than 5 mg/L renders the spent brine as hazardous waste, which make the direct disposal costly and unsustainable.\textsuperscript{4, 8} Management of hazardous brine has posed great challenges to implement IX process particularly at locations lack access to brine line or far from oceans.

To make IX process economically viable and sustainable, onsite brine treatment has been studied to integrate with IX process. This process can help reduce the quantity of hazardous waste, reuse of the treated brine for resin regeneration, and reduce the regenerant
salt consumption and discharge into environment.\textsuperscript{9} Existing treatment technologies for Cr(VI)- and nitrate-laden brine include chemical and catalytic reduction and biological removal.\textsuperscript{3, 4, 10, 11} Transformation of Cr(VI) and nitrate in spent brine is very challenging because brine has much higher salinity, alkalinity and ionic strength, compared with groundwater. The existing approaches, although functional, confront various challenges. For instance, catalytic reduction processes suffer from passivation effect of high levels of chloride and sulfate in IX brine\textsuperscript{11} Biological approaches require salinity-tolerant microorganisms and suffers from slow reaction kinetics.\textsuperscript{3, 12} Although chemical reduction can effectively remove Cr(VI) and make spent brine nonhazardous, this process generate a large quantity of waste sludge that required further disposal.\textsuperscript{13, 14}

Aliphatic carbon-centered radicals (e.g, CO$_2$·, ·CH$_2$OH, etc.), typically produced by hydrogen abstraction from carboxylate and alcohols, are strong reducing agents.\textsuperscript{15-17} Thermodynamically, they can reduce Cr(VI) and nitrate due to their negative reduction potentials.\textsuperscript{15} Prior study has proved that CO$_2$· generated from formate in heat-activated persulfate system effectively reduced Cr(VI) into Cr(III).\textsuperscript{18} In Chapter 3, CO$_2$· was produced by partial oxidation of formate with reactive radical species (e.g., HO· and NO$_2$·) from nitrate photolysis. The reduction induced by CO$_2$· integrated with photolysis of nitrate rendered a reductive transformation of nitrate into gas-phase nitrogen. Given the coexistence of Cr(VI) and nitrate in the spent IX brine and unique photochemistry of nitrate, UV irradiation of spent IX brine in the presence of formate or alcohols can potentially remove of Cr(VI) and nitrate concurrently. The elimination of solid catalysts and microorganisms avoids the issues associated with heterogeneous catalysis and
biological processes. In addition, the formed carbon-centered radicals are eventually mineralized into carbon dioxide, which reduce the production of hazardous sludge, compared with chemical reduction. Despite the promising application potentials, this process has not been studied for IX brine treatment.

In this chapter, photochemical reduction of Cr(VI) in spent IX brine was investigated with different carbon-centered radicals. The effects of formate dosage, ionic strength, pH, and major inorganic constituents (i.e., Cl⁻, SO₄²⁻, and HCO₃⁻) were examined on the reduction Cr(VI). The co-removal of Cr(VI) and nitrate was assessed in authentic IX brine.

5.3 Materials and Methods

5.3.1 Collection of spent IX regenerant brine

Spent brine waste was collected from a full-scale SBA-IX system that treated groundwater from a drinking well in California. Specifically, SBA-IX resin (Purolite A600E 9149, 2016) was utilized in a vessel with empty bed contact time of 2.4 min and hydraulic loading rate of 522 L min⁻¹ m⁻². The average concentrations of total chromium and nitrate in groundwater are 17.4 µg/L and 3.1 mg-N/L, respectively. As total chromium in effluent exceeded 10 µg/L, the resin was regenerated with 3 bed volumes of 2 M NaCl in softened groundwater followed by 3 bed volumes of softened groundwater for rinse. The combined waste solution was spent IX regenerant brine for treatment.

5.3.2 Photochemical experiments

Batch experiments of photochemical treatment of spent brine were conducted in 10-mL quartz tubes rotating around a 450 W medium-pressure UV lamp (Ace Glass, Inc.).
The lamp emitted photons mainly between 200 to 850 nm (Figure S5.1) with a total light intensity of 66 mW/cm² at the position of the quartz tubes. Prior to UV irradiation, 8 mL of spent IX brine (chemical composition in Table 5.1) was transferred to one quartz tube and spiked with a rather small volume of concentrated stock solutions of formate or alcohol (methanol, ethanol, or isopropanol) to make final formate or alcohol concentration ranging from 5 to 160 mM. To start an experiment, the reaction solution was exposed to UV irradiation. At predetermine time intervals, one sacrificial tube was taken out of photochemical reactor for further analysis. In the experiments to study the impact of pH, ionic strength, and major inorganic constituents, synthetic water matrices containing nitrate (45 mM), NaCl (0 - 2M), Na₂SO₄ (0 - 0.2 M), and NaHCO₃ (0 - 44 mM) were used. The solution pH was controlled between 3 and 11 by 100 mM phosphate buffer or borate buffer. The ionic strength of solution was adjusted by NaClO₄ (0 - 2 M) and maintained the same except the experiment to examine the impact of ionic strength.

5.3.3 Sample analysis

Prior to analysis, the sample was filtered by 0.2-µm PVDF membranes. The concentration of Cr(VI) was analyzed by the standard 1,5-diphenylcarbazide (DPC) method. The concentrations of nitrate, nitrite, and formate were analyzed by ion chromatography (DX-120, Thermo Fisher Scientific) with an anion column (Dionex Ion Pac AS22) and a conductivity detector. The eluent contained 4.5 mM NaHCO₃ and 1.4 mM Na₂CO₃ and had a flow rate of 0.86 mL/min. For solution with high levels of chloride, nitrite was analyzed by colorimetric methods with sulfanilamide and N-(1-naphtyl)-ethylenediamine dihydrochloride because the chromatographic peak of chloride strongly
interferes with that of nitrite. Total organic carbon and total nitrogen were analyzed by a TOC analyzer with nitrogen measurement module (Aurora 1030C). Total chromium concentration was analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, Agilent 7700 Series).

5.4 Results and Discussion

5.4.1 Water chemistry of spent IX brine

The spent brine from full-scale IX processes contained higher levels of toxic substances (e.g., chromium, nitrate, vanadium, etc.) and common water constituents (i.e., sulfate and chloride, Table 5.1), compared with raw groundwater. The spent brine is hazardous because the concentration of chromium (i.e., 34.1 mg/L) highly exceeds California hazardous soluble threshold limit concentrations (5 mg/L, Table 5.1). Despite the weak affinity on the resins, nitrate and sulfate were also accumulated in the spent brine because their concentrations in source water are much higher than chromium. After resin regeneration process, most of the chloride in the fresh brine was remained in the spent waste. Total organic matter in the spent brine was enriched up to 97.5 mg-C/L although its levels is negligible in the source groundwater.
Table 5.1 Composition of full-scale ion exchange spent brine and California Hazardous Soluble Threshold Limit Concentrations (STLC)

<table>
<thead>
<tr>
<th>Species</th>
<th>Chromium (mg/L)</th>
<th>Arsenic (mg/L)</th>
<th>Selenium (mg/L)</th>
<th>Vanadium (mg/L)</th>
<th>Uranium (mg/L)</th>
<th>Sulfate (mg/L)</th>
<th>Chloride (mg/L)</th>
<th>Nitrate (mg/L)</th>
<th>TOC (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>34.1</td>
<td>0.2</td>
<td>0.9</td>
<td>5.6</td>
<td>3.3</td>
<td>18,000</td>
<td>49,300</td>
<td>2945</td>
<td>97.5</td>
</tr>
<tr>
<td>STLC (mg/L)</td>
<td>5.0 *</td>
<td>5.0</td>
<td>1.0</td>
<td>24</td>
<td>0.05% by weight *</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*STLCs for both total chromium and Cr(VI) are 5 mg/L
*Nuclear regulatory commission low-level radioactive waste classification
UV-vis absorption spectrum shows that the spent brine has three major absorption bands: near 200 nm, 250-300 nm, and 320-400 nm (Figure 5.1). Optical spectra of the solutions with Cr(VI) and nitrate at the same levels as spent brine was utilized to deconvolute the overall absorption spectrum. The results showed that nitrate mainly contributed to the strong absorption near 200 nm. Cr(VI) resulted in the absorption band between 320 to 400 nm and partially contributed to the absorption between 250 and 300 nm. The unaccounted UV absorption beside that from Cr(VI) and nitrate was mainly due to the dissolved organic matters. The specific UV absorbance at 254 nm is 1.2 L/(mg-C·m), indicating low degree of aromaticity of organic matters accumulated in the spent brine.20

![Image](image_url)

**Figure 5.1** UV-vis absorption spectra of the spent IX regenerant brine and its major constituents.
5.4.2 Photochemical reduction of Cr(VI) in the spent brine

Figure 5.2 Photochemical reduction of Cr(VI) in the spent IX regenerant brine in the presence of different organic electron donors. [Formate] = [Methanol] = [Ethanol] = [Isopropanol] = 40 mM

Chromium predominantly exists as Cr(VI) in the spent brine. At alkaline pH (i.e., 8.6), the major speciation of Cr(VI) was CrO$_4^{2-}$. Transformation of CrO$_4^{2-}$ to sparingly soluble Cr(OH)$_3$ solids with subsequent filtration could remove chromium from spent brine and make it nonhazardous. Herein, photochemical reduction of Cr(VI) in the spent brine was investigated in the presence of formate and different alcohols. The results showed that Cr(VI) was removed much faster in the presence of formate than alcohols (Figure 5.2). Negligible reduction of Cr(VI) was observed in the absence of formate or alcohols. That indicated that the reduction of Cr(VI) demanded external electron donors and formate was better than three alcohols. Under UV irradiation, nitrate in the spent brine underwent photolysis and generated reactive radicals (e.g., HO· and NO$_2$·) that abstracted one hydrogen atom from formate or alcohols to form reductive carbon-centered radicals (i.e.,
CO_2^·, ·CH_2OH, CH_3ċHOH, and (CH_3)_3ċOH). The rate between HO· and HCOO^· (3.2×10^9 M^-1s^-1) is larger than that between HO· and alcohols (8.3×10^8 - 1.6×10^9 M^-1s^-1), which favored faster formation of CO_2^· than other carbon-centered radicals. In addition, the standard reduction potential of CO_2^· (E^o(CO_2/CO_2^·) = -1.90 V) is more negative than that of other carbon-centered radicals (E^0(HCHO/-CH_2OH) = -1.18 V, E^0(CH_3CHO/-CH_3ċHOH) = -1.25 V, and E^0((CH_3)_2CO/(CH_3)_3ċOH) = -1.39 V). Based on Marcus electron-transfer theory, more negative reduction potential of CO_2^· could render lower activation barrier between CO_2^· and CrO_4^{2-} than that between other carbon-centered radical and CrO_4^{2-}. These two factors probably caused faster reduction of Cr(VI) in the presence of formate than alcohols. In the following study, formate was chosen as the electron donor for Cr(VI) and nitrate reduction.

5.4.3 Impact of formate dosage

The impact of formate dosage on photochemical removal of chromium was investigated in the spent IX brine. As formate dosage increased from 5 to 120 mM, the reduction kinetics of Cr(VI) was dramatically accelerated (Figure 5.3). For instance, 120 minutes was required to reduce less than 20% of Cr(VI) in the presence of 5 mM formate, while only 40 minutes was required to completely reduce Cr(VI) in the presence of 120 mM formate. A similar trend was also observed for the removal of total chromium. With a formate dosage between 40 and 120 mM, the concentration of total chromium was reduced below regulatory standards (i.e., 5 mg/L) within 90 minutes (Figure S5.2). The reduction of total chromium over time indicated that Cr(VI) was transformed into Cr(OH)_3 solids and filtered out of solution. Formate at high dosages efficiently captured the reactive radicals
from nitrate photolysis, enhanced the production of CO$_2^-$, and consequently accelerated removal of chromium.

**Figure 5.3** Impact of formate dosage on photochemical reduction of Cr(VI) in the spent IX regenerant brine. [Formate] = 5-120 mM, pH = 8.4-8.7, and the sample was filtered through 0.2-µm PVDF membrane before analysis.

