

ARSENIC REMOVAL USING ADVANCED REDUCTION PROCESS

A Thesis

by

VISHAKHA KAUSHIK

Submitted to the Office of Graduate and Professional Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Chair of Committee,	Bill Batchelor
Committee Members,	Qi Ying
	Raghupathy Karthikeyan
Head of Department,	Robin Autenrieth

May 2016

Major Subject: Civil Engineering

Copyright 2016 Vishakha Kaushik

ABSTRACT

The effectiveness and feasibility of Advanced Reduction Process on arsenic has been studied. Advanced Reduction Process generates highly reducing radicals using a combination of a reducing reagent and UV light. These highly reducing radicals react with arsenic (oxidized specie) to convert it to elemental arsenic that is insoluble in water.

Screening experiments were conducted to identify the most effective ARP combination of a suitable reagent that gives maximum removal of arsenic. Three reagents (dithionite, ferrous ion and sulfite ion) were tested and dithionite was chosen to be the best amongst the three. This was based on faster kinetics and higher removal than other reagents.

Dithionite was further tested for effectiveness using various UV intensities, different initial dithionite concentrations and at 5 different pH (5, 6, 7, 8, and 9) conditions.

A kinetic study of changing arsenic and dithionite concentrations with time was done to better understand the reaction. Resolubilization of arsenic continues to be the challenge. However, pH 8 showed maximum removal of arsenic. And As (V) showed a better removal than As (III) species.

DEDICATION

This thesis is dedicated to my mother, Late Dr. Rama Kaushik, who will always be a source of inspiration for me.

ACKNOWLEDGEMENTS

This thesis has become possible with the guidance and the help of several individuals who in one way or another contributed and extended their valuable assistance in the preparation and completion of this study.

First and foremost I would like to acknowledge Texas A&M University and its dedicated faculty for helping me to acquire the theoretical knowledge which facilitated this research work.

I express my sincere gratitude towards Dr. Bill Batchelor, Committee chair, Professor and holder of the R.P. Gregory '32 Chair, Zachry Department of Civil Engineering, for giving me the opportunity to undertake this project work under his guidance. I would like to thank him for his patience in guiding me not only in my practical research work but also in completing thesis writing and supporting my research work financially. My heartfelt gratitude to my committee members Dr. Raghupathy Karthikeyan and Dr. Qi Ying for their guidance, encouragement and consistent support throughout my thesis. Their valuable suggestions and advice have facilitated the successful completion of my thesis.

I would also like to thank Mr. Venkata Sai Vamsi Botlaguduru, Ms. Yuhang Duan and Mr. Li Wang for their continuous guidance and support in teaching me to work with various instruments, sharing their best practices with lab work and making this experience a memorable one.

I am beholden to my parents, my grandparents, my siblings and my friends, who have always supported me in all my endeavors for their unconditional love and relentless encouragement.

Last but not the least I would like to thank God for his blessings.

NOMENCLATURE

ARP	Advanced Reduction Process
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
ECAR	ElectroChemical Arsenic Remediation
EPA	Environmental Protection Agency
FDA	Food and Drug Administration
ICP- MS	Inductively Coupled Plasma Mass Spectrometry
OSHA	Occupational Safety and Health Administration
PPE	Personal Protective Equipment
PTFE	Polytetrafluoroethylene
SAR	Subterranean Arsenic Removal
STP	Sewage Treatment Plant
TDS	Total Dissolved Solids
UV-L	Low pressure Ultraviolet lamps
UV-M	Medium pressure Ultraviolet lamps
UV-N	Narrowband Ultraviolet lamps
WHO	World Health Organization

TABLE OF CONTENTS

	Page
ABSTRACT.....	ii
DEDICATION.....	iii
ACKNOWLEDGEMENTS.....	iv
NOMENCLATURE.....	vi
TABLE OF CONTENTS.....	vii
LIST OF FIGURES.....	ix
LIST OF TABLES.....	xi
1. INTRODUCTION.....	1
1.1 Introduction.....	1
1.1.1 Arsenic.....	1
1.1.2 Arsenic Abundance.....	3
1.1.3 Regulations.....	6
1.2 Objectives.....	8
2. BACKGROUND.....	10
2.1 Fate and Transport of Arsenic.....	10
2.2 Arsenic Treatment Technologies.....	12
2.2.1 Advanced Reduction Process (ARP).....	17
2.3 Literature Review.....	18
3. ARSENIC REMOVAL BY ADVANCED REDUCTION PROCESS.....	22
3.1 Experimental Apparatus.....	22
3.1.1 Anaerobic Chamber.....	22
3.1.2 UV Light and UV Light Meter.....	22
3.1.3 Spectrophotometer.....	23
3.1.4 Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)..	23
3.1.5 Quartz Reactors.....	25
3.1.6 Cuvettes.....	25
3.2 Chemical Reagents.....	26
3.2.1 Deoxygenated Deionized Water.....	26

3.2.2 Chemicals.....	26
3.3 Experimental Work.....	27
3.3.1 Sample Preparation.....	27
3.3.1.1 Contaminated Wastewater Sample.....	27
3.3.1.2 Dithionite Solution.....	27
3.3.1.3 Ferrous Iron Solution.....	28
3.3.1.4 Sulfite Ion Solution.....	28
3.3.1.5 ICP Sample Preparation.....	28
3.3.1.6 Phosphate Buffer.....	28
3.3.2 Experimental Setup.....	29
3.3.3 Experimental Procedure.....	30
3.3.3.1 Screening Reagents.....	30
3.3.3.2 Kinetic Experiments.....	31
3.3.3.3 Kinetic Study.....	32
4. RESULTS AND DISCUSSION.....	34
4.1 Screening Experiments.....	34
4.2 Evaluating Resolubilization Process.....	36
4.3 Characterization of Kinetics.....	42
4.3.1 Arsenate (As(V)).....	42
4.3.2 Arsenite (As(III)).....	44
4.3.3 Effect of pH on Initial Dithionite Concentration.....	46
4.4 Approach to Model Development.....	47
4.4.1 Modelling Dithionite Concentration.....	48
4.4.2 Modelling Arsenic Concentration.....	50
5. SUMMARY.....	62
5.1 Conclusion.....	62
5.2 Recommendations.....	64
REFERENCES.....	65
APPENDIX A.....	73
APPENDIX B.....	75
PART a. Kinetic Experiment results – As(V) and corresponding dithionite concentration values.....	75
PART b. Kinetic Experiment results – As(III) and corresponding dithionite concentration values.....	85
APPENDIX C.....	95

LIST OF FIGURES

	Page
Figure 1. Chemical structure of some common arsenic compounds (Michael F. Hughes, 2011).....	2
Figure 2. Arsenic contaminated groundwater around the world (Mahzuz, 2014).....	4
Figure 3. Arsenic contaminated areas of Bangladesh based on data by Department of Public Health Engineering, Bangladesh (Smedley, 2001).....	5
Figure 4. Fate and transport of arsenic in the environment (Tanaka, 1988).....	10
Figure 5. Eh-pH diagram for Arsenic at STP with total arsenic 10 ⁻⁵ mol/l and total sulfur 10 ⁻³ mol/l (A. Gomez-Camirero, 2001).....	12
Figure 6. Dissociation of dithionite and sulfite with activation energy to form reducing radicals (Sunhee Yoon, 2014).....	20
Figure 7. ICP-MS principle (GLOBAL, 2016).....	24
Figure 8. Cylindrical UV reactor.....	25
Figure 9. Cuvette for UV-visible spectrophotometer.....	26
Figure 10. Experimental setup inside the anaerobic chamber.....	29
Figure 11. Soluble arsenic (V) concentration varying with time when different reagents are used and UV light is applied.....	35
Figure 12. Concentration of soluble arsenic (V) with time during irradiation by UV-L in presence of dithionite.....	37
Figure 13. UV scan for (a) T=0, no UV (b) T=5 min of UV (c) T=5 min of UV, added 500 μM dithionite and irradiated for another 5 min of UV (d) T= 5 min of UV, 55 min in dark (e) T= 10 min of UV (f) T=60 min of UV...	39
Figure 14. Effect of UV-L and sulfite addition on soluble arsenic. The blue diamonds are results without addition of sulfite and red diamonds are results with the addition of sulfite.....	40
Figure 15. UV scan for solutions of As (V) and dithionite with and without addition of sulfite after 5 minutes irradiation with UV-L.....	41

Figure 16. Effect of time on concentration of As (V) at different pH.....	43
Figure 17. Dithionite concentration curve at different pH for As (V).....	44
Figure 18. Effect of time on concentration of As (III) at different pH.....	45
Figure 19. Dithionite concentration curve at different pH for As (III).....	45
Figure 20. Initial dithionite present with As (V) with varying pH.....	46
Figure 21. Percent of added dithionite available at different pH.....	47
Figure 22. Measured and modeled concentrations of soluble As (III) at pH 5 as functions of time.....	52
Figure 23. Measured and modeled concentrations of soluble As (III) at pH 6 as functions of time.....	53
Figure 24. Measured and modeled concentrations of soluble As (III) at pH 7 as functions of time.....	54
Figure 25. Measured and modeled concentrations of soluble As (III) at pH 8 as functions of time.....	55
Figure 26. Measured and modeled concentrations of soluble As (III) at pH 9 as functions of time.....	56
Figure 27. Measured and modeled concentrations of soluble As (V) at pH 5 as functions of time.....	57
Figure 28. Measured and modeled concentrations of soluble As (V) at pH 6 as functions of time.....	58
Figure 29. Measured and modeled concentrations of soluble As (V) at pH 7 as functions of time.....	59
Figure 30. Measured and modeled concentrations of soluble As (V) at pH 8 as functions of time.....	60
Figure 31. Measured and modeled concentrations of soluble As (V) at pH 9 as functions of time.....	61