### 5.4.4 Impact of pH

**Figure 5.4** Impact of pH on photochemical removal of Cr(VI) in the spent IX regenerant brine. [Formate] or [Formic acid] = 40 mM.
The impact of pH on chromium removal in the spent brine was examined. Acidic pH favored photochemical reduction of Cr(VI). As the initial pH decreased from 10.8 to 3.1, the reduction kinetics of Cr(VI) was significantly accelerated (Figure 5.4). For instance, less than 85% of Cr(VI) was removed at initial pH 10.8 after 120 minutes, while more than 97% of Cr(VI) was reduced at initial pH 3.1 within 10 minutes. pH impacts speciation of the water constituents and reactive intermediates (H$_2$CO$_3$/HCO$_3^-$/CO$_3^{2-}$: pk$_1$=6.3 and pK$_2$=10.3; HCrO$_4^-$/CrO$_4^{2-}$: pK=6.5; HNO$_2$/NO$_2^-$: pK=3.3), the availability of protons, and thus the reduction process of Cr(VI). The spent brine contained high levels of carbonate species. As the initial pH decreased from 10.8 to 8.5, CO$_3^{2-}$ was protonated into HCO$_3^-$, which highly weakened the scavenging effect of carbonate species on HO· (4.0×10$^8$ M$^{-1}$s$^{-1}$ vs. 8.5×10$^6$ M$^{-1}$s$^{-1}$) and enhanced the production of CO$_2^.$ for Cr(VI) reduction. Further decrease of initial pH from 8.5 to 3.1 transformed CrO$_4^{2-}$ into more reducible HCrO$_4^-$ (E$^\circ$(HCrO$_4^-$/Cr$^{3+}$)= 1.35 V vs. E$^\circ$(CrO$_4^{2-}$/Cr(OH)$_3^-$)=-0.13 V). In addition, the protonated HNO$_2$ intermediate generated from nitrate photolysis had much higher quantum yield of HO· than NO$_2^-$. Overall, the enhanced formation of CO$_2^.$ from HO· and the generation of more reducible Cr(VI) species enhanced the reduction of Cr(VI) under acidic conditions. After treatment, the level of total chromium at initial pH 5.2 and 8.6 was below regulatory standard. Despite the fastest reduction of Cr(VI) at initial pH 3.1, total chromium remained unchanged because the formed Cr(III) was soluble (Figure S5.3). Subsequent pH adjustment prior to filtration was required to induce the precipitation of Cr(OH)$_3$ solids.
5.4.5 Impact of ionic strength

![Figure 5.5](image)

**Figure 5.5** Impact of ionic strength on photochemical reduction of Cr(VI) in the presence of nitrate and formate. [Cr(VI)] = 31.2 mg/L, [Nitrate] = 45 mM, [Formate] = 40 mM, [NaClO₄] = 0 - 2 M, and pH = 5.9-6.7 with 50 mM phosphate buffer.

The ionic strength of the spent brine was more than two orders of magnitude higher than groundwater. The impact of ionic strength on photochemical reduction of Cr(VI) was investigated. Buffered synthetic water matrices containing similar levels of Cr(VI) and nitrate to the spent IX brine but different ionic strength. The highest ionic strength (i.e., 2187 mM) in the synthetic water matrix was comparable with that in spent brine. As ionic strength increased, Cr(VI) reduction was not inhibited but accelerated (Figure 5.5). The enhanced removal of Cr(VI) at high ionic strength was due to the slight decrease of solution pH from 6.7 to 5.9 (pH was changed in the buffered solution because of the shifted equilibrium of phosphate buffer at different ionic strength). High ionic strength had no adverse effect on Cr(VI) removal. This phenomenon can be ascribed to homogenous nature of the reaction. In homogenous photochemical system, the produced CO₂⁻ even and
closely distributed with Cr(VI) in the solution, which avoided the mass-transfer issues and facilitate electron-transfer kinetics even that high ionic strength. In comparison, Cr(VI), in heterogenous catalytic reactions, needs to overcome high resistance from surrounding environment to access the active sites of the catalysts, which caused poor performance at high ionic strength.

5.4.6 Impact of inorganic constituents

![Figure 5.6 Impact of chloride, sulfate and bicarbonate on photochemical reduction of Cr(VI) in the presence of nitrate and formate. [Cr(VI)] = 31.2 mg/L, [NaCl] = 2 M, [Na$_2$SO$_4$] = 0.2 M, [NaHCO$_3$] = 45 mM, [NaClO$_4$] = 0 - 2 M, pH= 7.9-8.1 with 100 mM borate buffer.](image)

Spent brine contained high levels of chloride, sulfate, and bicarbonate. Their impact on photochemical reduction of Cr(VI) was quantified in synthetic water matrices with similar concentrations of Cr(VI), nitrate and targeted anions to that in the spent brine. NaClO$_4$ was used to maintain the same ionic under different conditions. The result showed that chloride strongly inhibited the reduction of Cr(VI) while sulfate and bicarbonate had slightly negative and negligible impact on Cr(VI) removal, respectively (Figure 5.6).
Prominent inhibition from chloride was due to its strong scavenging effect on NO$_2^-$ that made significant contribution to the formation of CO$_2^-$ based on Chapter 3. Prior study showed that chloride reacted with NO$_2^-$ with the formation of NOCl and NO$_3^-$. NOCl was unstable and subsequently transform into NO$_2^-$, NO· and Cl· through hydrolysis and photolysis reaction. High levels of chloride further transformed Cl· into Cl$_2^-$ The overall effect of chloride in the spent brine rendered the conversion of NO$_2^-$ into NO· and Cl$_2^-$ that are less reactive with formate, which reduced the formation of CO$_2^-$ and eventually slowed down the reduction of Cr(VI). Sulfate and bicarbonate have less significant impact than chloride because of their comparatively low concentrations and low reactivity with NO$_2^-$ and HO·.

5.4.7 Co-removal of Cr(VI) and nitrate

Co-removal of Cr(VI) and nitrate from the spent brine was investigated at different pHs under unbuffered conditions. The initial pH of the solution was adjusted by tuning the ratio between formic acid and formate. The results showed that acidic pH favored the removal of nitrate and total dissolved nitrogen. Despite the solution pH, the reduction kinetics of Cr(VI) was significantly faster than that of nitrate. For instance, complete reduction of Cr(VI) was achieved within 1.5 hours while at least 9 hours were required to achieve more than 95% removal of nitrate under the most favorable condition (i.e., pH = 2.1-3.5). The asynchronous removal between Cr(VI) and nitrate was mainly due to their different concentrations in the spent brine ([Cr(VI)] = 0.6 mM vs. [NO$_3^-$] = 47.5 mM). As pH decreased, the removal of total dissolved nitrogen was accelerated because protonated nitrite underwent fast photolysis and had insignificant accumulation. In addition, pH
strongly impacted the removal of total chromium. As photochemical reduction proceeded solution pH was increased (Figure S5.4) because of the consumption of protons. When the final pH was very acidic, total chromium was not removed because the formed Cr(III) mainly existed as a soluble form (Figure 5.7 A). Progressive pH change from acidic to alkaline condition caused initial lag phase followed by dramatic decrease of total chromium concentration (Figure 5.7B and Figure S5.4). Under alkaline pHs, the removal of total chromium followed the same track as that of Cr(VI) because the reduced Cr(VI) was simultaneously transformed into Cr(OH)$_3$ solids that was filtered out solution (Figure 5.7C). Overall, acidic pH favored the co-removal of Cr(VI) and total dissolved nitrogen but post adjustment of pH was required to precipitate Cr(III) for total chromium removal.
Figure 5.7 Photochemical removal of chromium and nitrate from the spent IX regenerant brine in the presence of formate: (A) pH = 2.1-3.5; (B) pH = 3.4-8.6; and (C) pH = 8.6-9.1. [Formate] = 160 mM.
5.5 Environmental Implications

This study demonstrated an alternative treatment technology to remove Cr(VI) and nitrate from the spent IX regenerant brine. It is advantageous over conventional chemical, catalytic, and biological treatment processes because of the reduced sludge production and high tolerance to ionic strength and concentrated coexisting constituents. High dosage of formate accelerated the reduction kinetics of Cr(VI) but left high levels of formate residual in the treated brine. Prior study showed the reuse of treated brine with 400-mM formate residual caused insignificant resin capacity loss. The leakage of formate into treated ground water can be eliminated by rinsing the resin regenerated by treated spent brine with small bed volumes of fresh NaCl solution. In addition, the stoichiometry of between formate and Cr(VI) plus nitrate can be investigated in further work to optimize the dosage of formate. Even though acidic pH favors the reduction of Cr(VI) and nitrate, post pH adjustment can be costly and should be avoided by optimizing the initial pH. Our study shows that the initial pH of the solution can be controlled by tuning the ratio of formic acid to formate with no need of extra acid. pH increase resulted from proton consumption during treatment can be potentially utilized to ensure fast removal of chromium and dissolved nitrogen as well as eliminate the post pH adjustment.

Successful removal of total chromium not only rely on the reductive transformation of Cr(VI) into Cr(OH)$_3$ solids but also the subsequent solid removal process. The presence of coexisting constituents can from complexes on the surface of Cr(OH)$_3$ and impact of surface charge and aggregation of Cr(OH)$_3$ particles. High ionic strength can compress diffusion double layer and promote the aggregation of particles. The aggregation and
growth behaviors of Cr(OH)$_3$ during photochemical treatment would eventually impact the precipitation and removal efficiency of Cr(OH)$_3$ solids. Therefore, it is important to understand the effect of water chemical parameters on the dynamics of particle formation and precipitation. In addition, our study also shows the co-removal other toxic oxyanions (e.g., arsenate and vanadate) with the precipitation of Cr(OH)$_3$ solids (Figure S5.5). The sequestration mechanism for arsenic and vanadium with the precipitation of Cr(OH)$_3$ solids remains unclear and will be investigated in future work.

5.6 Acknowledgement

The study was supported by U.S. National Science Foundation CAREER Program (CBET-1653931), GOALI Program (CBET-1611306), and Early-concept Grants for Exploratory Research Program (CBET-1619915). We acknowledge Corona Environmental Consulting to provide authentic spent IX brine. We also thank the support to G.C. from the Los Angeles Urban Natural Resources Sustainability Science Fellowship.
References


Chapter 6

Conclusions and Broader Impacts
The overall goal of this research was to understand the reduction processes of Cr(VI), vanadium(V), and nitrate under environment-relevant conditions and develop alternative redox-based treatment technologies for public water utilities to transform these contaminants into environmental benign products. To achieve this goal, photocatalytic reduction of Cr(VI) by newly designed and highly reductive TiO₂ nanocrystals (Chapter 2), nitrate reduction via CO₂⁻ induced photochemical denitrification (Chapter 3), and the reduction kinetics of vanadium(V) and their transformation products (Chapter 4) were investigated.

6.1 Photocatalytic Removal of Hexavalent Chromium by Newly Designed and Highly Reductive TiO₂ Nanocrystals

In Chapter 2, highly reductive TiO₂ nanocrystals were synthesized by thermal hydrolysis of TiCl₄ precursor in the DEG. FTIR characterization demonstrated that DEG was chemically bonded on TiO₂ surface via C-O-Ti covalent bonds. The suppressed formation of hydroxyl radical measured by terephthalic acid, compared with that of standard P25 TiO₂, indirectly evidenced the internal hole-scavenging effect of the synthesized TiO₂ nanocrystals. Hydrolysis time was the key synthesizing parameter that controlled the crystallinity of TiO₂ and the number of DEG bonded on TiO₂ surface. Optimization based on Cr(VI) reduction indicated that the optimal hydrolysis time was 3 hours.

With the same surface-area based dosage, the synthesized TiO₂ nanocrystal exhibited superior performance to standard P25 TiO₂ for the reduction of Cr(VI) with initial concentrations ranging from 100 µg/L to 50 mg/L. Increasing catalyst dosage dramatically
enhanced the reduction efficiency of Cr(VI). Catalyst surface analysis over time by XPS indicated the formation and accumulation of Cr(III) on TiO\(_2\) surface. Time-course FTIR study showed the formation of Cr-OH stretching, indicating that Cr(III) existed as Cr(OH)\(_3\)\(_\text{aq}\). Sequential filtration followed by total Cr analysis demonstrated the growth Cr(OH)\(_3\) solids over time. Single particle ICP-MS analysis showed the synthesized TiO\(_2\) nanocrystals had insignificant aggregation during Cr(VI) reduction process. The surface charges of TiO\(_2\) nanocrystals remained highly negative despite the changes caused by the oxidation of DEG during hole-scavenging processes and the deposition of Cr(OH)\(_3\) solids with Cr(VI) reduction.

The longevity experiments showed that the synthesized TiO\(_2\) nanocrystals can be reused at least 10 cycles with minor decay on Cr(VI) reduction performance. The total electron releasing capacity calculated based on 10-cycle experiment was 0.187 mol/g, indicating that the synthesized catalyst has a large electron-releasing capacity. Excellent Cr(VI) reduction performance in synthetic groundwater and tap water matrices indicated that the synthesized TiO\(_2\) nanocrystals was robust to remove Cr(VI) in diverse drinking water matrices.

6.2 Nitrate Removal via Formate Radical-induced Photochemical Process

In Chapter 3, a novel photochemical denitrification process was developed to transform nitrate into gas-nitrogen products under different water chemical conditions. Photolysis of nitrate in the presence of formate showed simultaneous removal of total dissolved nitrogen and organic carbon. Formate has been demonstrated to play an important role in driving denitrification process. The kinetic model including all possible
reactions showed that HO·, NO2· and CO3·− generated during nitrate photolysis oxidized formate into formate radical (CO2·−). Subsequently, CO2·− mainly reduced NO·, HNO, and N2O to gas-phase nitrogen (i.e., N2O and N2). The formation of CO2·− was confirmed by EPR analysis. Kinetic modeling showed that NO2· contributed most to CO2·− formation followed by HO· and CO3·−. NO· was the major sink of CO2·− followed by self-recombination and dissolved oxygen. The overall denitrification kinetics was controlled by photolysis rates of nitrate and nitrite. The reaction selectivity toward gas-phase products was mainly limited by the slow reaction between CO2·− and N2O. Products analysis showed N2 accounted for 30% of gas-phase products and the remaining 70% was N2O, indicating the accumulation of N2O in the final products.

Solution pH impacted the photolysis of nitrate and nitrite but had negligible effect on the removal of total dissolved nitrogen. Nitrate removal was slightly enhanced at alkaline pH compared with that at neutral and acidic pH, respectively, because catalytic hydration of dissolved CO2 into HCO3· inhibited formation of nitrate from ONOO−. The accumulation of nitrite was suppressed as pH decreased because protonated nitrite (i.e., HNO2) has larger molar extinction coefficient and higher photolysis quantum yield than the deprotonated form (i.e., NO2−). Collaborative effect of nitrate and nitrite caused insignificant effect of pH on the removal of total dissolved nitrogen.

DOM at levels similar to groundwater matrix had negligible impact on the denitrification performance. DOM at levels simulating eutrophic surface water and wastewater suppressed the photolysis of nitrate and slowed down the denitrification process. High concentrations of DOM impacted the denitrification process mainly because
of its light-shading and electron-donating effects. The reaction stoichiometry between formate and nitrate was determined as 3.1, regardless of pH and the presence of other inorganic and organic constituents at levels similar to groundwater matrix. Photochemical denitrification performance in synthetic groundwater was comparable with that in deionized water, indicating that the developed process had application potentials in nitrate-contaminated groundwater.

6.3 Understanding Reduction Kinetics of Aqueous Vanadium(V) and Transformation Products Using Rotating Ring-Disk Electrode

In Chapter 4, the reduction kinetics of vanadium(V) species and stability of their reduction products were investigated with rotating ring-disk electrode to fill the knowledge gap of vanadium redox chemistry under environment-relevant conditions. Four relevant vanadium(V) species were obtained through controlling solution pH, vanadium concentration, and ionic strength. Koutecky-Levich and Tafel analyses showed that the intrinsic reduction kinetics of vanadium(V) followed the order of $\text{Na}_x\text{H}_y\text{V}_{10}\text{O}_{28}^{(6-x-y)^-} > \text{VO}_2^+ > \text{H}_x\text{V}_4\text{O}_{12+x}^{(4+x)^-} > \text{HVO}_4^{2-}$. In addition, the reduction of vanadium(V) species on rotating ring-disk electrode surface was diffusion-controlled. Based on Koutecky-Levich plots and the correlation of reduction peak current vs. square root of scan rates from cyclic voltammetry curves, the calculation showed that the reduction of $\text{Na}_x\text{H}_y\text{V}_{10}\text{O}_{28}^{(6-x-y)^-}$ involved two-electron transfer while that of the other three species involved only one-electron transfer. Product collection efficiency on ring electrode showed the reduction product of $\text{Na}_x\text{H}_y\text{V}_{10}\text{O}_{28}^{(6-x-y)^-}$ is stable while that of $\text{VO}_2^+$, $\text{H}_x\text{V}_4\text{O}_{12+x}^{(4+x)^-}$, and $\text{HVO}_4^{2-}$ had a half-life ranging from milliseconds to seconds. The fast reduction kinetics of
Na$_x$H$_y$V$_{10}$O$_{28}$($^{6-x-y}$)$^-$, unique two-electron mechanism, and high stability of reduction products were resulted from cage-like superstructure.

As the molar ratios of phosphate to vanadium(V) increased from 0 to 1, phosphate accelerated the reduction kinetics of Na$_x$H$_y$V$_{10}$O$_{28}$($^{6-x-y}$)$^-$ and H$_x$V$_4$O$_{12+x}$($^{4+x}$)$^-$ but had a minimal effect on that of VO$_2^+$ and HVO$_4^{2-}$. At pH 4, Phosphate mainly as H$_2$PO$_4^-$ formed complexes with Na$_x$H$_y$V$_{10}$O$_{28}$($^{6-x-y}$)$^-$, which lowered the electron density of vanadium and therefore the reduction barrier. At pH 7, phosphate mainly as H$_2$PO$_4^-$ and HPO$_4^{2-}$ promoted the decomposition of H$_x$V$_4$O$_{12+x}$($^{4+x}$)$^-$ to H$_2$VO$_4^-$ and further complexed with latter, which made vanadium more reducible. The weak complexation of phosphate with VO$_2^+$ and HVO$_4^{2-}$ caused negligible effect on their reduction kinetics. Phosphate also complexed with and stabilized reduction products of VO$_2^+$, H$_x$V$_4$O$_{12+x}$($^{4+x}$)$^-$, and HVO$_4^{2-}$ and inhibited their re-oxidation to vanadium(V).

6.4 Photochemical Removal of Cr(VI) and Nitrate in Spent Ion-exchange Regenerant Brine

In Chapter 5, photochemical reduction of Cr(VI) and nitrate in spent IX brine regenerant brine was investigated to reduce the quantity of hazardous waste and increase the viability and sustainability of ion-exchange processes for water treatment. CO$_2$.·, ·CH$_3$OH, CH$_3$·CHOH, and (CH$_3$)$_3$·COH) were produced by hydrogen abstraction of formate, methanol, ethanol, and isopropanol with reactive radicals from nitrate photolysis (i.e., HO·). CO$_2$.· exhibited better Cr(VI) reduction performance than the other three radicals. The increase of formate dosage enhanced the production of CO$_2$.· and consequently
accelerated the reduction kinetics of Cr(VI) as well as total chromium. The decrease of pH significantly improved the reduction efficiency of Cr(VI) because the change of speciation of carbonate, nitrite species, and chromate enhanced the production of CO$_2$· and the formation of more reducible HCrO$_4$·. In contrast to fast reduction of Cr(VI), negligible removal of total chromium at acidic pH, indicating that post pH adjustment was required to precipitate the generated Cr(III). Ionic strength exhibited no adverse effect on Cr(VI) reduction because CO$_2$· was homogenously and closely distributed with Cr(VI) with insignificant mass-transfer resistances. Chloride scavenged NO$_2$·, suppressed the formation of CO$_2$·, and consequently inhibited the reduction of Cr(VI), while bicarbonate and sulfate had insignificant impact. The reduction kinetics of Cr(VI) was much faster than that of nitrate mainly because of the concentration of Cr(VI) was much lower than that of nitrate. Co-removal of chromium and dissolved nitrogen in the spent brine was achieved at prolonged the reaction time.

6.5 Broader Impacts and Future Studies

Findings from this research provide alternative treatment technologies for public water facilities to remove Cr(VI) and nitrate from their water resources. The obtained insight on the reduction process of vanadium(V) can help develop novel treatment processes for vanadium(V) and prevent the re-oxidation of the reduction products. The synthesized TiO$_2$ nanocrystals exhibited high reductive capacity and can be reused multiple time before disposal. To make a treatment unit for Cr(VI), the synthesized TiO$_2$ can be suspended in a completely-mixed reactor with membrane-separation module. This reaction system can allow complete recovery and recirculation of the catalyst back to the reactor and treated
water passing through the membrane. Periodically, the spent catalyst with surface-coated Cr(OH)$_3$ can be regenerated by strong acid or replaced with fresh catalyst. In addition, the synthesized TiO$_2$ nanocrystals can be immobilized on substrate surface to eliminate the need for catalyst recovery. For instance, they can be deposited as a uniform film on optical fiber in which the light can be effectively delivered. The catalyst on the fiber surface can be activated by refraction light out of the fiber. Compact light-emitting diode can be integrated with TiO$_2$-coated optical fibers to reduce energy consumption. Given the advantage of magnetic separation, future work will also attempt to graft the synthesized TiO$_2$ to magnetic materials. For instance, Fe$_3$O$_4$/SiO$_2$/TiO$_2$ core-shell-shell nanocomposite will be designed and synthesized.

The newly developed denitrification process is based on homogenous radical chemistry. Unlike the conventional photocatalytic reduction, this process does not require a solid catalyst and therefore eliminated the issues associated with catalyst recovery, surface passivation, and mass-transfer limitation. In addition, the denitrification efficiency of this process has little dependence on pH and inorganic constituents and has moderate tolerance on dissolved organic matters, which allow its wide application in diverse water matrices. Even though formate has been demonstrated as an effective electron donor, other organics including alcohols and carboxylate will be examined for photochemical denitrification given their capability to generate reductive carbon-centered radicals. Photochemical denitrification in actual water matrix can potentially form potent carcinogen N-Nitrosodimethylamine (NDMA) because reactive nitrogen intermediate (e.g., NO$^-$) generated from denitrification process can react with dissolved organic matters with amine
functional groups to form NDMA. NDMA precursor compounds should be carefully recognized, monitored and removed before the denitrification process. The sluggish kinetics between CO$_2^-$ and N$_2$O causes the accumulation of N$_2$O in gas-phase product (70%). N$_2$O is one major green-house gas. Future work will strive to transform N$_2$O to N$_2$ by introducing reducing reagents that have high reactivity with N$_2$O (e.g., hydrated electrons).

The proposed process can also remove both nitrate and Cr(VI) in the spent IX regenerant brine despite its high ionic strength and concentration of interference constituents, compared with groundwater matrices. To avoid the accumulation of nitrite and reduce energy footprint, acidic pH was recommended for photochemical treatment. Post pH adjustment is required to induce the precipitation of Cr(III) as Cr(OH)$_3$(s) with subsequent filtration. Photolysis of nitrate is the rate-determining step for the photochemical reduction process. However, the major photon output of conventional UV lamps (e.g., low-pressure and medium-pressure UV lamps) has poor overlap with the high absorption and photolysis quantum yield of nitrate (< 220 nm). In the practical applications, UV lamps with high photon flux below 220 nm (e.g., deuterium arc lamp and excimer lamps) are recommended to intensify nitrate photolysis. Given the enhanced photolysis of nitrate on water-air interface, aerosolization of spent brine is promising to further reduce energy consumption of treatment process. Operational and reaction parameters (e.g., the size of aerosol droplet and flow rate) should be optimized to improve the energy efficiency of the system. Prior to full implementation, pilot-scale test should be performed to evaluate the feasibility and the cost of the developed process. The full-scale reactor can be operated
either at batch reaction mode or continuous flow mode with lamp fully immersed in the bulky water. To reduce energy consumption, photons should be effectively trapped inside the reactor for full use. The configuration of the reactor should be designed to maximize the exposure of the solution to UV irradiation.

Electrochemical investigation of the redox process of vanadium(V) species and their transformation products reveal that the speciation of vanadium(V) significantly impacts its reactivity and stability in aquatic environment. The complexation of vanadium(V) with phosphate changed the coordination and electron density of vanadium and therefore affect the reduction kinetics of vanadium(V) and stability of its transformation products. Future work can be conducted to investigate the impact of other environment-relevant ligands (e.g., bicarbonate and natural organic matters) on redox chemistry of vanadium(V) species and their transformation products. As the total discharge of vanadium into aquatic environment increases because of increasing demands of vanadium in industries, the findings in this research can help water facilities to design efficient treatment units to minimize their presence in drinking water. They can also help environmentalists and geochemists understand the interaction of vanadium with natural environment and its transformation under various aquatic and geological conditions. Furthermore, vanadium serves as building blocks in biological structures and plays an important functional role in proteins. The presence of different vanadate species in biological systems can impact the enzymatic activities and induce toxicity. These new findings on the redox properties of vanadium probably can help biologists to understand the metabolism of vanadium in the biological systems.
The electrochemical techniques developed in this research combined classical theories on static and rotating electrode and exhibited robustness to study physical and redox properties of vanadium(V) species and their transformation products. The application of this technique can be further expanded to other redox-reactive aquatic contaminants (e.g., selenate, halogenated organic compounds, etc.). For some contaminants with extremely slow electron-transfer kinetics and very unstable transformation products, this electrochemical technique cannot accurately extract their kinetic information because of limited current response on both disk and ring electrode. In this case, redox active mediators that have high electron-exchange rates with both electrode surface and the targeted contaminants can serve as indicator to study the kinetic behaviors of the targeted contaminants. Future studies will explore the feasibility of this strategy to unveil the redox properties of redox-inactive contaminants.
Appendix A

Supporting Information for Chapter 2
Text S2.1: Calculation of UV fluence in photocatalytic system

UV fluence represents the total energy input to photocatalytic system. The fluence calculation took account of the wavelengths over the whole spectrum (Figure S2.1) even though some low-energy photons in the spectrum were not utilized by catalyst. It was calculated by equation S2.1:

\[
\text{UV fluence (J/cm}^2\text{)} = \text{Irradiance (W/cm}^2\text{)} \times \text{Light exposure time (s)} \quad (S2.1)
\]

In this equation, the irradiance of the lamp is 42 mW/cm\(^2\) and light exposure time is the reaction time.

Text S2.2: Surface area calculation

The normalized surface area of TiO\(_2\) nanocrystals was calculated by equation S2.2:

\[
S = \frac{6000}{\rho d} \quad (S2.2)
\]

Where S is the normalized surface area of TiO\(_2\) nanocrystals (m\(^2\)/g), \(\rho\) is the density of anatase TiO\(_2\) (3.8 g/cm\(^3\)), and d is the diameter of TiO\(_2\) nanocrystals in suspension (10 nm).

Text S2.3: Single-Particle ICP-MS (SP-ICP-MS) analysis for TiO\(_2\) nanoparticles

Fundamentals

The size of TiO\(_2\) nanoparticles during Cr(VI) treatment was analyzed by SP-ICP-MS. This method has been applied to characterize metal colloids in aqueous solution\(^1,2\). Briefly, under appropriately short dwell time, constant flow rate and sufficiently low particle number concentration, each pulse of MS signal during the ICP-MS measurement can
represent a single particle event. The frequency of the pulses is proportional to the number concentration of particles and the intensity of the pulses is related to particle size.  