LIST OF TABLES

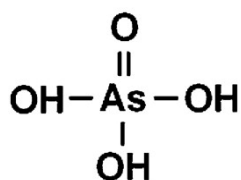
	Page
Table 1. Limitations of existing arsenic removal methods (Mollehuara, September 2012).....	16
Table 2. Results of experiments with As (V) in dithionite solutions irradiated with UV-L.....	38
Table 3. Effects of UV-L and sulfite addition on soluble arsenic.....	40
Table 4. Dissolution of elemental arsenic using thiosulfate.....	42
Table 5. Value of rate constants for arsenic at different pH as computed from MATLAB modelling and their goodness of fit.....	51
Table 6A. Soluble concentrations of As (V) at various times when reacted with 500 μ M dithionite at nominal pH 8. (Highlighted concentration is minimum value observed).....	73
Table 7A. Soluble concentrations of As (V) at various times when reacted with 500 μ M ferrous ion solution at nominal pH 8. (Highlighted concentration is minimum value observed).....	73
Table 8A. Soluble concentrations of As (V) at various times when reacted with 500 μ M Sulfite ion solution at nominal pH 8. (Highlighted concentration is minimum value observed).....	74
Table 9A. Soluble concentrations of As (V) at various times when reacted with 100 μ M ferrous ion solution at nominal pH 8. (Highlighted concentration is minimum value observed).....	74
Table 10A. Soluble concentrations of As (III) at various times when reacted with 500 μ M ferrous ion solution at nominal pH 8. (Highlighted concentration is minimum value observed).....	74
Table 11C. Values of quantum yield (Q) and initial concentration of dithionite (D _o) for arsenic at various pH. The Q values were calculated using nonlinear regression on measured concentrations of dithionite.....	97

1. INTRODUCTION

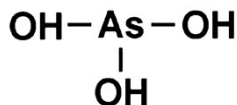
1.1 Introduction

1.1.1 Arsenic

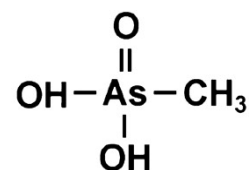
Arsenic is the 33rd element in the periodic table having a relative atomic mass of 74.92 u and density (of most abundant allotrope of arsenic) of 5.33g/cm³ (Holleman, Wiberg, & Wiberg, 1985). Arsenic is believed to be named after a Greek word ‘arsenikos’ meaning potent (Bentor, 2012). Arsenic is also known as arsénico in Spanish, Arsen in German, and arsenico in Italian (Henke, 2009). The atomic weight and density classifies arsenic as a heavy metal (Duffus, 2002); however, it has also been characterized as a crystalline metalloid (Live Science Staff, 2013). The most abundantly found allotrope of arsenic is steel gray in color and very brittle (Norman, 1998). Yellow and black isotopes also exist (Norman, 1998). The most common oxidation states of arsenic found in the earth’s crust are oxidation states of +5 in the arsenates, +3 in the arsenites, and -3 in the arsenides. The most abundant forms are arsenates and arsenites, which are more harmful than arsenide or elemental arsenic. In fact, elemental arsenic is relatively inert (Sanderson, 2014). Figure 1 shows the chemical structure of some of the arsenic compounds that are of importance in the environment.



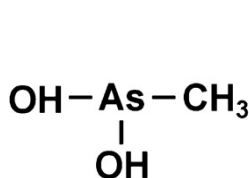
Arsenic Acid, Arsenate



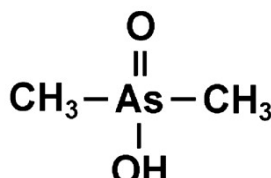
Arsenious Acid, Arsenite



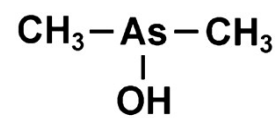
Monomethylarsonic Acid



Monomethylarsonous Acid



Dimethylarsinic Acid



Dimethylarsinous Acid

Figure 1. Chemical Structure of some common arsenic compounds (Michael F. Hughes, 2011)

Arsenic finds a variety of uses. It is used as a doping agent in semiconductors for solid-state devices; it is used in bronzing, hardening and improving the sphericity of shot, pyrotechny and in insecticides and other poisons (Helmenstine, 2015). As for the ancient uses, Victorian era women used a mixture of arsenic, chalk and vinegar to lighten their complexions (Helmenstine, 2015). The same era also used arsenic compound, Dr. Fowler's Solution (potassium arsenate dissolved in water) as a popular cure-all tonic. It also finds use in a variety of products like pigments, medicines, alloys, pesticides, herbicides, glassware, embalming fluids, etc. (Henke, 2009). Arsenic is also used as a depilatory in leather manufacturing plants (Henke, 2009). Hence, arsenic has been in use for many centuries.

1.1.2 Arsenic Abundance

Arsenic is chosen as the contaminant of study because it becomes life threatening in living beings even at concentrations as low as 5 mg/m³ according to EPA and OSHA. (EPA, 2009) (Bentor, 2012). Furthermore, this contaminant is present widely in the biosphere. In the Earth's crust, its abundance is about five grams per ton, while the cosmic abundance is estimated as about four atoms per million atoms of silicon (Sanderson, 2014). Towards the end of the twentieth century, scientists detected widespread poisoning in Bangladesh, India (West Bengal), parts of Argentina, Cambodia, Chile, mainland China, Mexico, Nepal, Pakistan, Taiwan, Vietnam, and the United States (Henke, 2009) as can be seen in figure 2. Most of these poisonings are from consumption of arsenic-bearing groundwater, which is a threat to more than 100 million human beings (Henke, 2009). Arsenic exposure to humans is known to cause cancer. The endpoints of arsenic attack are still being studied with two major theories. One is the interaction of trivalent arsenicals with sulfur present in human protein; and second being the capability of arsenic generating oxidative stress in humans (Michael F. Hughes, 2011). Ingestion of arsenic is also known to be the cause of skin diseases, neurological defects, cardiovascular problems and diabetes (NRC, 2001).

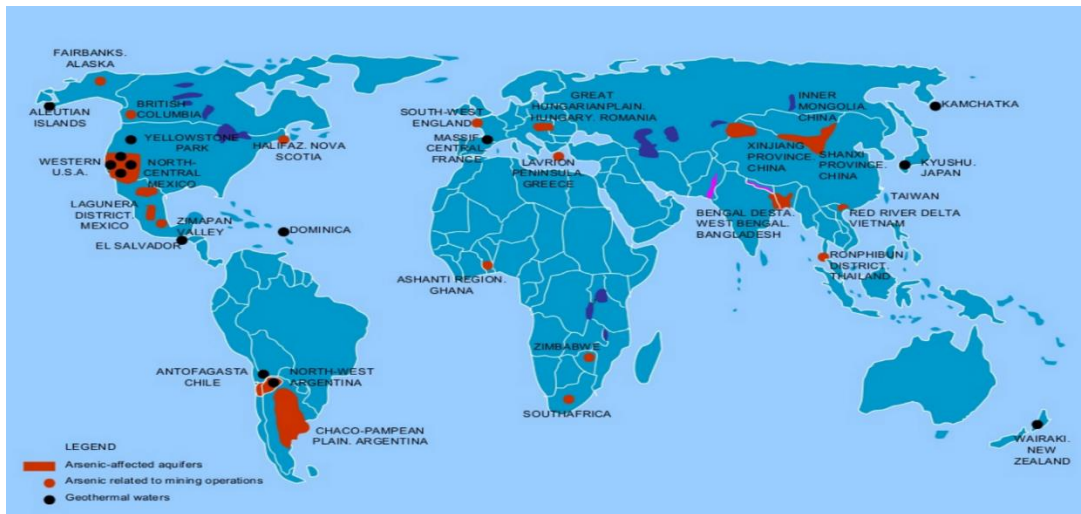


Figure 2. Arsenic Contaminated groundwater around the world (Mahzuz, 2014)

Out of all the arsenic in the Earth’s atmosphere, one-third is of natural origin. Volcanic activities and arsenic salts that volatilize at low temperatures are the two major natural sources of arsenic. Arsenic causes many problems, especially when it is found in groundwater that is used as drinking water by many countries like Bangladesh, India and Taiwan (Barlow, 2015). These countries have levels of arsenic ranging from 5 to 100 times the usual concentration of arsenic in their drinking water (Figure 3) and this leads to adverse health effects like skin diseases and cancer (Barlow, 2015). Increased levels of arsenic cause arsenic poisoning in our bodies. Arsenic bearing waters are not only caused by industrial spills, improper disposal of wastes leading to its leaching in groundwater, but also from natural activities of the geothermal waters leading to its mobilization from rocks. The natural processes of oxidation and reduction of chemicals like arsenosulfides are responsible for dissolution of arsenic stored in rocks and sediments to dissolve and contaminate waters. During the oxidation-dissolution process, arsenides and arsenosulfides already present naturally or with contaminated wastewaters, release arsenic

to groundwater and other fresh water sources (Henke, 2009). In addition, microbes oxidize organic matter present in waters into bicarbonates and carbonates. In some special cases, like that of Bangladesh, due to the presence of goethite and other metallic rocks, these bicarbonates and carbonates increase the pH of the waters causing arsenic to desorb from mineral surfaces (Appelo, 2002). On the other hand, reductive dissolution of arsenic occurs under anaerobic conditions that develop in soils, rocks or sediments which leads to dissolution of arsenic bearing iron oxides/ hydroxides (Henke, 2009).

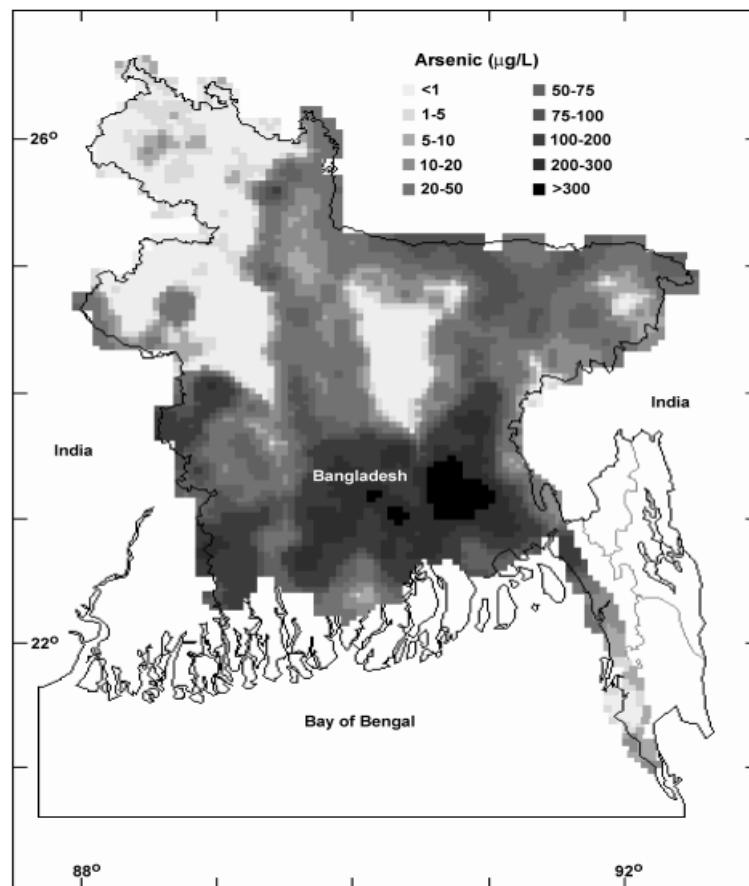


Figure 3. Arsenic contaminated areas of Bangladesh based on data by Department of Public Health Engineering, Bangladesh (Smedley, 2001)

Our bodies don't easily absorb elemental arsenic, which is less harmful than As (III). As (III) compounds like H_3AsO_3 , that are carcinogenic with high levels of toxicity, are easily absorbed by our body (Chemicool Periodic Table, 2012). As a matter of fact, arsenic was known as "King of Poisons" for many centuries (Helmenstine, 2015).

1.1.3 Regulations

The drinking water standard set by EPA for total arsenic concentration in drinking water is 10 ppb (EPA, Arsenic in Drinking Water, 2013). Although there are no limits on arsenic in most foods, the Food and Drug Administration (FDA) has also set the limit of 10 ppb on bottled water and apple juice (US-Food&DrugAdmin, 2015). On the other hand, EPA has also set limits for amounts of arsenic that can be discharged to the environment by various industries and has also put restrictions on the use of arsenic. For example, many governments have put regulations on discharge of arsenic wastewater from ore smelters and coal combustion power plants (Henke, 2009). Efforts have been made in this regard with laws like the Superfund in the United States, which aims at remediation of 1209 contaminated sites that were identified in 1999. Arsenic-contaminated sites rank second (568 sites out of 1209) only after lead contaminated sites in that list (EPA US, 2002). Arsenic has also been listed in the Priority List of Hazardous Substances prepared by the Agency for Toxic Substances and Disease Registry (ATSDR) on the basis of occurrence, toxicity and potential for human exposure. This action was required by the Comprehensive, Environmental, Response, Compensation and Liability Act (CERCLA) and arsenic was listed as the most important substance in the 2007 ATSDR (ATSDR, 2007).

The Occupational Safety & Health Administration (OSHA) has put restrictions on exposure to inorganic arsenic in the workplace at 10 micrograms per cubic meter of air (USDept.ofLabor, 1978). This limit is averaged over an 8-hour period. OSHA also requires workers to use Personal Protective Equipment (PPE), like respirators, if the exposure to arsenic is higher.

The World Health Organization (WHO) standard for arsenic in drinking water is 10 µg/l. The U.S. Geological Survey estimated median groundwater concentration of arsenic to be about 1 µg/l in 1999. Although the median level of arsenic in US drinking water are well within the WHO drinking water limits, maximum concentrations in Nevada were as high as 8 µg/l (Focazio MJ, 1999) and levels of 1000 µg/l have also been detected in natural waters in the United States (Steinmaus C, 2003). This value is much above the WHO drinking water standard and would be extremely toxic if used as potable water without arsenic removal.

Recent changes in regulations by the Environmental Protection Agency have put restrictions on power plants for discharging mercury, arsenic, selenium and lead, which are recognized to cause cancer and learning disabilities (Devaney, 2015). Impacting more than 1000 steam powered electric power plants, the new water pollution rules, which were issued on November 3, 2015, are expected to reduce toxic pollutants by 1.4 billion pounds annually (Hayat, 2015). According to the EPA, the new standards would provide net benefits valued at \$463 million each year to America by reducing cancer, neurological and drinking water risks (Hayat, 2015). The new rule known as the Steam Electric Power Generating Effluent Guidelines, is the first update in electric power plant guidelines since

1982 (Valentine, 2015). These new regulations put more pressure on industries to treat their discharges with additional investment in their treatment technologies. These rules call for cost effective wastewater treatment technologies that are effective against such pollutants and Advanced Reduction Processes have the potential to meet these requirements.

1.2 Objectives

- i. Study the effect of Advanced Reduction Processes on reducing the concentration of arsenic (As (III) and As (V)) that would help industries discharge wastewater within safe arsenic limits.
- ii. Study the kinetics of arsenic removal using selected reagent with Advanced Reduction Process in order to optimize the process

For achieving the above, following steps will be undertaken:

A) Develop analytical and experimental procedures

The developed analytical procedures would be accurate, reproducible and reliable. Procedures will be developed to measure arsenic using ICP-MS (Inductively Coupled Plasma Mass Spectrometry) within the machine's detection limit.

B) Screen reagents and activation methods for effectiveness against As(III) and As(V)

This step would include the combination of all the reagents and target compounds to find the best combination of reagent able to remove the target compounds (As (III) and As (V)). The time periods for experiments would be such that they help estimate the second-order rate constant. Various pH conditions and variation in UV light intensity would be used in experiments to find removal efficiencies and rate constants. The purpose is to study

the rates of all reactions under a range of reaction conditions, so that the possibility of applying the reactions in industrial treatment processes can be evaluated.

C) Develop design model for arsenic removal using ARP.

A model will be developed that describes rates of reduction of the target compound as functions of local conditions (pH, concentration of target, concentration of reagent and UV intensity). The model will include the rate of reaction of dithionite as a function of its own concentration and the intensity of UV- L light. The coefficient of the rate equations will be calculated by conducting non-linear regressions using MATLAB and MS Excel.

2. BACKGROUND

2.1 Fate and Transport of Arsenic

Of the arsenic present in Earth's atmosphere, two-third is anthropogenic in origin (Barlow, 2015). The anthropogenic origin of arsenic is attributed to its extensive use in agricultural applications, wood preservation, glass production (Welch, 2000), mining and waste treatment sites.

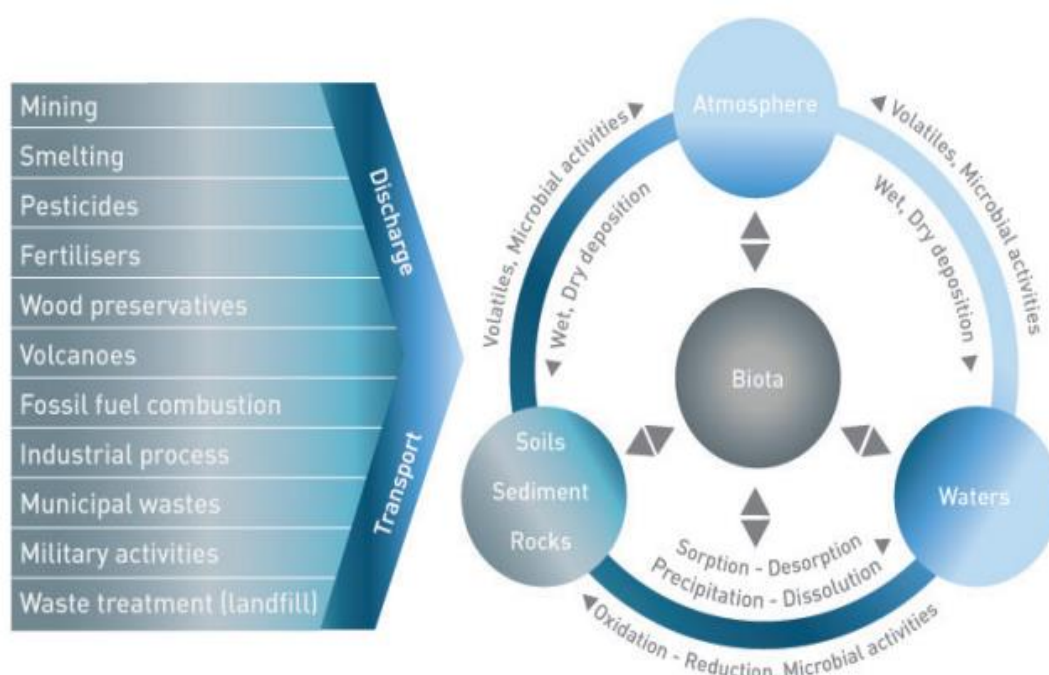


Figure 4. Fate and transport of Arsenic in the Environment (Tanaka, 1988)

Figure 4 shows the various sources of arsenic and how various physical, chemical and biological processes lead to its transfer in the environment. As discussed in the introduction, activities and industries like mining, smelting, pesticides, fertilizers, wood preservatives, waste treatment, military activities, municipal waste dumping, and other

industrial processes along with human activities of fossil fuel combustion and natural volcanic activities, are some of the many sources of increasing the concentration of arsenic in the environment. Once arsenic is introduced into the environment, then natural process and the interaction of various biota keep transferring arsenic from one form to another between soil, water and atmosphere. This movement of arsenic between different biota is interesting to examine. First, fossil fuel combustion is responsible for releasing arsenic into the air, primarily as arsenic trioxide (A. Gomez-Caminero, 2001). Microbial activity in soil, sediments and rocks also converts arsenic into volatile forms and releases it into the atmosphere. The oxidation processes that volatile arsenic undergoes in the atmosphere converts it back into non-volatile forms. (A. Gomez-Caminero, 2001). Similar activities occur that transport and distribute concentrations of arsenic amongst water soil and atmosphere. The more common state of arsenic found in oxygenated water and soil is its pentavalent state. Depending on the redox potential, alkalinity and biochemical processes occurring in soil and water, arsenic exists as arsenate and arsenite. More description of prevalent forms of arsenic are depicted in Figure 4. An increase in the “source” activities (Figure 4) just adds more arsenic to the biota cycle that keeps it in the environment forever. Hence, it is very important to limit release of arsenic that is harmful for living beings and dispose of it in the environment in a form that does not lead to environmental degradation. Figure 5 shows that at high Eh arsenate oxyanions exist, while under reducing conditions arsenite predominates.