**SP-ICP-MS analysis**  

At predetermined intervals of reaction time, reaction suspension with synthesized TiO\textsubscript{2} nancrystals (50 mg/L) and Cr(VI) (initial concentration: 20 mg/L) was withdrawn from the UV reactor, diluted 5 million times and sonicated for 15 minutes. Well dispersed suspension of TiO\textsubscript{2} nanocrystals with a concentration of 10 ng/L was introduced to Agilent 7700 series ICP-MS with time-resolved mode for particle size analysis. The duration of data acquisition for each sample is 60 seconds with a dwell time of 3 milliseconds. The sample flow rate was 0.36 mL/min. During SP-ICP-MS analysis, isotope Ti\textsuperscript{48} was monitored for TiO\textsubscript{2} samples.  

**Data processing**  

An established procedure described previously was followed for data processing. Data points with very high intensity were first removed as outliers due to their skewed influence on the calculation of the mean intensity. Average intensity of entire data set plus five-fold standard deviation (\(\mu + 5\sigma\)) was used as the threshold limit to differentiate particle event from background signals. An iterative algorithm was carried out to identify all particle events. In each iteration, data points with values higher than \(\mu + 5\sigma\) were removed as particle events. New threshold limit was calculated from the remaining data points. The iteration was not ceased until no further data point could be removed from the remaining data points.
Particle size calculation

The particle size was calculated from SP-ICP-MS analysis following the protocol described by pace et al. Transport efficiency was determined using 60 nm gold reference nanoparticles (PerkinElmer) based on previously described particle size method. Typically, monodispersed Au nanoparticles were used to create two-point calibration curve which related pulse intensity to particle mass. Dissolved Au standard was used to develop the second calibration curve. The transport efficiency is the ratio of the slope of dissolved calibration curve to the slope of two-point calibration curve.

Dissolved Ti standard (Aristar Plus) was used to develop the calibration curve for sizing synthesized TiO$_2$ nanocrystals. The relationship between the mass observed per event and Ti concentration was described by equation S2.3:

\[ W = \eta q t_{dt} C \quad (S2.3) \]

Where \( W \) (μg/event) is the mass observed per event, \( \eta \) is transport efficiency which is defined as the ratio of the amount of Ti entering the plasma to the amount of Ti aspirated, \( t_{dt} \) (millisecond/event) is the dwell time for each particle event, and \( C \) (μg/L) is the dissolved Ti standard concentration.

Based on this relationship, a newly transformed calibration curve which related pulse intensity to total mass transported into plasma per event was developed. The particle mass \( m_p \) (μg/event) was obtained by inserting the intensity of each individual pulse Ip to the equation of newly transformed calibration curve (equation S2.4):
\[ m_p = f_a \left[ \frac{\left( I_p - I_{Bgd} \right) \eta_i}{m} \right]^{-b} \]  

(S2.4)

Where \( f_a \) is the mass fraction of Ti in TiO\(_2\) (60%), \( \eta_i \) is the particle ionization efficiency (100% was used as reported) \(^3\) which is defined as the ratio of the ionization efficiency of synthesized TiO\(_2\) nanocrystals to the ionization efficiency of the corresponding dissolved Ti solution, \( I_{Bgi} \) (counts/event) is the background intensity, \( m \) and \( b \) are the slope and \( y \)-intercept of the newly transformed calibration curve, respectively.

Assuming a spherical geometry of nanoparticle, particle size was calculated with TiO\(_2\) density \( \rho \) (4.2 g/cm\(^3\)) based on equation S2.5 \(^3\):

\[ d = \left( \frac{6m_p}{\pi \rho} \right)^{\frac{1}{3}} \]  

(S2.5)

**Text S2.4: Particle size analysis for Cr(III) precipitates**

1 mg/L of Cr(VI) was treated by 50 mg/L of the synthesized TiO\(_2\) nanocrystals under UV irradiation. Cr(VI) and total chromium concentration were monitored throughout the reaction (Figure S2.10). For the solution without filtration, total chromium concentration was 1 mg/L. After filtration by membrane with pore size of 25 and 220 nm, total chromium concentration in the filtrate was measured, respectively. The increase of chromium concentration (\( \Delta C_1 \)) from black square curve to red circle curve resulted from Cr(OH)\(_3\)(S) passing through 25-nm membrane. The increase of chromium concentration from red circle curve to blue triangle curve (\( \Delta C_2 \)) was ascribed to Cr(OH)\(_3\) with sizes between 25 and 220 nm. The decrease of total chromium concentration (\( \Delta C_3 \)) from orange star curve to
blue triangle curve was attributed to Cr(OH)$_3$$_{(s)}$ removed by 220-nm membrane. The mass fraction of Cr(OH)$_3$$_{(s)}$ within different particle size range was calculated by equation S2.6, 2.7 and 2.8,

\[
F_1 = \frac{\Delta C_1}{(\Delta C_1 + \Delta C_2 + \Delta C_3)} \times 100\% \quad (S2.6)
\]

\[
F_2 = \frac{\Delta C_2}{(\Delta C_1 + \Delta C_2 + \Delta C_3)} \times 100\% \quad (S2.7)
\]

\[
F_3 = \frac{\Delta C_3}{(\Delta C_1 + \Delta C_2 + \Delta C_3)} \times 100\% \quad (S2.8)
\]

Where $F_1$, $F_2$ and $F_3$ are the fraction of Cr(OH)$_3$$_{(s)}$ with particle sizes smaller than 25 nm, between 25 and 220 nm and greater than 220 nm, respectively.

**Text S2.5: Sherrer Equation**

\[
\tau = \frac{(k\lambda)}{(\beta \cos \theta)}
\]

$\tau$ is the average crystalline domain size, $k$ is the shape factor with a typical value of 0.9, $\lambda$ is the X-ray wavelength, $\beta$ is the line broadening full width at half maximum (FWHM) peak height of the (101) peak, and $\theta$ is the Bragg angle ($12.640^\circ$).

**Text S2.6: Optimization of synthesis parameters**

The hydrolysis time during TiO$_2$ synthesis was optimized because it impacted the content of DEG bonded on the TiO$_2$ surface, which is central to the catalyst performance. Formation of Ti-O-C bonding organic complex by mixing Ti precursors and ethylene glycol has been reported previously $^5$-$^7$. The Ti-DEG complex was used as a precursor to synthesize TiO$_2$ via hydrolysis and condensation upon thermal treatment. TiO$_2$
nanocrystals were generated from the hydrolysis and condensation of the Ti-DEG complex on the basis of the following reactions:

\[
\text{TiCl}_4 + 4\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} \rightarrow \text{Ti(OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH)}_4 + 4\text{HCl} \quad (S2.9)
\]

\[
\text{Ti(OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH)}_4 + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} \quad (S2.10)
\]

Reaction S2.9 showed the formation of Ti-DEG complex. Reaction S2.10 represented the hydrolysis and condensation of the Ti-DEG complex. As reaction 10 proceeded, C-O-Ti bonds in Ti-DEG complex were transformed to Ti-O-Ti bonds and TiO\textsubscript{2} nanocrystals were formed with the time. As hydrolysis and condensation time increased, the number of DEG molecules bonded on the surface of TiO\textsubscript{2} nanocrystals decreased and the degree of crystallization of TiO\textsubscript{2} was improved.

Table S2.1 summarized the impact of hydrolysis time on the performance of synthesized catalysts. As the hydrolysis time increased from 1.5 to 3 hours, the percentage of Cr(VI) removal after 20 min of reactions increased from 88% to 98%. Further increasing the hydrolysis time from 3 to 12 hours decreased Cr(VI) removal efficiency to 51%. As shown in Reaction S2.10, hydrolysis time was associated with the extent of TiO\textsubscript{2} crystallization and the number of DEG molecules bonded on TiO\textsubscript{2}. TiO\textsubscript{2} had low crystalinity when synthesized with a short hydrolysis time, \textit{i.e.}, 1.5 hours. As a result, Photogenerated holes and electrons had a strong tendency to recombine and less electrons were available for Cr(VI) reduction \textsuperscript{8}. As the hydrolysis time increased, TiO\textsubscript{2} nanocrystals became more crystalized, however, less DEG was chemically bonded on the TiO\textsubscript{2} surface.
Therefore, there existed an optimal hydrolysis time of 3 hours. The Cr(VI) removal kinetics profile by catalysts synthesized with different hydrolysis time was shown in Figure S2.2.

**Text S2.7: Calculation of electron capacity**

The electron capacity (mole e'/g TiO$_2$) of the synthesized TiO$_2$ nanocrystals for the first 10 cycles was calculated through equation S2.11:

$$EC = \frac{\Delta n_{\text{Cr(VI)}} \times 3}{m_{\text{TiO}_2}} \quad (S2.11)$$

Where $\Delta n_{\text{Cr(VI)}}$ represents the variation of molar number of Cr(VI) during the reaction, 3 is the number of electron transferred from Cr(VI) to Cr(III), and $m_{\text{TiO}_2}$ is the mass of the synthesized TiO$_2$ nanocrystals used.
Table S2.1 Composition of the synthetic groundwater and Riverside tap water chemical matrixes.\textsuperscript{9,10}

<table>
<thead>
<tr>
<th>Species</th>
<th>Synthetic groundwater (mg/L)</th>
<th>Riverside tap water (mg/L) \textsuperscript{10}</th>
<th>Species</th>
<th>Synthetic groundwater (mg/L)</th>
<th>Riverside tap water (mg/L) \textsuperscript{10}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexavalent chromium</td>
<td>0.1</td>
<td>2.1E-3 \textsuperscript{a}</td>
<td>Sodium</td>
<td>13.6</td>
<td>43</td>
</tr>
<tr>
<td>Nitrate</td>
<td>40.3</td>
<td>25</td>
<td>Potassium</td>
<td>3.9</td>
<td>3.0</td>
</tr>
<tr>
<td>Chloride</td>
<td>13.1</td>
<td>33</td>
<td>Calcium</td>
<td>24.4</td>
<td>68</td>
</tr>
<tr>
<td>Bicarbonate</td>
<td>37.9</td>
<td>87.8</td>
<td>Magnesium</td>
<td>6.0</td>
<td>10</td>
</tr>
<tr>
<td>Sulfate</td>
<td>32.9</td>
<td>73</td>
<td>TOC\textsuperscript{c}</td>
<td>4.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Silica</td>
<td>36.6</td>
<td>18</td>
<td>pH</td>
<td>8.0</td>
<td>7.6</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Hexavalent chromium concentration in Riverside tap water was spiked to 0.1 mg/L prior to use
\textsuperscript{b} NOM: natural organic matter
\textsuperscript{c} TOC: total organic carbon

Table S2.2 The effects of hydrolysis time during TiO\textsubscript{2} synthesis on the performance of Cr(VI) removal. Reaction time=20 minutes, initial [Cr(VI)] =1 mg/L, TiO\textsubscript{2} dosage = 50 mg/L, pH = 7.0 with 6 mM phosphate buffer, and ionic strength =12 mM.

<table>
<thead>
<tr>
<th>DEG (mL)</th>
<th>H\textsubscript{2}O (mL)</th>
<th>TiCl\textsubscript{4} concentration (mM)</th>
<th>Hydrolysis time (hour)</th>
<th>Cr(VI) removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.2</td>
<td>89</td>
<td>1.5</td>
<td>88±3</td>
</tr>
<tr>
<td>20</td>
<td>0.2</td>
<td>89</td>
<td>3</td>
<td>98±2</td>
</tr>
<tr>
<td>20</td>
<td>0.2</td>
<td>89</td>
<td>6</td>
<td>94±5</td>
</tr>
<tr>
<td>20</td>
<td>0.2</td>
<td>89</td>
<td>9</td>
<td>88±4</td>
</tr>
<tr>
<td>20</td>
<td>0.2</td>
<td>89</td>
<td>12</td>
<td>51±1</td>
</tr>
</tbody>
</table>
Figure S2.1 Spectra of the 450-W UV immersion lamp used for photochemical Cr(VI) reduction experiments.

Figure S2.2 The effect of hydrolysis time used for synthesizing TiO$_2$ nanocrystals on the photocatalytic reduction of Cr(VI) under UV irradiation. Initial [Cr(VI)]=1 mg/L, TiO$_2$ dosage = 50 mg/L, and pH = 7.0 with 6 mM phosphate buffer.
Figure S2.3 Zeta potential of the synthesized TiO$_2$ nanocrystals and P25 TiO$_2$ at different pHs. pHs were controlled by phosphate buffer; ionic strength = 12 mM; TiO$_2$ dosage = 50 mg/L.
**Figure S2.4** The photocatalytic removal of Cr(VI) under UV irradiation by TiO₂ catalysts. pH = 7.0 with 6 mM phosphate buffer. (A) Initial [Cr(VI)] = 1 mg/L, surface area-based catalyst dosage = 7.8 m²/L; (B) Initial [Cr(VI)] = 50 mg/L, surface area-based TiO₂ dosage = 78 m²/L.
Figure S2.5 The effect of catalyst dosage on photocatalytic reduction of Cr(VI) with initial concentration of (A) 100 μg/L, (B) 1 mg/L and (C) 50 mg/L over the synthesized TiO$_2$ nanocrystals under UV irradiation. pH = 7.0 with 6mM phosphate buffer.
Figure S2.6 Impact of initial Cr(VI) concentration on surface area normalized second-order rate constants of Cr(VI) removal by TiO$_2$. pH = 7.0 with 6 mM phosphate buffer.