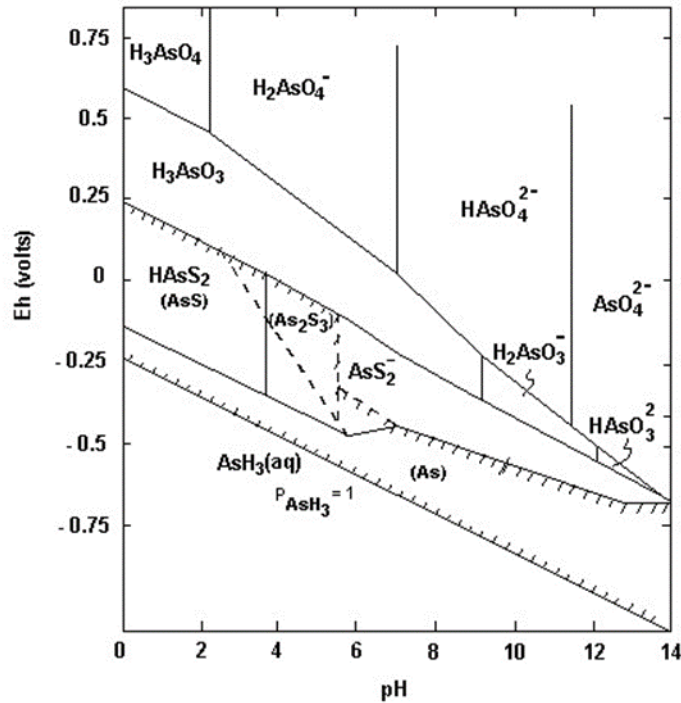


Figure 5. Eh-pH diagram for Arsenic at STP with total arsenic 10-5 mol/l and total sulfur 10-3 mol/l (A. Gomez-Caminero, 2001)

2.2 Arsenic Treatment Technologies

Treatment of arsenic-contaminated wastewater and management of wastes to prevent further depletion of environmental quality should be focused on preventing further addition of this toxic substance to the environment. Previous releases have stimulated a sense of fear in many across the globe. Waste management strategies include preventing environmental contamination by avoiding accidental leakage and intentional disposal of arsenic from point sources, so that no more arsenic enters the biota. One such waste management strategy for disposal of arsenic-bearing wastewater is treating the wastewater to remove arsenic.

Removal of arsenic depends on many factors, depending on which technology is used. Some of the major characteristics of water that will determine the best treatment process are the physical and chemical characteristics of the water such as pH (acidic waters are easier to treat), concentration of arsenic present, the concentration level that is required to be achieved by treatment, volume of water to be treated, presence of co-ions and their interference. Apart from these, training of personnel and cost of treatment processes are also important aspects to look for. More commonly used, cost efficient technologies for the removal of the more common forms of inorganic arsenate include sorption, coprecipitation with iron oxides and iron hydroxides, ion exchange, and separation technologies like filtration. Nevertheless, coprecipitation generates a lot of sludge that is difficult to dewater (Deliyanni, 2003).

Wastewaters may contain arsenic in the trivalent or pentavalent form, depending on the pH and other factors as discussed above in Figure 5. As (III) is more toxic and primarily exists as H_3AsO_3^0 at a pH of less than 9. Due to its zero charge, it is difficult to remove arsenite from wastewaters using technologies like sorption and ion exchange (Henke, 2009). To overcome this challenge, arsenite is oxidized to arsenate, which exists as oxyanions and can be removed with ion exchange, sorption and coprecipitation (Henke, 2009).

Oxidation of arsenite is not a spontaneous reaction in oxygenated water (Bisceglia, 2005). Various activation methods are used to attain the activation energy for the oxidation process like solar energy (Garcia, 2004), radiation (Hug, 2001), chemical methods (Dodd, 2006), gamma radiation (Henke, 2009), etc.

Ion exchange and sorption techniques look promising in terms of their capability to treat large volume of water, regeneration, and durability in water. But hardly any such systems have practically proven their efficiency to treat arsenic from water (Henke, 2009). Using such techniques would also require a lot of pretreatment of wastewater such that the Total Dissolved Salts is brought down to levels that would not choke the sorbent or ion exchange resin.

Coprecipitation also has a disadvantage in that it is affected by interfering ions; however, knowledge of chemistry and correct dosage can easily overcome this problem (EPA US, 2002). However, production of much toxic sludge is a problem, because it is difficult to dispose. Many technologies and sequences of processes are used in industries to remove arsenic from wastewater. Some of these are a combination many processes. Studies are going on to attain maximum removal of arsenic from wastewater. For example one study recommends oxidation of all arsenic to arsenate, followed by arsenic precipitation using ferric sulfate at a fixed pH and finally removal using adsorption by activated carbon and organic adsorbent (Yue LI, 2009). The main drawback with these techniques that remove a high percentage (99.9%) of arsenic is the large volume of toxic arsenic bearing sludge (Yue LI, 2009).

Apart from the chemical treatment methods discussed above, many biological methods are also used to remove arsenic from wastewater. One such technology is ABMet. Biological processes always have been slower than chemical processes and this one uses a retention time of 4 to 8 hours to attain the desired arsenic removal. The technology only uses a biological nutrient to feed its bacteria. This technology has even removed arsenic

under high TDS and low temperature conditions (Reinsel, 2015). THIOTEQ is another biological treatment technology used for arsenic removal. The technology oxidizes iron from biologically formed bioscorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) to react with arsenic (Reinsel, 2015). But biological methods have always been slow and are susceptible to shock loads and shock volumes of wastewater. In biological processes, it is difficult to monitor the amounts of electron donor and acceptor so that one does not become a limiting reagent (Vellanki BP, 2013). Limitations of present arsenic removal methods are summarized in Table 1 and call for development of new treatment methods.

Process	Disadvantages	References
<i>Precipitation Methods</i>		
Precipitation with lime	-Sludge contaminated with arsenic -Poor removal of As(III) -Requires constant process conditions - High sludge production	(Van_der_Meer, 2011)
Precipitation with ferric iron	- Sludge contaminated with arsenic -Poor removal of As(III)	(Henke, 2009)
Coagulation with Al(III), Fe(III) followed by precipitation	- Sludge contaminated with arsenic	
Biological Precipitation	-Arsenic might release back to environment after organic matter decay or organism death	(Rubidge, 2004)
<i>Non-Precipitation Methods</i>		
Adsorption	-Constant monitoring -Poor removal of As(III) -Monitoring of water flow and influent concentration	
Ion Exchange	-Effluent must be of low sulfate (<50 mg/L) -Effluent must be low nitrate (<5mg/L)	
Membrane Separation	-Expensive to install and operate -Higher concentration arsenic contaminated brine waste	
Biological Methods	-Susceptible to shock loading of other toxins -Long retention times	(Reinsel, 2015)

Table 1. Limitations of existing arsenic removal methods (Mollehuara, September 2012)

Apart from these conventional ways of treating arsenic in wastewater, many other cost effective novel ways of treating arsenic are being investigated. For example, some scientists are trying to help people in developing nations with cost effective treatment

technologies, which would help countries like Bangladesh to treat their arsenic at the village level. ElectroChemical Arsenic Remediation (ECAR) one such technology. This technology makes use of low current and produces rust from iron plates, which binds to arsenic in wastewater and forms a precipitate. This precipitate can be removed by sedimentation and decantation. To attain better quality water, filtration techniques could be used (Reinsel, 2015).

Nanomaterials with arsenic-adsorbing functional groups are being used for adsorbing even low concentrations of arsenic. The specialty of these nanomaterials is their ability to change color with adsorption of arsenic. Nanomaterials like this one are light, cost effective and have fast kinetics (El-Safty, 2012). Another new technology for arsenic removal is Subterranean Arsenic Removal (SAR). SAR uses an in-situ process in which water is first oxidized above the ground, then injected back to the aquifer creating an aerobic environment that oxidizes ferrous iron to ferric iron. Finally, ferric arsenate particles are produced and filtered by and adsorbed onto soil particles (Reinsel, 2015).

2.2.1 Advanced Reduction Process (ARP)

Knowing the disadvantages of current chemical and biological means of arsenic removal from water, this thesis focuses on Advanced Reduction Processes (ARP) and their role in arsenic removal from wastewater in a time and cost efficient manner. Advanced Reduction Processes (ARP) make up an upcoming group of treatment methods that looks promising for arsenic removal from wastewater.

Advanced Reduction Processes are chemical reduction processes that produce highly reactive reducing radicals by the reaction of reagents and activation methods.

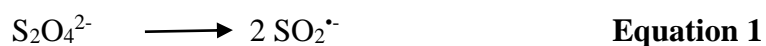
Irradiation with UV light is an example of an activation method and the sulfur dioxide radical is an example of a reducing radical. The concentrations of reagents, target compounds and the intensity of UV light determine the kinetics of removal of the target, which is an important aspect because it determines the ultimate feasibility of the process (Vellanki BP, 2013).

2.3 Literature Review

Advanced Reduction Processes (ARP) are a group of recently explored treatment processes for oxidized contaminants in wastewater (Vellanki BP, 2013). The basic principal of these processes is to produce highly reactive reducing radicals in situ, which react with the target compound to make stable products. The reducing free radicals are produced by providing the necessary activation energy to solutions of appropriate reagents. Most commonly used reagents to produce the reducing radicals are sulfite, sulfide, dithionite and ferrous iron (Liu, 2013). Studies have been conducted on removal of nitrate by the ARP with dithionite as the reducing reagent and ultraviolet radiation using medium pressure lamps as the activating energy. One such study showed almost complete removal of nitrate with an initial concentration of 25 mg NO_3^-/L at pH 7 (Abdel-Wahab, 2014). The study also showed the effects of changes in the dithionite dose, pH, initial target ion concentration, and intensity of UV light source on the kinetics of the reaction. Much work has been done in the field of reducing free radicals (Buxton, 1988), but very little has been done to apply that to the field of wastewater treatment. The effectiveness of ultraviolet light as an activation method in ARP depends on its wavelength and the reagent, which determines the type of radical to be formed. As far as ultraviolet activation methods

are concerned, low pressure ultraviolet lamps (UV-L), narrowband ultraviolet lamps (UV-N), or medium pressure ultraviolet lamps (UV-M) are being used in wastewater treatment (Kowalski, 2009).