Figure S2.7 The LogC-pH diagram showing the solubility of chromium (total chromium) and the speciation of Cr(III) hydroxyl complexes in equilibrium with Cr(OH)$_3$(s).
Figure S2.8 Optical photograph of the filters (pore size: 25 nm) after the filtration of Cr(VI)/TiO\textsubscript{2} suspension at different durations of UV irradiance. Initial [Cr(VI)] = 20 mg/L, TiO\textsubscript{2} dosage = 50 mg/L, and pH=7.0 with 6 mM phosphate buffer.

Figure S2.9 The variation of Cr(VI) and total chromium concentration with respect to reaction time. Initial [Cr(VI)] =1 mg/L, pH=7.0 with 6 mM phosphate buffer, and TiO\textsubscript{2} dosage=50 mg/L. ΔC\textsubscript{1}: the increase of chromium concentration from Cr(OH)\textsubscript{3(S)} through 25-nm filter; ΔC\textsubscript{2}: the increase of chromium concentration from Cr(OH)\textsubscript{3(s)} with sizes between 25 and 220 nm; ΔC\textsubscript{3}: the decrease of total chromium concentration from Cr(OH)\textsubscript{3(s)} removed by 220-nm filter.
**Figure S2.10** Fraction of the formed Cr(OH)$_3$(s) within different particle size range as a function of reaction time. TiO$_2$ dosage = 50 mg/L, initial [Cr(VI)] = 1 mg/L, and pH=7 with 6 mM phosphate buffer.
Figure S2.11 The effect of pH on the photocatalytic reduction of Cr(VI) over the synthesized TiO₂ nanocrystals under UV irradiation. Initial Cr(VI) concentration and catalyst dosage: (A) 100 μg/L and 20 mg/L and (B) 20 mg/L and 50 mg/L.
Figure S2.12 The effect of pH on the photocatalytic reduction of Cr(VI) with initial concentration of (A) 1 mg/L and (B) 50 mg/L over the synthesized TiO\textsubscript{2} nanocrystals under UV irradiation. TiO\textsubscript{2} dosage = 50 mg/L.
Figure S2.13 The change of Cr(VI) concentration and zeta potential of the synthesized TiO$_2$ nanocrystals with reaction time. Ionic strength = 12 mM, initial [Cr(VI)] = 20 mg/L, TiO$_2$ dosage = 50 mg/L, and pH=7.0 with 6 mM phosphate buffer.

Figure S2.14 Zeta potential of the synthesized Cr(OH)$_3(s)$ particles at different pHs. Ionic strength = 12 mM, Cr(OH)$_3(s)$ dosage = 200 mg/L, and pH was adjusted by phosphate buffer.
Figure S2.15 Particle size distribution at (A) 0 minutes, (B) 14 minutes, (C) 60 minutes, (D) 90 min, (E) 120 minutes, and (F) the variation of average particle size of the synthesized TiO$_2$ nanocrystals and Cr(VI) concentration from 0 to 120 minutes. Initial [Cr(VI)] = 20 mg/L, TiO$_2$ dosage = 50 mg/L, and pH = 7.0 with 6 mM phosphate buffer.
Figure S2.16 The electron capacity of the synthesized TiO$_2$ nanocrystals as a function of cycle number. Initial [Cr(VI)] = 20 mg/L, pH = 2.7 with 0.2 M phosphate buffer, and TiO$_2$ dosage = 50 mg/L.

Figure S2.17 The effect of water matrices on the photocatalytic reduction of Cr(VI) over the synthesized TiO$_2$ nanocrystals under UV irradiation. Initial [Cr(VI)] = 100 μg/L, TiO$_2$ dosage = 50 mg/L, and pH = 7 with 6 mM phosphate buffer.
References


Appendix B

Supporting Information for Chapter 3
**Figure S3.1** UV-vis absorption spectra of nitrate, nitrite and formate and output spectrum of medium pressure UV lamp.

**Table S3.1** Composition of the synthetic groundwater

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Concentration (mg/L)</th>
<th>Constituents</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate</td>
<td>28\textsuperscript{a}</td>
<td>Sodium</td>
<td>13.6</td>
</tr>
<tr>
<td>Chloride</td>
<td>13.1</td>
<td>Potassium</td>
<td>3.9</td>
</tr>
<tr>
<td>Bicarbonate</td>
<td>37.9</td>
<td>Calcium</td>
<td>24.4</td>
</tr>
<tr>
<td>Sulfate</td>
<td>32.9</td>
<td>Magnesium</td>
<td>6.0</td>
</tr>
<tr>
<td>Silica</td>
<td>36.6</td>
<td>DOM\textsuperscript{b}</td>
<td>1.9\textsuperscript{c}</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td></td>
<td>8.0</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Nitrate concentration was expressed as nitrogen  
\textsuperscript{b} DOM: Suwannee River natural organic matter was used as dissolved organic matter  
\textsuperscript{c} DOM concentration was expressed as total organic carbon
For gaseous phase nitrogen analysis, photochemical denitrification in the presence of formate was carried out in a homemade gas-tight cylindrical reactor (70 mL) which contained 40 mL of reaction solutions. Prior to start, the headspace over the solution was repeatedly vacuumed and filled with helium gas five times to displace the air and then pressurized by helium gas at 7 psi in the last cycle. 2 mL of gas samples taken at irradiation time 0 and 6 hours from the headspace of the reactor was injected into gas chromatography (GC), respectively. The temperature and pressure before and after sampling ((T₁, T₂) and (P₁, P₂)) were monitored, respectively. The molar number of N₂ in the gas samples (nₛ) was calculated based on its peak area of the GC spectra (Figure S3.7). Based on ideal gas law, the molar number of N₂ in the headspace (n₁) was calculated using Equation S3.1:

\[
  n₁ = \frac{P₁ T₂ nₛ}{(P₁ T₂ - P_{12} T₁)} \quad (S3.1)
\]

The mole concentration of dissolved N₂ in the solution was calculated based on Henry’s Law. It was negligible because the partial pressure in the headspace and Henry’s Law constant of N₂ were very small. The molar concentration of N₂ generated from denitrification process with respect to reaction solution ([N₂], mM) was calculated using Equation S3.2:

\[
  [N₂] = \frac{n₁}{40} \quad (S3.2)
\]

N₂O formed was calculated based on the mass balance using Equation S3.3:
\[ [\text{N}_2\text{O}] = \frac{(|\Delta[DN]|-2[N_2])}{2} \quad (S3.3) \]

in which, \([\text{N}_2\text{O}]\) (mM) was the molar concentration of \(\text{N}_2\text{O}\), and \(\Delta[DN]\) (mM) was the molar concentration change of total dissolved nitrogen.

The fractions of \(\text{N}_2\) (\(F(\text{N}_2)\)) and \(\text{N}_2\text{O}\) (\(F(\text{N}_2\text{O})\)) generated during photochemical denitrification were calculated using Equations S3.4 and S3.5:

\[ F(\text{N}_2) = \frac{2[N_2]}{|\Delta[DN]|} \times 100\% \quad (S3.4) \]

\[ F(\text{N}_2\text{O}) = \frac{2[N_2\text{O}]}{|\Delta[DN]|} \times 100\% \quad (S3.5) \]

**Text S3.2 Kinetic modeling and optimization**

Kinetic modeling with parameter optimization was performed using chemical kinetic modeling software (Kintecus V6.01).\(^2\)\(^3\) Specifically, all relevant reactions with rate constants collected from literatures were compiled in Kintecus program (Table S3.2). For 13 protonation reactions in the model, they typically occur at diffusion-controlled rate. Those rate constants were assumed as \(5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}\) as have been commonly used in the previous modeling.\(^4\)\(^5\) The deprotonation reaction rates were calculated based on equilibrium constants and protonation rate constants. Other rate constants which cannot be measured directly or found in prior literature were obtained through fitting the experimental datasets using the kinetic model. The four photolysis rates of nitrate and nitrite in the model were fitted individually under the specific experimental condition to quantify the impacts of pH and DOM on the denitrification performance. The remaining
five unknown rate constants that do not vary with experimental conditions were obtained through a globally fitting with 27 experimental datasets (i.e., more than 210 data points) under nine different experimental conditions. If the fitted rate constants enable the model to well predict the reaction kinetics of the reactants and products, they will be utilized in the model for further uncertainty, sensitivity and principal component analyses. Specifically, an initial input with constrained optimization range was used as the starting values of rate constants that required fitting in the kinetic modeling. Powell method that is sensitive to optimization tolerance (the minimum difference between the experimental data and simulated data that must be met before the data is considered optimized) was chosen as optimization algorithm. Standard least square was chosen as the comparison operator to compare the experimental data and simulated data and return their difference to the optimizer. To assure sufficient optimization and avoid substantial optimization time, the optimization tolerance was set as $1 \times 10^{-5}$. Uncertainty analysis was performed by Kintecus program by introducing 20% relative standard deviation (relative standard deviation should be less than 30% to avoid negative initial rate constants generated randomly by Gaussian distribution) to the fitted rate constants. 95% confidence interval was specified for the Kinetic program to calculate confidence band. 100 simulations were performed to gather the final average concentration and confidence predictions. Time profiles of average concentrations with 95% confidence intervals were eventually output form Kintecus program.
Text S3.3 Principal component analysis

Principal component analysis was performed with computer programs (Kintecus V6.01 & Atropos V 1.00).\textsuperscript{2,3} Normalized sensitivity coefficient (NSC) of each reaction for certain species was calculated by Kintecus program using Equation S3.6 below:\textsuperscript{6}

\[
NSC = \left( \frac{\partial [\text{Species}]}{\partial k_i} \right)_{k_{ji}} \left( \frac{\partial \ln[\text{Species}]}{\partial \ln k_i} \right)_{k_{ji}} \quad (S3.6)
\]

where [Species] is the concentration of certain species, \( k_i \) is the rate constants of the targeted reaction. NSC reflects the influence of one reaction on certain species. Large positive NSC represents a significant source of certain species and large negative NSC represents a significant sink of that species.

For one simulation run, the whole reaction time was evenly divided into 60 intervals and NSC matrix for each interval was calculated by Kintecus program. A big NSC matrix (S) was constructed by combining NSC matrixes at all intervals. Principal component analysis is based on the eigenvalue-eigenvector of \( S^TS \) matrix by Atropos program and it provides an absolute measure of significant reactions out of detailed mechanism and mutual dependency of reactions. The reactions with significant entries in the eigenvectors (\textit{i.e.}, principal components) with the largest eigenvalues were the most influential. The appearance of significant values in the same principal components reflected the mutual dependency of the reactions. A safety factor of 0.5 was used in Atropos program to sufficiently eliminate the most of unimportant reactions in the kinetic model. A trial-and-error method was further used to manually eliminate reactions that contributed negligibly
to the major reaction mechanism. Importance of each reaction was determined by the analysis of principal components with top eigenvalues. Principal components with small eigenvalues (\(i.e., < 450\) and absolute entries (\(i.e., < 0.01\)) were not displayed considering their negligible contribution to the analysis.

**Figure S3.2** Nitrate photolysis under the irradiation of medium-pressure UV lamp. [Nitrate] = 2 mM, and pH = 7 with 20 mM phosphate buffer. Markers represent the data from experiments; lines with shaded bands represent the predicted time profiles of the average concentrations with 95% confidence intervals from the kinetic modeling.
Figure S3.3 Photochemical denitrification in the presence of formate: (A) 1.9 mM, (B) 3.2 mM, (C) 10.4 mM, and (D) 20.6 mM. [Nitrate] = 2.0 mM, and pH = 7 with 20 mM phosphate buffer. Makers represent the data from experiments; Lines with shaded bands represent the predicted time profiles of the average concentrations with 95% confidence intervals from the kinetic modeling.