The reagents used in ARP also undergo different chemical reactions depending on the reagent and its bonding atoms. Dithionite is a reducing reagent used in ARP. It has a long and hence a weak S-S bond that breaks to form two sulfur dioxide radical anions (SO_2^-) (Makarov, 2001). The vast applications of dithionite across various industries makes it an easily available and cost effective chemical.



Since this reaction has a low equilibrium constant of 1.4×10^{-9} M, the sulfur dioxide radical exists at very low concentrations in aqueous dithionite solutions. The sulfur dioxide anion has characteristics of being a strong reductant with reduction potential of -0.66 V (S.G., 1978). The absorption peak of dithionite is at 315 nm (E.V., 2005) so irradiating the dithionite solution near this wavelength would produce the sulfur dioxide radical anions by breaking the weak S-S bond.

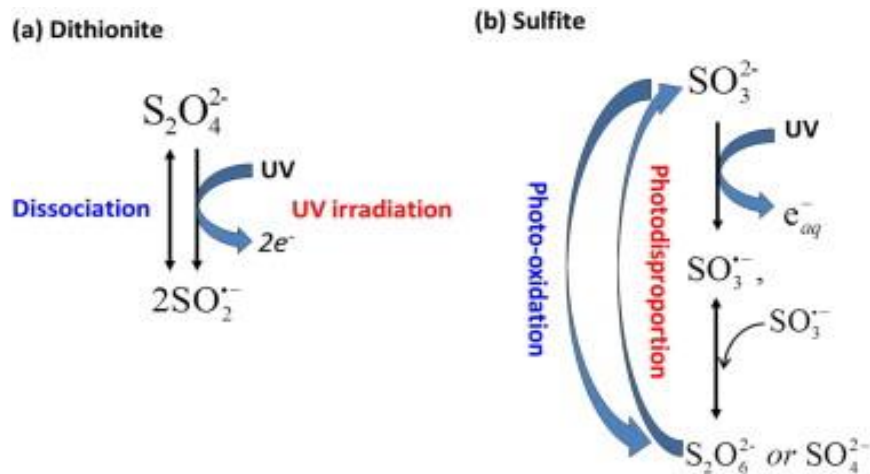
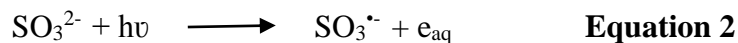
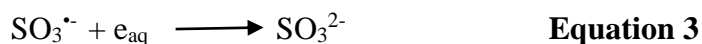


Figure 6. Dissociation of dithionite and sulfite with activation energy to form reducing radicals (Sunhee Yoon, 2014)

Sulfite is another reducing agent used with ARP to produce sulfite radical anions. The UV spectrum absorption peak of sulfite is not at a single wavelength but depends on the pH and concentration of the sulfite solution, due to the different species that exist at different pH (F.H., 1926). Irradiation of sulfite solution produces sulfite radical anion (R.W., 1989) and a hydrated electron (J.J., 1968).



In the above photolysis reaction, the sulfite anion breaks into two reducing species. It is important to note that the sulfite radical anion could also act as an oxidant by accepting an electron and be converted to sulfite.



Sulfide and ferrous ion solutions absorb UV light with maxima at 230 nm and 220 nm, respectively which promotes formation of hydrogen (Vellanki BP, 2013).

The basic and most important advantage of using a redox reaction in water/wastewater treatment is that these chemical reactions destroy environmental contaminants. Rapid and cost effective treatments are being investigated for contaminants like arsenic, which are highly injurious. ARP technology looks promising as it is non-selective, and hence, good at producing reducing agents for arsenic-bearing wastewater treatment. Use of ARP in arsenic-bearing waters will not only remove this poisonous contaminant from waters, such as done by other water/ wastewater treatment technologies, but it will also convert it into a form that is not harmful. ARP does not just change the medium in which the contaminant exists from water to sludge. Research studies have shown ARP to be a valid method to treat waters and wastewaters (Vellanki BP, 2013).

To the best of my knowledge, there has yet not been any study reported in the literature to show the effects of process variables on the ability of Advanced Reduction Processes to remove arsenic from wastewater. The objective of this study is to study the impact of different reagents (dithionite, sulfite, sulfide and ferrous iron), different light intensities, pH values and initial concentrations of arsenic on arsenic removal from wastewater. A kinetic model that describes the reaction better will also be derived to aid investigation of the effect of pH on the rate of arsenic removal. Direct photolysis, i.e. when no reagent is used with UV irradiation of the target compound will also be studied in order to compare these reactions with ARP.

3. ARSENIC REMOVAL BY ADVANCED REDUCTION PROCESS

3.1 Experimental Apparatus

3.1.1 Anaerobic Chamber

Since all the experiments use an Advanced Reduction Process, all of them were conducted in an environment where oxygen would not interfere with the reduction process. The anaerobic chamber was a perfect place to conduct all of the ARP experiments. A Coy Laboratory Products Inc. anaerobic chamber was used for all the experiments. To maintain the anaerobic atmosphere within the chamber it was filled with a gas mixture of 95% nitrogen and 5% hydrogen from Praxair Distribution Inc. The amount of oxygen in the chamber was monitored by an analyzer that detected levels of oxygen and hydrogen in the chamber. A palladium catalyst was used in the chamber to catalyze the reaction that turned the oxygen in the chamber into water by reacting it with hydrogen. This catalyst was recharged depending upon the speed of the reaction that reduced the little oxygen that would enter into the chamber during transfer of materials. Hence, concentration of hydrogen was maintained in the chamber by vacuuming and refilling the chamber with gas mix.

3.1.2 UV Light and UV Light Meter

The source of activation energy for the experiments was UV light. This short wave UV light was provided by Phillips Model TUV PL-L36W/4P low pressure mercury bulb having a peak light output at 253.7 nm. To measure the intensity of light provided in the experiments, we used the General UV digital light meter, model number UV 512C.

3.1.3 Spectrophotometer

A UV-Visible spectrophotometer (Helios, Thermo Spectronic) was used to determine the concentration of dithionite in the solution. Dithionite is very unstable and extremely sensitive to oxygen in the atmosphere. Dithionite showed peak absorbance at 316 nm. A calibration curve was developed to verify the relationship between the absorbance and concentration of dithionite at 316 nm. The absorbance was converted to concentration using Beer's Law which gives the equation:

$$A = \epsilon l c \quad \text{Equation 4}$$

where, "A" is the Absorbance as read from the spectrophotometer at 316 nm; "ε" is the molar extinction coefficient at 316 nm, which was calculated by the research group at our lab as 8043 L/mole-cm (Appendix A); "l" is the cell path length which was noted as 1 cm; and "c" was the calculated concentration.

3.1.4 Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)

Concentration of arsenic was measured using the ICP- MS NexION™ 300D which is an analytical instrument to determine elements using Mass Spectrometry (Training, 2014). Mass spectrometer separates the ions introduced by the ICP according to their mass to charge ratio. A detector quantifies the number of selected mass/charge ions.

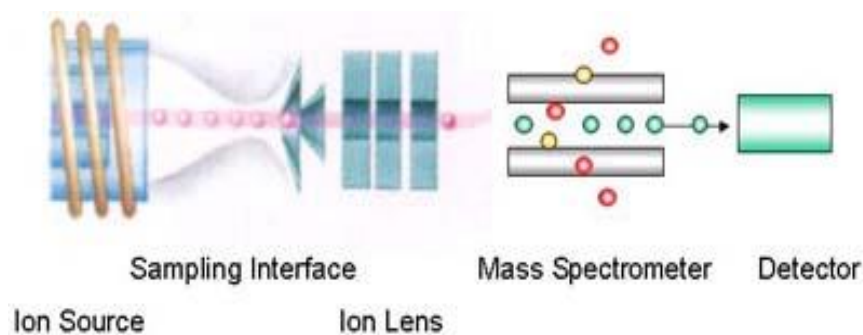


Figure 7. ICP-MS principle (GLOBAL, 2016)

The above figure is a description of the working of an ICP-MS which can broadly be divided into four sections. The first part is the ion source which generates ions which are to be introduced into the sampling interface. The second is the sampling interface which couples the ion source to the spectrophotometer. The third section is the mass spectrometer which is responsible for separating ions by mass/charge. And the final section is the detector which measures the rate of ions reaching the detector (Training, 2014). Argon was the carrier gas in all my experiments.

The advantage of ICP-MS is that it has low detection limits for quantitative analysis and is a rapid technique for semi-quantitative analysis.

A daily performance test was conducted to check the performance of the instrument with doubly charged, singly charged and a few specified elements as it was calibrated. Failure in the daily performance check would demand a change of gas flow, lens adjustment, or alignment of nebulizer in the instrument. After adjustments were made, it was again checked for daily performance. This procedure was repeated till the machine passed the daily performance test.

A set concentration of calibration tubes was to be freshly prepared each time samples were analyzed. The machine had an upper detection limit of 100 ppb so experimental samples were diluted to fall with the range of the machine.

3.1.5 Quartz Reactors

The reactors used were the quartz reactors from Starna Cells, Inc. These reactors were cylindrical cell units having a light path length of 10 mm, external diameter of 50 mm, and had a nominal volume of 17 ml. The two windows of these reactors were polished.



Figure 8. Cylindrical UV reactor

3.1.6 Cuvettes

Type 21 rectangular cells with PTFE (Polytetrafluoroethylene) stopper from Starna Cells, Inc. were used for UV-visible spectrophotometer analysis. Each cell had two polished windows having an external width of 12.5 mm, height of 48 mm and length of 12.5 mm. The path length for these cuvettes is 10 mm.



Figure 9. Cuvette for UV-visible spectrophotometer

3.2 Chemical Reagents

3.2.1 *Deoxygenated Deionized Water*

All solutions used in experiments were prepared with deoxygenated, deionized water. It was deoxygenated so that there would be no interference of oxygen with the reduction process and it was deionized so it did not have any ions to interfere with the reactions between target compound and reducing reagent. Preparation of this water required ultra-pure water at 18 M Ω cm. This water was purged with Ultra High Purity nitrogen (99%) by Praxair Distribution Inc. for 3 hours and then purged with gas mixture containing 5% hydrogen and 95% nitrogen for 12 hours in the airtight anaerobic chamber.

3.2.2 *Chemicals*

All chemicals used for target compounds and as reductants are discussed in the following sections and were used as received.

3.3 Experimental Work

3.3.1 Sample Preparation

3.3.1.1 Contaminated Wastewater Sample

A stock solution of 10 mM As (V) was made by taking 3.75 ml of Fluka Analytical's Arsenic (V) Standard for ICP measuring $999 \text{ mg/l} \pm 3 \text{ mg/l}$. This was made up to 5 ml using deoxygenated water inside the anaerobic chamber.

A stock solution of 10 mM As(III) was prepared by taking 0.04945 g of Alfa Aesar's Arsenic(III) oxide, adding 0.5 ml of NaOH for complete dissolution of the salt in water and the solution was made up to 50 ml using deoxygenated water inside the anaerobic chamber.

3.3.1.2 Dithionite Solution

A 50 mM dithionite stock solution was made by taking 0.2176 g of sodium dithionite powder salt by J.T. Baker and making it up to 25 ml by adding deoxygenated water inside the anaerobic chamber. This was done by taking an empty tube inside the anaerobic chamber and taking an approximate amount of dithionite salt in the tube (Due to the highly reactive nature of dithionite towards oxygen, it is kept inside the anaerobic chamber). This tube was then sealed air tight and taken out to weigh the salt by subtracting the weight of empty tube and weight of tube with salt. The amount of deoxygenated water was then back calculated to obtain a 50 mM dithionite solution, if there was a difference between the theoretical and practical weight of the salt.

3.3.1.3 Ferrous Iron Solution

A 10 mM ferrous iron stock was made by weighing 0.0994 g of Sigma Aldrich's Iron II chloride tetrahydrate powdered salt on a weighing scale, putting it in a 50 ml vial and adding 50 ml deoxygenated deionized water to it inside the anaerobic chamber.

3.3.1.4 Sulfite Ion Solution

A 50 mM stock solution of sulfite was made by weighing 0.3151 g of J.T. Baker's anhydrous Sodium Sulfite salt and putting it in a 50 ml vial. This vial was then taken into the anaerobic chamber and 50 ml water was added to it.

3.3.1.5 ICP Sample Preparation

The ICP requires all solutions to be in 1% volume/volume nitric acid and 15 ml vials were used for this purpose. A 0.1 ml volume of concentrated nitric acid was added to the tube and the tube was transferred to the anaerobic chamber where 7.9 ml deoxygenated deionized water was added to it. A 2 ml volume of the final experiment sample was added to this to make a total volume of 10 ml for ICP analysis of arsenic. Samples had to be diluted to meet with the limit of ICP machine of 100 ppb. All samples were diluted 5 times and results of analysis of the diluted samples were multiplied by a factor of 5 to determine final results.

ICP standards were also prepared for calibrating the ICP machine each time before use. These standards contained 0, 5, 10, 25, 50 and 100 ppb arsenic.

3.3.1.6 Phosphate Buffer

A 100 mM stock buffer solution was prepared using Alfa Aesar's potassium dihydrogen phosphate (KH_2PO_4), Alfa Aesar's potassium hydrogen phosphate (K_2HPO_4)

and NaOH or HCl to make pH buffers with pH values from 5 to 9. The buffers were prepared inside the chamber using deoxygenated deionized water for make-up volume.

3.3.2 *Experimental Setup*

The following figure shows the experimental setup that was used inside the anaerobic chamber.

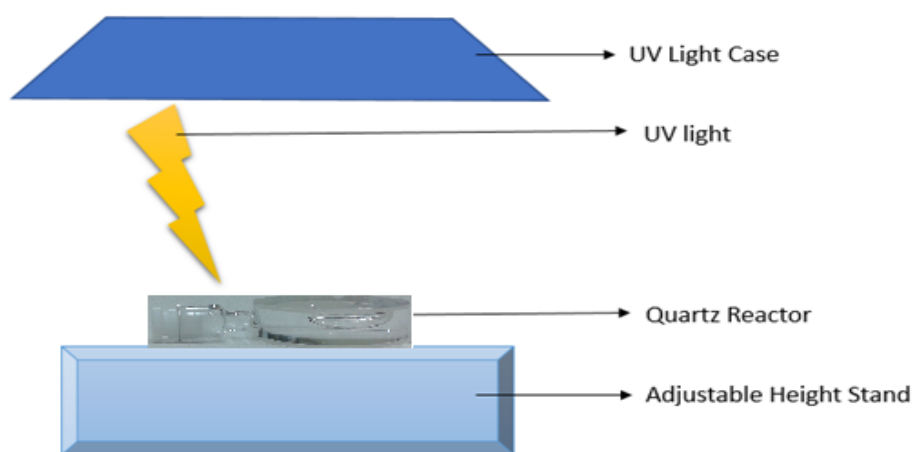


Figure 10. Experimental Setup inside the Anaerobic Chamber

An adjustable height stand was used to adjust the distance between the UV light source and the top of the quartz reactor in order to vary the UV irradiance entering the reactor. The quartz reactor contains the target compound which is arsenic and reducing agents dissolved in deoxygenated deionized water.

3.3.3 Experimental Procedure

3.3.3.1 Screening Reagents

Based on the experiments previously done in our lab, three reagents (sulfite, dithionite and ferrous iron) were chosen as the reducing reagents for screening experiments due to their effectiveness with ARP (Vellanki BP, 2013). There were two target compounds, arsenic (III) and arsenic (V) and all screening experiments were conducted at pH 8. Screening experiments were conducted using an initial concentration of arsenic of 5 μM and an initial reagent concentration of 0.5 mM. The UV-L lamp irradiance was kept constant at 6 mW/cm^2 . Phosphate buffer was used at a concentration of 10 mM to maintain pH 8.

Quartz reactors were used to carry out all experiments in the anaerobic chamber. A 15 ml reaction mixture containing freshly prepared samples of 0.5 mM reducing reagent, 5 μM arsenic and 10 mM buffer of desired pH was put in the quartz reactor. This reactor was placed in the experimental system discussed above with one side facing the UV light. A UV meter was used to measure the light intensity falling on the quartz reactor and the quartz reactor was placed at a height such that it received a light intensity of about 6 mW/cm^2 .

Three conditions were used for the screening experiments. The first was a light control in which arsenic was exposed for the specified time to UV light without reagent being added to the sample. The second was a reagent control wherein arsenic and reagent were present, but were kept in dark away from UV light. The third included arsenic in the presence of both UV light and reducing reagent. Light control reactors were sampled

initially and after 300 minutes. Reagent controls were sampled at 3, 30, and 300 minutes. Reactors with reagent and arsenic exposed to UV light were sampled at 3, 30 and 300 and were identified as “ARP” or Advanced Reduction Process experiments.

A small volume of the sample taken from the reactors was used to check the pH and was then discarded. The remaining part of each sample was transferred into a 10 ml BD Luer-Lok tip syringe using a BD PrecisionGlide needle. The needle was removed and the syringe was put into a filter holder containing a Whatman 0.2 μm filter paper. The filtrate was the final sample from which 2 ml was taken and added to the ICP dilution tube for analysis of total arsenic.

3.3.3.2 Kinetic Experiments

To study the kinetics of the reaction in the ARP experiments, it was important to reduce the pace of the reaction so sample times could be set at reasonable intervals. This was accomplished by reducing the initial concentration of the reagent and the incident UV irradiance relative to values used in screening experiments. The initial concentration of reagent was reduced to 0.2 mM from 0.5 mM and the intensity of UV light was reduced to 1 mW/cm^2 from the initial intensity of 6 mW/cm^2 . Sampling times were increased with samples from multiple reactors being taken at 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, 20, 25, 30, 40, 60, 90 and 120 min. Each reactor was set to be sampled at one of the sampling times, that is, reactor 1 was sampled at 0 minutes, reactor 2 was sampled at 1 minute and so on. Time zero corresponds to when all reactors were first exposed to UV in the presence of dithionite. The solution containing arsenic and dithionite were prepared from stock solutions and added to each reactor. Since it was established in screening experiments that

ARP was better than just light control or reagent control in removing arsenic from solution, only ARP experiments were performed. Dithionite was selected as the reagent because it was found to be more effective than other reagents in the screening experiments.

Analysis of dithionite in the filtered sample was conducted using an ultraviolet-visible spectrophotometer as rapidly as possible without contact with air. A part of the final filtered sample was immediately transferred to air-tight quartz cuvettes and its absorbance measured with the UV- visible spectrophotometer, which was outside the anaerobic chamber. The measurement was made within 30 to 60 seconds after taking the sample.

3.3.3.3 Kinetic Study

A simplified, second-order kinetic model for removal of soluble arsenic by the dithionite/UV-L ARP was developed. The model described photolysis of the reagent in a completely mixed reactor that was irradiated. It considered the change in light intensity through the reactor by calculating a spatially averaged light intensity. The batch material balance for reagent was integrated to obtain an explicit equation for the concentration of reagent as a function of time. The important parameters of the model are the quantum yield for photolysis, the molar extinction coefficient for reagent, the length of the light path in the reactor and the initial concentration of reagent. This relationship for the concentration of reagent was substituted into a second-order rate equation for removal of soluble arsenic. The result was a differential equation that was solved numerically for the concentration of soluble arsenic as a function of time. This was done in conjunction with a non-linear regression applied to experimentally measured concentrations of soluble

arsenic to obtain values of the second-order rate constants. This was done for a number of kinetic experiments for removal of soluble arsenic by the dithionite/UV-L ARP. This simulation was done using MATLAB modelling of data using the MATLAB function ode45 in combination with the MATLAB function nlinfit to conduct non-linear regressions with measured data for soluble arsenic to obtain second-order rate constants for the process.