Figure S3.4 Model-predicted concentrations of radical species formed during photochemical denitrification in the presence of formate. [Nitrate] = 2.0 mM, [Formate] = 6.2 mM, and pH = 7 with 20 mM phosphate buffer.
Text S3.4 Calculation of cumulative contribution of different reaction pathways to the formation and consumption of certain species

The cumulative contribution of different reaction pathways to the formation and consumption of specific species was calculated through the integration of their individual contribution at different reaction time through the whole reaction process. Take the contribution of HO\(^-\), NO\(_2\)-, and CO\(_3\)- to the formation of CO\(_2\)- as an example. The concentrations of HO\(^-\), NO\(_2\)-, and CO\(_3\)- at different time were output from kinetic modeling (Figure S4) and the reaction rate constants were obtained from literatures or fitted through kinetic modeling. The relative contribution of HO\(^-\), NO\(_2\)-, and CO\(_3\)- to CO\(_2\)- formation varies with the reaction time because their concentrations were changed over time. Cumulative contribution of HO\(^-\), NO\(_2\)-, and CO\(_3\)- to CO\(_2\)- formation was calculated using Equation S3.7-S3.9, respectively.

\[
F(\text{HO}^-) = \frac{\sum_{i=0}^{n-1} k_{\text{HO}} \cdot [\text{HO}^-]_i \cdot [\text{HCOO}^-]_i (t_{i+1})}{(\sum_{i=0}^{n-1} k_{\text{HO}} \cdot [\text{HO}^-]_i \cdot [\text{HCOO}^-]_i (t_{i+1})) + (\sum_{i=0}^{n-1} k_{\text{NO}2} \cdot [\text{NO}_2^-]_i \cdot [\text{HCOO}^-]_i (t_{i+1}) + (\sum_{i=0}^{n-1} k_{\text{CO}3} \cdot [\text{CO}_3^-]_i \cdot [\text{HCOO}^-]_i (t_{i+1}))} \times 100\% \quad (S3.7)
\]

\[
F(\text{NO}_2^-) = \frac{\sum_{i=0}^{n-1} k_{\text{NO}_2} \cdot [\text{NO}_2^-]_i \cdot [\text{HCOO}^-]_i (t_{i+1})}{(\sum_{i=0}^{n-1} k_{\text{HO}} \cdot [\text{HO}^-]_i \cdot [\text{HCOO}^-]_i (t_{i+1})) + (\sum_{i=0}^{n-1} k_{\text{NO}_2} \cdot [\text{NO}_2^-]_i \cdot [\text{HCOO}^-]_i (t_{i+1}) + (\sum_{i=0}^{n-1} k_{\text{CO}_3} \cdot [\text{CO}_3^-]_i \cdot [\text{HCOO}^-]_i (t_{i+1}))} \times 100\% \quad (S3.8)
\]

\[
F(\text{CO}_3^-) = \frac{\sum_{i=0}^{n-1} k_{\text{CO}_3} \cdot [\text{CO}_3^-]_i \cdot [\text{HCOO}^-]_i (t_{i+1})}{(\sum_{i=0}^{n-1} k_{\text{HO}} \cdot [\text{HO}^-]_i \cdot [\text{HCOO}^-]_i (t_{i+1})) + (\sum_{i=0}^{n-1} k_{\text{NO}_2} \cdot [\text{NO}_2^-]_i \cdot [\text{HCOO}^-]_i (t_{i+1}) + (\sum_{i=0}^{n-1} k_{\text{CO}_3} \cdot [\text{CO}_3^-]_i \cdot [\text{HCOO}^-]_i (t_{i+1}))} \times 100\% \quad (S3.9)
\]

Where, \(k_{\text{HO}}\), \(k_{\text{NO}_2}\), and \(k_{\text{CO}_3}\) are the rate constants of HO\(^-\), NO\(_2\)-, and CO\(_3\)- with formate, respectively; \([\text{HO}^-]_t\), \([\text{CO}_3^-]_t\), and \([\text{HCOO}^-]_t\) are the concentrations of HO\(^-\), NO\(_2\)-, and CO\(_3\)- at time \(t\); \(n\) is the total number of time point intervals over the whole reaction time. Similarly, cumulative contribution of different reaction pathways to the consumption of CO\(_2\)- and HNO was calculated using the same procedure.
Figure S3.5 Model-predicted concentrations of dissolved oxygen and formate radical during photochemical denitrification in the presence of formate. [Nitrate] = 2.0 mM, [Formate] = 6.2 mM, and pH = 7 with 20 mM phosphate buffer.
Figure S3.6 Model-predicted cumulative contribution of HNO and CO₂· to HNO consumption during photochemical denitrification in the presence of formate. [Nitrate] = 2.0 mM, [Formate] = 6.2 mM, and pH=7 with 20 mM phosphate buffer.

Figure S3.7 Gas chromatography spectra of gaseous product formed during nitrate photolysis in the presence of formate. [Nitrate] = 2.0 mM, [Formate] = 6.1 mM and pH = 7 with 20 mM phosphate buffer.
**Figure S3.8** Model-predicted time profiles of gaseous nitrogen formation during photochemical denitrification in the presence of formate. [Nitrate] = 2.0 mM, [Formate] = 6.2 mM and pH = 7 with 20 mM phosphate buffer.

**Text S3.5 Calculation of theoretical formate-to-nitrate stoichiometry**

The reactions of formate and nitrate to form N₂O and N₂ were shown in Equation S3.10 and S3.11, respectively. At formate-to-nitrate molar ratio of 3.1, the final product distribution of gas-phase nitrogen is 70% of N₂O and 30% of N₂. The overall denitrification reaction can be written as Equation S3.12 through combing Equation S3.10 with Equation S3.11. Based on Equation S3.12, the theoretical formate-to-nitrate stoichiometry is determined as 2.2.

\[
\text{NO}_3^- + 4\text{HCOO}^- + \text{H}_2\text{O} \rightarrow \text{N}_2\text{O} + 4\text{CO}_2 + 6\text{OH}^- \quad (S3.10)
\]

\[
\text{NO}_3^- + 5\text{HCOO}^- + \text{H}_2\text{O} \rightarrow \text{N}_2 + 5\text{CO}_2 + 7\text{OH}^- \quad (S3.11)
\]

\[
\text{NO}_3^- + 2.15\text{HCOO}^- + 0.5\text{H}_2\text{O} \rightarrow 0.15\text{N}_2 + 0.35\text{N}_2\text{O} + 2.15\text{CO}_2 + 3.15\text{OH}^- \quad (S3.12)
\]
<table>
<thead>
<tr>
<th>No.</th>
<th>Reactions</th>
<th>Rate constants</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{NO}_3^- \xrightleftharpoons \text{NO}_2^+ + \text{O}^-$</td>
<td>1.7 × 10^4 s(^{-1}) (pH = 2)</td>
<td>Fitted</td>
</tr>
<tr>
<td>2</td>
<td>$\text{NO}_2^+ \xrightarrow{hv} \text{ONO}^-$</td>
<td>4.6 × 10^4 s(^{-1}) (pH = 7)</td>
<td>Fitted</td>
</tr>
<tr>
<td>3</td>
<td>$\text{ONO}^- + \text{H}^+ \rightarrow \text{ONO}^\cdot\text{OH}$</td>
<td>6.5 × 10^4 M(^{-1}) s(^{-1})</td>
<td>Globally Fitted</td>
</tr>
<tr>
<td>4</td>
<td>$\text{ONO}^- \rightarrow \text{NO}^+ + \text{O}_2^-$</td>
<td>2.3 × 10^2 s(^{-1})</td>
<td>7</td>
</tr>
<tr>
<td>5</td>
<td>$\text{ONO}^- \rightarrow \text{NO}_2 + \text{O}^-$</td>
<td>1.0 × 10^6 s(^{-1})</td>
<td>7</td>
</tr>
<tr>
<td>6</td>
<td>$\text{ONO}^- + \text{OH} \rightarrow \text{NO}^+ + \text{O}_2 + \text{OH}^-$</td>
<td>5.0 × 10^6 M(^{-1}) s(^{-1})</td>
<td>8</td>
</tr>
<tr>
<td>7</td>
<td>$\text{ONO}^- + \text{HCOO}^- \rightarrow \text{ONO}_2 + \text{CO}_2^- + \text{OH}^-$</td>
<td>7.7 × 10^6 M(^{-1}) s(^{-1})</td>
<td>9</td>
</tr>
<tr>
<td>8</td>
<td>$\text{OH}^- + \text{CO}_2^- \rightarrow \text{NO}_2^- + \text{CO}_2$</td>
<td>2.9 × 10^6 M(^{-1}) s(^{-1})</td>
<td>10</td>
</tr>
<tr>
<td>9</td>
<td>$\text{NO}_3^- + \text{H}_2\text{O} \rightarrow \text{NO}_2 + 2\text{OH}^-$</td>
<td>5.0 × 10^8 M(^{-1}) s(^{-1})</td>
<td>11</td>
</tr>
<tr>
<td>10</td>
<td>$\text{HCOO}^- + \text{H}_2\text{O} \rightarrow \text{HCO}_2^- + \text{H}_2\text{O}$</td>
<td>6.3 × 10^2 s(^{-1})</td>
<td>12</td>
</tr>
<tr>
<td>11</td>
<td>$\text{OH}^- + \text{HCOO}^- \rightarrow \text{CO}_2^- + \text{H}_2\text{O}$</td>
<td>3.2 × 10^4 M(^{-1}) s(^{-1})</td>
<td>13</td>
</tr>
<tr>
<td>12</td>
<td>$\text{HCOO}^- \rightarrow \text{CO}_2^- + \text{H}_2\text{O}$</td>
<td>1.3 × 10^8 M(^{-1}) s(^{-1})</td>
<td>14</td>
</tr>
</tbody>
</table>

**Assumed** *a*

**Calculated** *b*
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$NO_2 + OH \rightarrow ONOOH$</td>
<td>$4.5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NO_2 + OH \rightarrow NO_2^+ + H^+$</td>
<td>$4.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NO_2 + HO_2 \rightarrow ONOOOH$</td>
<td>$1.8 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NO_2 + O_2^- \rightarrow ONOOO^-$</td>
<td>$4.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$ONOOO^- + H^+ \rightarrow ONOOOH$</td>
<td>$5.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$</td>
<td>Assumed</td>
</tr>
<tr>
<td>$ONOOO^- \rightarrow NO_2^- + O_2$</td>
<td>$1.35 \text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$ONOOO^- \rightarrow NO_2^- + O_2^-$</td>
<td>$1.05 \text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$ONOOO^- + OH \rightarrow NO_2^- + O_2 + OH^-$</td>
<td>$1.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$ONO_2OH \rightarrow ONOOO^- + H^+$</td>
<td>$7.9 \times 10^4 \text{s}^{-1}$</td>
<td>Calculated</td>
</tr>
<tr>
<td>$ONO_2OH \rightarrow NO_2^+ + HO_2$</td>
<td>$2.6 \times 10^2 \text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$ONO_2OH \rightarrow HNO_2 + O_2$</td>
<td>$7.0 \times 10^4 \text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$ONO_2OH + OH \rightarrow NO_2^- + O_2 + H_2O$</td>
<td>$1.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$</td>
<td>Calculated</td>
</tr>
<tr>
<td>$O_2^- + H^+ \rightarrow HO_2$</td>
<td>$5.0 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$</td>
<td>Assumed</td>
</tr>
<tr>
<td>$HO_2 \rightarrow O_2^- + H^+$</td>
<td>$7.9 \times 10^4 \text{s}^{-1}$</td>
<td>Calculated</td>
</tr>
<tr>
<td>$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$</td>
<td>$8.3 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$N_2O_4 \rightarrow NO_2^- + NO_2^-$</td>
<td>$6.9 \times 10^4 \text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$N_2O_4 + H_2O \rightarrow NO_2^- + NO_2^- + 2H^+$</td>
<td>$1.0 \times 10^5 \text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NO_2^-_{hv} \rightarrow NO^+ + O^-$</td>
<td>$7.9 \times 10^4 \text{s}^{-1} (pH = 7)$</td>
<td>Fitted</td>
</tr>
<tr>
<td>$NO_2^- + CO_2 \rightarrow NO_2^- + CO_2$</td>
<td>$1.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NO_2^- + O_2^- \rightarrow NO_2^- + O_2$</td>
<td>$5.0 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NO_2^- + HO_2 \rightarrow NO_2^- + O_2 + H^+$</td>
<td>$5.0 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NO_2^- + H_2O \rightarrow NO^- + 2OH^-$</td>
<td>$4.3 \times 10^4 \text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NO_2^- + O_2 + ONO^- \rightarrow NO_2^- + NO_2^- + ONO^-$</td>
<td>$5.3 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$</td>
<td>Calculated</td>
</tr>
<tr>
<td>$NO^+ + NO_2 \rightarrow N_2O_3$</td>
<td>$1.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NO^+ + CO_2 \rightarrow NOCO_2^-$</td>
<td>$2.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NO^+ + NOCO_2^+ \rightarrow N_2O_3 + CO_2$</td>
<td>$6.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NO^+ + N_2O_2^- \rightarrow N_2O_3^-_2$</td>
<td>$2.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NO^+ + NO + O_2 \rightarrow NO_2^- + NO_2^-$</td>
<td>$2.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NO^+ + OH \rightarrow HNO_2$</td>
<td>$6.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NO^+ + HO_2 \rightarrow ONOOH$</td>
<td>$3.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NO^+ + O_2^- \rightarrow ONOO^-$</td>
<td>$4.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NO^+ + NO^- \rightarrow N_2O_2^-_2$</td>
<td>$1.7 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$HNO_2 \rightarrow H^+ + NO_2^-$</td>
<td>$7.9 \times 10^6 \text{s}^{-1}$</td>
<td>Calculated</td>
</tr>
<tr>
<td>$H^+ + NO_2^- \rightarrow HNO_2$</td>
<td>$5.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$</td>
<td>Assumed</td>
</tr>
<tr>
<td>$HNO_2_{hv} \rightarrow NO^- + OH$</td>
<td>$2.5 \times 10^3 \text{ s}^{-1} (pH = 2)$</td>
<td>Fitted</td>
</tr>
<tr>
<td>$N_2O_3 \rightarrow NO^- + NO_2^-_2$</td>
<td>$8.1 \times 10^5 \text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$N_2O_3 + ONOO^- \rightarrow NO_2^- + NO_2^- + NO_2^-$</td>
<td>$3.1 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$N_2O_3 + H_2O \rightarrow NO_2^- + NO_2^- + 2H^+$</td>
<td>$9.9 \times 10^4 \text{s}^{-1} (pH = 2)$</td>
<td></td>
</tr>
<tr>
<td>Reaction</td>
<td>Rate Constant</td>
<td>Notes</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>$N_2O_2$ → $N_2O + O^-$</td>
<td>$3.5 \times 10^2 \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$N_2O_2$ → $NO^+ + NO^-$</td>
<td>$6.6 \times 10^4 \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$N_2O_2^- + N^0 \rightarrow N_2O_3$</td>
<td>$2.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$N_2O_2^- + H^+ \rightarrow HN_2O_2$</td>
<td>$8.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td>Calculated</td>
</tr>
<tr>
<td>$HN_2O_2 \rightarrow HNO + NO^-$</td>
<td>$5.5 \times 10^6 \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$HN_2O_2 + NO^- \rightarrow HN_3O_3$</td>
<td>$8.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$N_2O_3^- \rightarrow NO_2^- + N_2O$</td>
<td>$2.4 \times 10^6 \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$N_2O_3^- + H^+ \rightarrow HN_3O_3$</td>
<td>$5.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$</td>
<td>Assumed</td>
</tr>
<tr>
<td>$HN_2O_3 \rightarrow NO_2^- + N_2O$</td>
<td>$3.9 \times 10^6 \text{ s}^{-1}$</td>
<td>Calculated</td>
</tr>
<tr>
<td>$HN_2O_3 \rightarrow HNO_2 + N_2O$</td>
<td>$1.6 \times 10^6 \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NO^- + O_2 \rightarrow ONOO^-$</td>
<td>$2.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NO^- + H_2O \rightarrow HNO + OH^-$</td>
<td>$1.2 \times 10^7 \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$HNO + OH^- \rightarrow NO^- + H_2O$</td>
<td>$4.9 \times 10^4 \text{ s}^{-1}$</td>
<td>Calculated</td>
</tr>
<tr>
<td>$HNO + NO^- \rightarrow HN_2O_3$</td>
<td>$5.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$HNO + CO_2^- + H_2O \rightarrow HN_2O^- + CO_2 + OH^-$</td>
<td>$1.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$HN_2O_3 \rightarrow NO_2^- + H_2O$</td>
<td>$8.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$N_2O + CO_2^- + H_2O \rightarrow N_2 + OH^- + OH^- + CO_2$</td>
<td>$1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$HN_3O^- + HN_2O^- + H_2O \rightarrow N_2 + H_2O + H_2O$</td>
<td>$2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$HN_3O^- + CO_2^- + H_2O \rightarrow NH_2OH^- + CO_2 + OH^-$</td>
<td>$1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NH_2OH^- + OH^- \rightarrow NH_3 + NH_2OH + 2OH^-$</td>
<td>$1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NH_2OH^- + CO_2^- + H_2O \rightarrow NH_3 + CO_2 + 2OH^-$</td>
<td>$1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NH_3 + OH^- \rightarrow NH_2 + H_2O$</td>
<td>$9.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NH_3 + H^+ \rightarrow NH_4^+$</td>
<td>$5.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$</td>
<td>Assumed</td>
</tr>
<tr>
<td>$NH_4^+ \rightarrow NH_3 + H^+$</td>
<td>$2.8 \times 10^7 \text{ s}^{-1}$</td>
<td>Calculated</td>
</tr>
<tr>
<td>$NH_2 + O^- \rightarrow NH_2OH$</td>
<td>$9.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NH_2 + CO_3^- \rightarrow NH_3 + CO_2$</td>
<td>$1.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NH_2 + O_2 \rightarrow NH_3O_2$</td>
<td>$3.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NH_2 + NO^- \rightarrow N_2 + H_2O$</td>
<td>$1.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NH_2 + NH_2 \rightarrow N_2H_4$</td>
<td>$2.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$NH_2O_2^- + O^- \rightarrow ONOO^- + H_2O$</td>
<td>$2.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$CO_2 + OH^- \rightarrow HCO_3^-$</td>
<td>$6.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$CO_2 + H_2O \rightarrow HCO_3$</td>
<td>$3.7 \times 10^2 \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$H_2CO_3 \rightarrow CO_2 + H_2O$</td>
<td>$1.8 \times 10^3 \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$HCO_3^- \rightarrow HCO_3 + H^+$</td>
<td>$2.5 \times 10^4 \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$H_3CO_3 + OH^- \rightarrow CO_3^- + H_2O + H^+$</td>
<td>$1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$HCO_3^- \rightarrow CO_3^- + H^+$</td>
<td>$2.5 \times 10^7 \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Reaction</td>
<td>Rate Constant</td>
<td>Comments</td>
</tr>
<tr>
<td>----------</td>
<td>---------------</td>
<td>----------</td>
</tr>
<tr>
<td>$HCO_3^- + OH^- \rightarrow CO_2^- + H_2O$</td>
<td>$8.5 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
<td>Assumed: general rapid and assumed as $5 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$CO_3^{2-} + H^+ \rightarrow HCO_3^-$</td>
<td>$5.0 \times 10^{10}$ M$^{-1}$ s$^{-1}$</td>
<td>Calculated: $1.0 \times 10^8$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$CO_3^- + OH^- \rightarrow CO_2^- + OH^-$</td>
<td>$3.9 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
<td>Assumed: general rapid and assumed as $5 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$CO_3^- + NO_2^- \rightarrow CO_2 + NO_3^-$</td>
<td>$1.0 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
<td>Calculated: $3.2 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$CO_3^- + NO_2^- \rightarrow CO_3^{2-} + NO_2^-$</td>
<td>$4.0 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
<td>Assumed: general rapid and assumed as $5 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$CO_3^- + NO^- \rightarrow CO_2 + NO_2^-$</td>
<td>$3.5 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
<td>Calculated: $1.0 \times 10^8$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$CO_3^- + HCOO^- \rightarrow CO_3^- + HCOO^-$</td>
<td>$1.1 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
<td>Assumed: general rapid and assumed as $5 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$CO_3^- + CO_2^- \rightarrow CO_3^- + CO_2$</td>
<td>$5.0 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
<td>Assumed: general rapid and assumed as $5 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$CO_3^- + O^-_2 \rightarrow CO_3^- + O_2$</td>
<td>$5.5 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
<td>Assumed: general rapid and assumed as $5 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$OH^- + OH^- \rightarrow H_2O_2$</td>
<td>$9.9 \times 10^3$ M$^{-1}$ s$^{-1}$</td>
<td>Calculated: $3.2 \times 10^3$ s$^{-1}$</td>
</tr>
<tr>
<td>$OH^- + O_2^- \rightarrow OH^- + O_2$</td>
<td>$1.1 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
<td>Assumed: general rapid and assumed as $5 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$OH^- + H_2O_2 \rightarrow H_2O + H_2O$</td>
<td>$2.7 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
<td>Calculated: $2.5 \times 10^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$HCOO^- + H^+ \rightarrow HCOOH$</td>
<td>$5.0 \times 10^6$ M$^{-1}$ s$^{-1}$</td>
<td>Assumed: general rapid and assumed as $5 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$HCOOH \rightarrow HCOO^- + H^+$</td>
<td>$8.5 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
<td>Calculated: $4.0 \times 10^8$ s$^{-1}$</td>
</tr>
<tr>
<td>$H_3PO_4 \rightarrow H_2PO_4^- + H^+$</td>
<td>$4.0 \times 10^6$ s$^{-1}$</td>
<td>Assumed: general rapid and assumed as $5 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$H_2PO_4^- + H^+ \rightarrow H_3PO_4$</td>
<td>$5.0 \times 10^6$ M$^{-1}$ s$^{-1}$</td>
<td>Assumed: general rapid and assumed as $5 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$H_2PO_4^- \rightarrow HPO_4^{2-} + H^+$</td>
<td>$3.2 \times 10^6$ s$^{-1}$</td>
<td>Calculated: $2.5 \times 10^8$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$HPO_4^{2-} + H^+ \rightarrow H_2PO_4^-$</td>
<td>$5.0 \times 10^6$ M$^{-1}$ s$^{-1}$</td>
<td>Assumed: general rapid and assumed as $5 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$HPO_4^{2-} \rightarrow PO_4^{3-} + H^+$</td>
<td>$2.5 \times 10^2$ s$^{-1}$</td>
<td>Calculated: $5.0 \times 10^{10}$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$PO_4^{3-} + H^+ \rightarrow HPO_4^{2-}$</td>
<td>$5.0 \times 10^6$ M$^{-1}$ s$^{-1}$</td>
<td>Assumed: general rapid and assumed as $5 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$OH^- + H_2PO_4^- \rightarrow H_2PO_4^- + OH^-$</td>
<td>$2.4 \times 10^6$ M$^{-1}$ s$^{-1}$</td>
<td>Calculated: $1.5 \times 10^6$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$OH^- + HPO_4^{2-} \rightarrow HPO_4^- + OH^-$</td>
<td>$1.5 \times 10^6$ M$^{-1}$ s$^{-1}$</td>
<td>Assumed: general rapid and assumed as $5 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$H_2PO_4^- + HCOO^- \rightarrow H_2PO_4^- + CO_2^-$</td>
<td>$1.5 \times 10^6$ M$^{-1}$ s$^{-1}$</td>
<td>Calculated: $2.5 \times 10^6$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$HPO_4^- + HCOO^- \rightarrow HPO_4^{2-} + CO_2^-$</td>
<td>$2.5 \times 10^6$ M$^{-1}$ s$^{-1}$</td>
<td>Assumed: general rapid and assumed as $5 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$HPO_4^- + H_2O_2 \rightarrow HPO_4^{2-} + O_2^- + 2H^+$</td>
<td>$2.7 \times 10^3$ M$^{-1}$ s$^{-1}$</td>
<td>Calculated: $5.5 \times 10^3$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$H_2PO_4^- + H_2O_2 \rightarrow H_2PO_4^- + O_2^- + 2H^+$</td>
<td>$5.5 \times 10^3$ M$^{-1}$ s$^{-1}$</td>
<td>Assumed: general rapid and assumed as $5 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$H_2PO_4^- \rightarrow HPO_4^- + H^+$</td>
<td>$6.3 \times 10^4$ s$^{-1}$</td>
<td>Calculated: $5.0 \times 10^6$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$HPO_4^- + H^+ \rightarrow H_2PO_4^-$</td>
<td>$5.0 \times 10^6$ M$^{-1}$ s$^{-1}$</td>
<td>Assumed: general rapid and assumed as $5 \times 10^9$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$H_2O \rightarrow H^+ + OH^-$</td>
<td>$1.0 \times 10^3$ s$^{-1}$</td>
<td>Calculated: $1.0 \times 10^{11}$ M$^{-1}$ s$^{-1}$</td>
</tr>
</tbody>
</table>

\(^a\) Assumed: the rates of protonation reactions are generally very rapid and are assumed as $5 \times 10^9$ M$^{-1}$ s$^{-1}$

\(^b\) Calculated: the rates of deprotonation reactions were calculated using equilibrium constants multiplying protonation rate constants.
Figure S3.9 Fraction of light absorbed by nitrate, SRNOM, and formate at the initial stage of the reaction and output spectrum of medium-pressure UV lamp. [Nitrate] = 2.0 mM, [Formate] = 6.2 mM, [SRNOM] = 72 mg-C/L, and pH = 7 with 20 mM phosphate buffer.

Figure S3.10 Time profiles of nitrate decay in UV/formate systems at different concentrations of dissolved organic matter. [Nitrate] = 2.0 mM, [Formate] = 6 mM, and pH = 7 with 20 mM phosphate buffer.
Figure S3.11 Evolution of nitrite in UV/formate systems at different concentrations of dissolved organic matter. [Nitrate] = 2.0 mM, [Formate] = 6 mM, and pH = 7 with 20 mM phosphate buffer.

Table S3.3 Impact of water chemical parameters of optimal formate-to-nitrate molar ratio

<table>
<thead>
<tr>
<th>Solution pH</th>
<th>Dissolved organic matter (mg-C/L)</th>
<th>Optimal Formate-to-nitrate molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>0</td>
<td>3.1</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>2.8</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>2.9</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>2.8</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>3.0</td>
</tr>
<tr>
<td>11</td>
<td>0</td>
<td>3.0</td>
</tr>
<tr>
<td>Synthetic groundwater</td>
<td>3.1</td>
<td></td>
</tr>
</tbody>
</table>
References