4. RESULTS AND DISCUSSION

4.1 Screening Experiments

Screening experiments were conducted with dithionite, sulfite, and ferrous ion as the reducing reagents with arsenic. However, the results indicated more complex reaction mechanisms than anticipated, so additional experiments were conducted to better understand the behavior of arsenic during ARP treatment. The results will be presented in this section.

The results of the experiments conducted with As (III) and As (V) at pH 8 are shown in figure 11. Samples were taken from reactors at specified times and filtered to remove all solid phases. Each series of experiments included blanks (no reagent, no UV light), reagent controls (reagent present, but no UV light), light control (no reagent, but UV light irradiation) and the ARP (reagent and UV light). UV-L light only without any reagent was not able to remove arsenic from water. None of the three types of reagents without any activation were effective in arsenic removal. However, some combinations of reagents and activation methods were effective. The ARP that combines ferrous chloride and UV-L was able to continuously remove arsenic over the time period of the experiments (300 minutes) with a maximum removal of about 45% as shown in figure 11. Dithionite combined with activation by UV-L has able to remove arsenic very rapidly, with substantial removal (about 32%) occurring in the first 3 minutes. However, soluble arsenic increased at later sampling times. This was not expected and the mechanism is not known, but was investigated. One hypothesis is that the ARP is reducing As (III) and

As (V) to the elemental form rapidly and then slowly reducing As (0) to arsine (As (-III)), which is dissolved in the solution. The combination of sulfite and UV-L has almost no effect on As (V) removal. The kinetics for As (V) removal is much slower than that observed for As (III) removal, which should be expected because As (V) requires more electrons to be reduced to elemental arsenic.

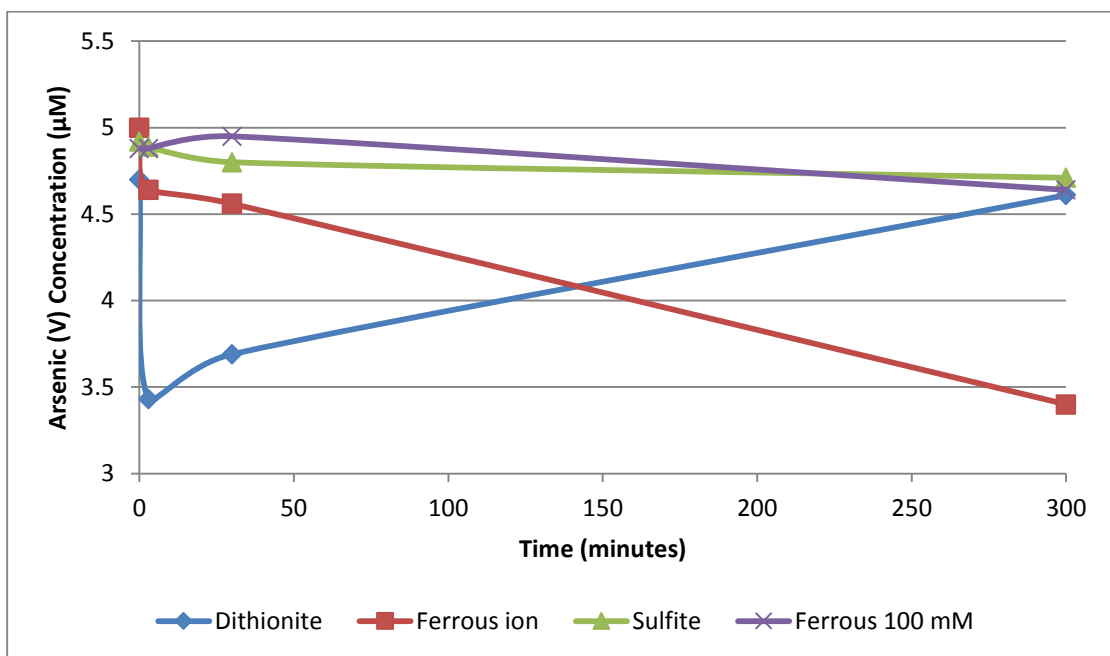
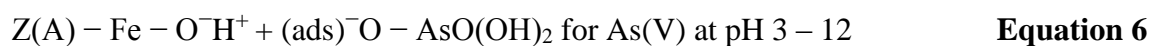


Figure 11. Soluble arsenic (V) concentration varying with time when different reagents are used and UV light is applied

Results with ferrous iron indicate the possibility of an adsorption mechanism after an initial chemical reduction of arsenic. This hypothesis is based on the shape of the curve in Figure 11 for experiments with ferrous iron, which shows a rapid initial decrease in concentration of soluble arsenic followed by a slower decrease. The initial stages could be caused by the chemical reduction of soluble arsenic to particles of zero valent arsenic as expected in an advanced reduction process. The later stage shows a comparatively slow decrease in the levels of soluble arsenic indicating an adsorption mechanism of arsenic on ferric ions. Ferric ions and aqueous electrons are produced by photolysis of ferrous iron. Literature shows that arsenic and ferric ion have a strong tendency to precipitate. Also, ferric hydroxide is an effective adsorbent for soluble arsenic and forms mono-dentate and bi-dentate complexes with arsenic at high pH, as shown in Equations 5 and 6 (Abdel-Fattah, 2005).



Dithionite was identified during these experiments as the most effective reagent for treating arsenic in water. Experience in the laboratory and a review of the literature indicated that dilute solutions of dithionite are unstable, so additional work was conducted to investigate dithionite stability and to develop guidelines for conducting experiments with dithionite.

4.2 Evaluating Resolubilization Process

Experiments were conducted to evaluate factors affecting the precipitation/resolubilization process. These experiments used 5 μM As (V), 500 μM dithionite from

sodium dithionite and a 10 mM phosphate buffer (9.5 mM KH_2PO_4 and 90.5 mM K_2HPO_4 , diluted 1/10) at pH 8. Figure 12 shows results for one experiment.

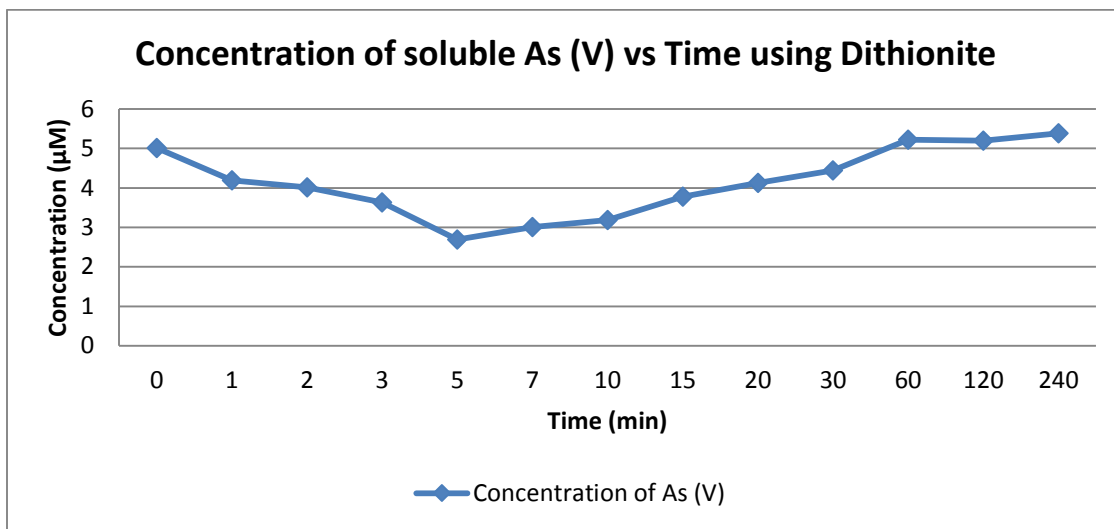


Figure 12. Concentration of soluble Arsenic (V) with time during irradiation by UV-L in presence of dithionite

Figure 12 shows resolubilization of As (V) after 5 minutes from the start of the experiment. The expected mechanism for precipitation of As (V) is that it reacts with dithionite or the product of dithionite photolysis (sulfur dioxide radical) and is reduced to solid elemental arsenic. Resolubilization could occur by reduction of elemental arsenic to arsine (AsH_3).

A set of experiments was carried out with dithionite to check for the presence of any volatile arsenic species such as arsine. This was done by purging the samples from the ARP experiments with a gas mix of 95% nitrogen and 5% hydrogen in the anaerobic chamber for about 30 minutes before analysis by ICP. Results for purged samples were compared with samples that were not purged with the gas mix and it was concluded that

there were no volatile arsenic species present.

Experiments were performed to evaluate the mechanism of resolubilization and results are shown in Table 2.

Exp. ID	Experimental Conditions	Soluble As(V) Replicate 1 (μM)	Soluble As(V) Replicate 2 (μM)	pH 1	pH 2
a.	T=0; no UV	5.31	5.12	7.97	7.96
b.	T=5 min of UV	2.90	2.69	7.76	7.76
c.	T=5 min of UV, add 500 μM dithionite, irradiate for another 5 min of UV	1.48	1.21	7.56	7.54
d.	T= 5 min of UV, 55 min in dark	2.91	2.80	7.71	7.73
e.	T= 10 min of UV	3.06	3.05	7.73	7.73
f.	T=60 min of UV	4.79	4.56	7.86	7.83

Table 2. Results of experiments with As (V) in dithionite solutions irradiated with UV-L

These results show that As (V) was precipitated after 5 minutes of UV-L irradiation (compare Exp. ID “a” and “b”) and that resolubilization occurred between 5 minutes and 10 minutes (compare Exp. ID “b” and “e”). However, addition of more dithionite after 5 minutes resulted in further precipitation (compare Exp. ID “b” and “c”). The results also show that UV irradiation is required for resolubilization (compare Exp. ID “b” and “d”; “b” and “f”).

The samples were also subjected to a UV scan (180 – 350 nm) and the results are shown in Figure 13. The samples were put in cuvettes that were sealed with caps to prevent oxidation.