Appendix C

Supporting Information for Chapter 4
Figure S4.1 Speciation profiles of vanadium(V) as a function pH at the different vanadium(V) concentration: (A) 2 µM, (B) 20 µM, (C) 200 µM, (D) 2 mM, and (E) 20 mM. [NaClO₄] = 0.6 M, and ionic strength = 0.6 M. V₁₀ is a combination of H₃V₁₀O₂₈³⁻, H₂V₁₀O₂₈⁴⁻, NaHV₁₀O₂₈⁴⁻, Na₂V₁₀O₂₈⁴⁻, HV₁₀O₂₈⁵⁻ and NaV₁₀O₂₈⁵⁻; V₄ is a combination of V₄O₁₂⁴⁻ and HV₄O₁₃⁵⁻; V₂ is a combination of H₂V₂O₇²⁻ and HV₂O₇³⁻.
Figure S4.2 Predominance diagram of vanadium(IV) species as a function of pH. Total [vanadium(IV)] = 10 µM, [NaClO₄] = 0.6 M, and ionic strength = 0.6 M.
Text S4.1 Reactions and equilibrium constants of vanadium(V) and vanadium(IV) species

\[
\begin{align*}
\text{HVO}_2^2+3\text{H}^+ &\leftrightarrow \text{VO}_2^2+2\text{H}_2\text{O} & (1) & \log K_1=15.89 \\
10\text{HVO}_2^2+17\text{H}^+ &\leftrightarrow \text{H}_3\text{V}_{10}\text{O}_{28}^5+12\text{H}_2\text{O} & (2) & \log K_2=150.38 \\
10\text{HVO}_2^2+16\text{H}^+ &\leftrightarrow \text{H}_2\text{V}_{10}\text{O}_{28}^5+12\text{H}_2\text{O} & (3) & \log K_3=145.70 \\
10\text{HVO}_2^2+15\text{H}^+ &\leftrightarrow \text{HV}_{10}\text{O}_{25}^2+12\text{H}_2\text{O} & (4) & \log K_4=141.50 \\
10\text{HVO}_2^2+15\text{H}^++\text{Na}^+ &\leftrightarrow \text{NaHV}_{10}\text{O}_{25}^2+12\text{H}_2\text{O} & (5) & \log K_5=143.68 \\
10\text{HVO}_2^2+14\text{H}^++2\text{Na}^+ &\leftrightarrow \text{NaHV}_{10}\text{O}_{28}^4+12\text{H}_2\text{O} & (6) & \log K_6=139.33 \\
10\text{HVO}_2^2+14\text{H}^++\text{Na}^+ &\leftrightarrow \text{NaV}_{10}\text{O}_{25}^5+12\text{H}_2\text{O} & (7) & \log K_7=137.03 \\
5\text{HVO}_2^2+5\text{H}^+ &\leftrightarrow \text{V}_5\text{O}_{15}^5+5\text{H}_2\text{O} & (8) & \log K_8=52.02 \\
4\text{HVO}_2^2+4\text{H}^+ &\leftrightarrow \text{V}_4\text{O}_{12}^4+4\text{H}_2\text{O} & (9) & \log K_9=42.60 \\
4\text{HVO}_2^2+3\text{H}^+ &\leftrightarrow \text{HV}_4\text{O}_{12}^3+3\text{H}_2\text{O} & (10) & \log K_{10}=42.60 \\
2\text{HVO}_2^2+2\text{H}^+ &\leftrightarrow \text{H}_2\text{V}_2\text{O}_7^2+\text{H}_2\text{O} & (11) & \log K_{11}=19.80 \\
2\text{HVO}_2^2+\text{H}^+ &\leftrightarrow \text{HV}_2\text{O}_7^2+\text{H}_2\text{O} & (12) & \log K_{12}=10.20 \\
\text{HVO}_2^2+\text{H}^+ &\leftrightarrow \text{H}_2\text{VO}_4 & (13) & \log K_{13}=8.75 \\
\text{HVO}_2^2 &\leftrightarrow \text{VO}_4^3+\text{H}^+ & (14) & \log K_{14}=10.20 \\
\text{VO}^{2+}+\text{H}_2\text{O} &\leftrightarrow \text{VO(OH)}^+ + \text{H}^+ & (15) & \log K_{15}=-5.94 \\
\text{VO}^{2+}+2\text{H}_2\text{O} &\leftrightarrow \text{V(OH)}_2^+ + \text{H}^+ & (16) & \log K_{16}=-5.70 \\
2\text{VO}^{2+}+2\text{H}_2\text{O} &\leftrightarrow \{\text{V(OH)}_2\}^2+ + 2\text{H}^+ & (17) & \log K_{17}=-6.69 \\
\text{VO}^{2+}+3\text{H}_2\text{O} &\leftrightarrow \text{VO(OH)}_3^+ + 3\text{H}^+ & (18) & \log K_{18}=-18.00 \\
2\text{VO}^{2+}+5\text{H}_2\text{O} &\leftrightarrow \{\text{V(OH)}_2\}^2+ + 5\text{H}^+ & (19) & \log K_{19}=-22.50 \\
\text{V}_2\text{O}_4(\text{s})+2\text{H}^+ &\leftrightarrow \text{VO}^{2+}+\text{H}_2\text{O} & (20) & \log K_{20}=4.27 \\
\text{VO(OH)}_2(\text{s})+2\text{H}^+ &\leftrightarrow \text{VO}^{2+}+2\text{H}_2\text{O} & (21) & \log K_{21}=5.89 
\end{align*}
\]
Figure S4.3 Correlations between the cathodic peak current of vanadium (V) species and the square root of scan rates. Total \([\text{vanadium(V)}] = 20 \text{ mM}, [\text{NaClO}_4] = 0.6 \text{ M}, \) and ionic strength = 0.6 M. The EC current at disk electrode potentials of 0.10, -0.54, -0.74, and -1.15 V was taken for VO\(^2^+\), V\(_{10}\), V\(_4\) and HVO\(_4^{2-}\), respectively.
Text S4.2 Calculations of the electron-transfer number and diffusion coefficient

The electron-transfer number (n) and diffusion coefficient of vanadium(V) species (D, cm/s) were calculated through combing the slope of Koutecky-Levich plots (Figure 4.4 in the main text) from Equation 1 with the slope from correlation of cathodic peak current vs. square root of scan rates (Figure S4.1) from Equations S4.2 below.¹

\[
\frac{1}{i} = \frac{1}{i_K} + \frac{1}{i_D} = \frac{1}{i_K} + \frac{1}{0.62nFAD^{2/3}\omega^{1/2}\theta^{-1/6}C_0} \quad (S4.1)
\]

\[
I_p = (2.69 \times 10^5)n^{3/2}AD^{1/2}C_0V^{1/2} \quad (S4.2)
\]

where \( i \) is the current measured on the disk electrode (A), \( i_K \) represents the kinetic current in the absence of diffusion limitation (A), \( i_D \) is the diffusion current (A), F is Faradic constant (C/mol), A is the electrode surface area (cm²), \( \omega \) is angular frequency of the rotation (s⁻¹), \( \nu \) is the kinematic viscosity of the solution (cm²/s), \( V \) is the scan rate (V/s) and \( C_0 \) is the bulk concentration of vanadium(V) species (mol/cm³).

Text S4.3 Calculations of rate constant, charge transfer coefficient and intrinsic rate constant

The kinetic current of vanadium(V) reduction at different potentials was determined by the intercept of Koutecky-Levich plots (Figure S4.3 and Figure S4.4). The rate constant of vanadium(V) reduction (k) was further calculated from Equation 4.3:¹

\[
k = \frac{i_k}{nFAC_0} \quad (S4.3)
\]

where \( k \) is the rate constant at a targeted potential (cm/s), \( i_k \) is the kinetic current of vanadium(V) reduction, \( n \) is the electron-transfer number, F is Faradic constant (C/mol),
A is the electrode surface area (cm$^2$), and $C_0$ is the bulk concentration of vanadium(V) species (mol/cm$^3$).

To obtain charge transfer coefficient ($\alpha$), Tafel analysis was conducted on RRDE data of vanadium(V) reduction with rotation speed from 1600 to 2700 rpm (Figure S4.5 and Figure S4.6). $\alpha$ was determined from the slope of the Tafel plots at three rotation speeds (Equation S4.4) and the average was taken in Table 2.2 of the main text,

$$\log i = \log i_0 - \frac{\alpha n F}{2.3RT} \eta$$

(S4.4)

Where $i$ is the measured current (A), $i_0$ is the exchange current (A), $\alpha$ is the charge transfer coefficient, $n$ is the electron-transfer number, $\eta$ is overpotential (the difference between applied potential and reduction onset potential, V), $R$ is gas constant (J/(mol·K)), and $T$ is the temperature (K).

The intrinsic rate constants were calculated based on Butler-Volmer electrode kinetics (Equation S4.5)$^1$

$$k_0 = k / \exp \left( - \frac{\alpha n F \eta}{RT} \right)$$

(S4.5)

Where $k_0$ is the intrinsic rate constant (cm/s), $k$ is the rate constant at a targeted potential (cm/s), $\alpha$ is the charge transfer coefficient, $n$ is the electron-transfer number, $F$ is Faradic constant (C/mol), $\eta$ is overpotential (the difference between applied potential and reduction onset potential, V), $R$ is gas constant (J/(mol·K), and $T$ is the temperature (K).
With multiple rate constants at different overpotentials and the average charge transfer coefficient, multiple intrinsic rate constants \( k_0 \) were calculated based on Equation S4.5. The average intrinsic rate constant was used in Table 2.2 of the main text.

**Figure S4.4** Koutecky-Levich plots of linear sweep voltammetry of the reduction of vanadium(V) on a rotating gold ring-disk electrode: (A) \( \text{VO}_2^{\text{+}} \), (B) \( \text{V}_{10} \), (C) \( \text{V}_4 \) and (D) \( \text{HVO}_4^{2-} \). Total [vanadium(V)] = 20 mM, [\( \text{NaClO}_4 \)] = 0.6 M, ionic strength = 0.6 M, and scan rate = 50 mV/s.
Figure S4.5 Koutecky-Levich plots of linear sweep voltammetry of the reduction of VO$_2^+$ at pH=1 on a rotating gold ring-disk electrode in the presence of phosphate: (A) 1 mM, (B) 5 mM, (C) 10 mM and (D) 20 mM. Total [vanadium(V)] = 20 mM, [NaClO$_4$] = 0.6 M, ionic strength = 0.6 M, and scan rate=50 mV/s.
Figure S4.6 Tafel plots of linear sweep voltammetry of the reduction of vanadium(V) on a rotating gold ring-disk electrode: (A) VO$_2^+$, (B) V$_{10}$, (C) V$_4$ and (D) HVO$_4^{2-}$. Total [vanadium(V)] = 20 mM, [NaClO$_4$] = 0.6 M, ionic strength = 0.6 M, and scan rate= 50 mV/s.
Figure S4.7 Tafel plots of linear sweep voltammetry of the reduction of of VO$_2^+$ at pH=1 on a rotating gold ring-disk electrode in the presence of phosphate: (A) 1 mM, (B) 5 mM, (C) 10 mM and (D) 20 mM. Total [vanadium(V)] = 20 mM, [NaClO$_4$] = 0.6 M, ionic strength = 0.6 M, and scan rate = 50 mV/s.
**Text S4.4 Calculation of half-life of the intermediate products**

Half-life of the intermediate products of vanadium(V) was calculated based Equations S4.6 and 4.7.²

\[
\frac{N_0}{N} = 1 + 1.28 \left( \frac{\nu}{D} \right)^{\frac{1}{3}} \left( \frac{k}{\omega} \right) \quad (S4.6)
\]

\[
t_{1/2} = \frac{\ln 2}{k} \quad (S4.7)
\]

where \( N \) is the experimental collection efficiency, \( N_0 \) is theoretical collection efficiency (24%), \( \nu \) is the kinematic viscosity of the electrolyte (cm\(^2\)/s), \( D \) is the diffusion coefficient of the intermediate products (cm\(^2\)/s), \( \omega \) is the rotation speed (rad/s), \( k \) is first-order decay rate constant of the reduction product (s\(^{-1}\)), and \( t_{1/2} \) is the half-life of the intermediate products (s).

**Figure S4.8** Impact of rotation speed on the collection efficiency reduction products produced at a gold rotating ring-disk electrode. Total [vanadium(V)] = 20 mM, [NaClO\(_4\)]
= 0.6 M, ionic strength = 0.6 M, scan rate = 50 mV/s, and ring potential was fixed at 1.3, 1.0, 0.8, and 0.7 V for VO$_2^+$, V$_{10}$, V$_4$ and HVO$_4^{2-}$, respectively.

Figure S4.9 Impact of phosphate on the linear sweep voltammetry of vanadium(V) at a rotating gold ring-disk electrode: (A) VO$_2^+$, (B) V$_{10}$, (C) V$_4$ and (D) HVO$_4^{2-}$. Total [vanadium(V)] = 20 mM, [NaClO$_4$] = 0.6 M, ionic strength = 0.6 M, scan rate = 50 mV/s, rotation speed = 2400 rpm, and ring potential was fixed at 1.3, 1.0, 0.8, and 0.7 V for VO$_2^+$, V$_{10}$, V$_4$ and HVO$_4^{2-}$, respectively.
Figure S4.10 Predominance diagram of phosphate as a function of pH. Total [phosphate] = 20 mM, [NaClO₄] = 0.6 M, and ionic strength = 0.6 M.

Figure S4.11 Impact of phosphate on the collection efficiency of the reduction products produced on a rotating ring-disk electrode. Total [vanadium(V)] = 20 mM, [NaClO₄] = 0.6 M, ionic strength = 0.6 M, rotation speed = 2400 rpm, scan rate = 50 mV/s, and Ring electrode potential was fixed at 1.5, 1.0, 0.8, and 0.7 V for VO₂⁺, V₁₀, V₄ and HVO₄²⁻, respectively.
References


Figure S5.1 Spectrum of the 450-W UV immersion lamp used for photochemical treatment of the spent IX brine.

Figure S5.2 Impact of formate dosage on photochemical removal of total chromium in the spent IX regenerant brine. [Formate] = 5-120 mM, pH = 8.4-8.7, and the sample was filtered through 0.2-µm PVDF membrane before analysis.
Figure S5.3 Impact of initial pH on photochemical removal of total chromium in the spent IX regenerant brine. [Formate] + [Formic acid] = 40 mM.

Figure S5.4 The change of solution pH during photochemical treatment of the spent IX regenerant brine in the presence of formate. [Formate] + [Formic acid] = 160 mM.
Figure S5.5 Photochemical removal of toxic heavy metals in the spent IX brine in the presence of formate. [Formate] + [Formic acid] = 160 mM and initial pH = 3.4.