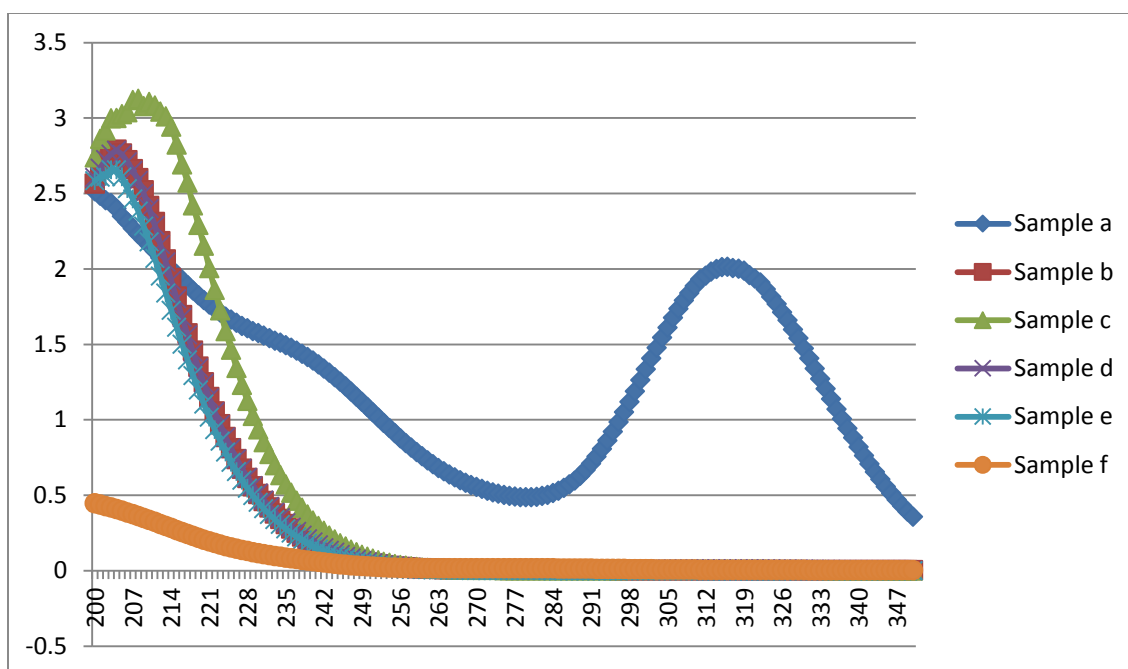


Figure 13. UV scan for (a) T=0, no UV (b) T=5 min of UV (c) T=5 min of UV, added 500 μ M dithionite and irradiated for another 5 min of UV (d) T= 5 min of UV, 55 min in dark (e) T= 10 min of UV (f) T=60 min of UV

The dithionite peak is clearly visible at 315nm in the sample taken at zero time (Exp. ID “a”) and is not present in samples taken after 5 minutes of UV-L irradiation (Exp. ID “b”, “c”). This data, along with that in Table 2, indicate that the presence of dithionite is needed for precipitation of As (V) and its absence results in resolubilization during irradiation. The typical dithionite peak at 315 nm is attributed to the sulfur dioxide radical ($\text{SO}_2^{\bullet-}$) (Mckenna CE, 1991) (Amonette JE, 1994).

A potential mechanism for resolubilization during UV-L irradiation is that a product of dithionite photolysis is photolyzed and its photolysis products react with solid phase arsenic to solubilize it. To evaluate this hypothesis, experiments were performed by introducing 5 mM of sulfite at different irradiation times and measuring the effect on

arsenic precipitation/resolubilization. The results are shown in Table 3 and Figure 14.

Exp. No.	Experimental Conditions	Concentration (μM)	pH
1.	T=0; no UV; reagent present	4.16 \blacklozenge	8.22
2.	T=5 min of UV	2.97 \blacklozenge	7.88
3.	T= 10 min of UV	3.45 \blacklozenge	7.90
4.	T=5 min of UV; Added 5mM of sulfite; UV for another 5 min	2.94 \blacklozenge	8.12
5.	T=10 min of UV; Added 5mM of sulfite; UV for another 5 min	3.43 \blacklozenge	8.12

Table 3. Effects of UV-L and sulfite addition on soluble arsenic

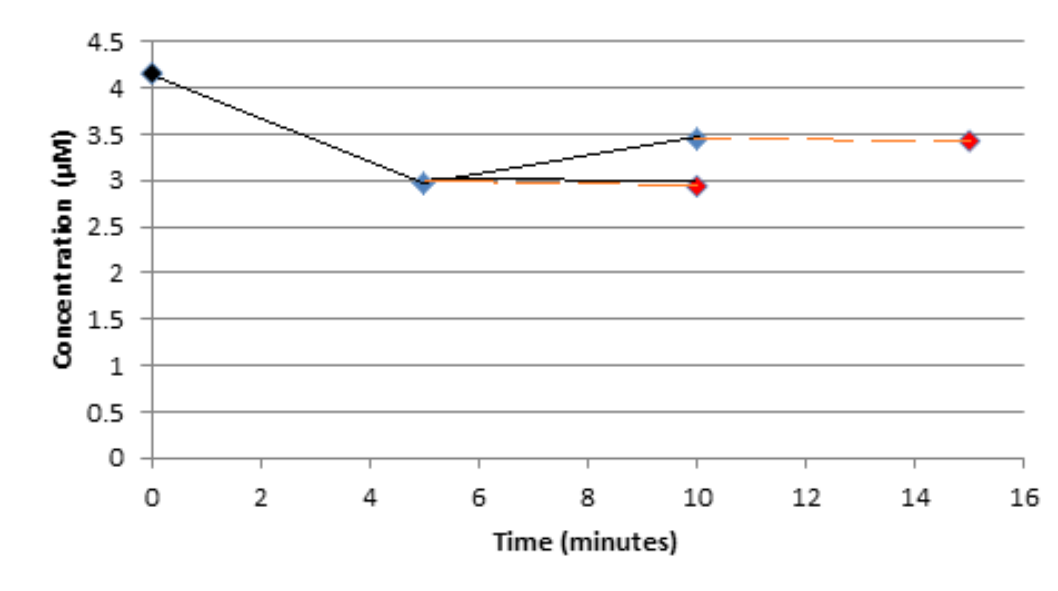


Figure 14. Effect of UV-L and sulfite addition on soluble arsenic. The blue diamonds are results without addition of sulfite and red diamonds are results with the addition of sulfite

Results indicated that addition of sulfite not only failed to increase resolubilization of arsenic, it inhibited it. Figure 15 shows UV scans of the solutions in these reactors.

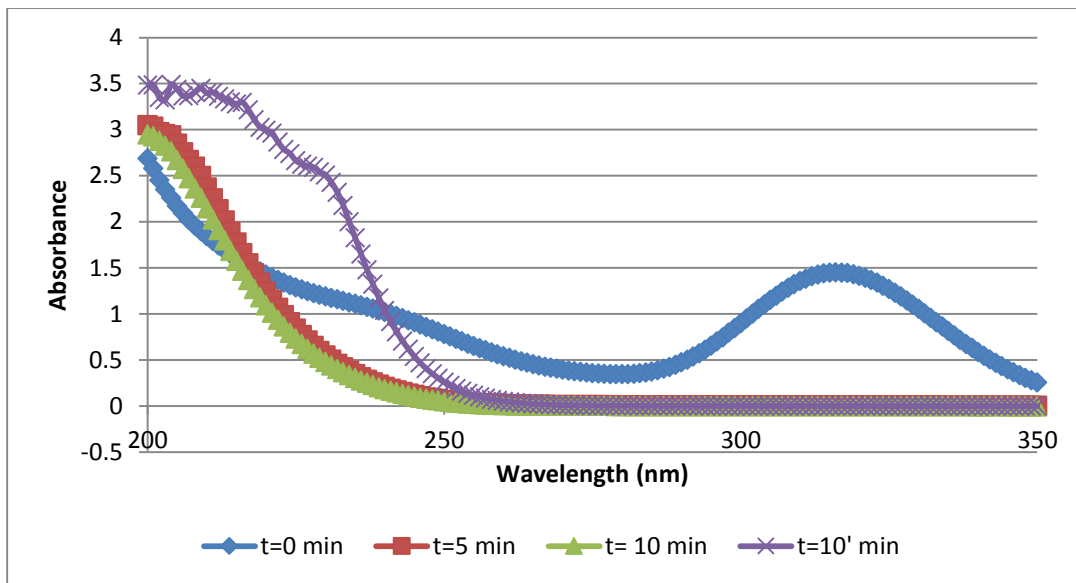


Figure 15. UV scan for solutions of As (V) and dithionite with and without addition of sulfite after 5 minutes irradiation with UV-L

Figure 15 shows that dithionite was depleted after 5 minutes and that addition of sulfite resulted in increased absorbance at wavelengths below 250 nm.

Another product of dithionite decomposition that could be responsible for resolubilization is thiosulfate. Therefore, additional experiments were conducted to evaluate the effect of additions of thiosulfate. For this zero valent arsenic, -20 mesh size from Alfa Aesar was weighed to prepare what would be a 10 mM arsenic solution, if all the solid dissolved. Thiosulfate ion was added as the solubilizing reagent at a concentration of 1 M and the pH of the solution was buffered at 8. These samples were subject to an irradiance of 6 mW/cm². The results are shown in Table 4 and they indicate that thiosulfate was not responsible for the resolubilization of arsenic observed in previous experiments.

	Light + Thiosulfate	
Time (min)	Concentration (μM)	pH
0	-2.87	7.16
2	-2.14	7.20
3	-2.64	7.15
5	-2.55	7.16
7	-2.92	7.15
10	-3.12	7.19
30	-2.41	7.22

Table 4. Dissolution of Elemental Arsenic using Thiosulfate

4.3 Characterization of Kinetics

4.3.1 Arsenate (As(V))

Experiments were performed to further characterize the kinetics of As (V) precipitation in irradiated solutions of dithionite with reduced UV-L irradiance (approximately 1 mW/cm^2). Experiments were performed at pH 5, 6, 7, 8 and 9 using a 10-mM phosphate buffer with initial concentrations of dithionite and As (V) being 0.2 mM and $5 \mu\text{M}$, respectively. Dithionite analysis was also performed by measuring absorbance at 316 nm with a UV-Visible spectrophotometer.

Figure 16 shows the variation of concentration of As (V) with time at different pH.

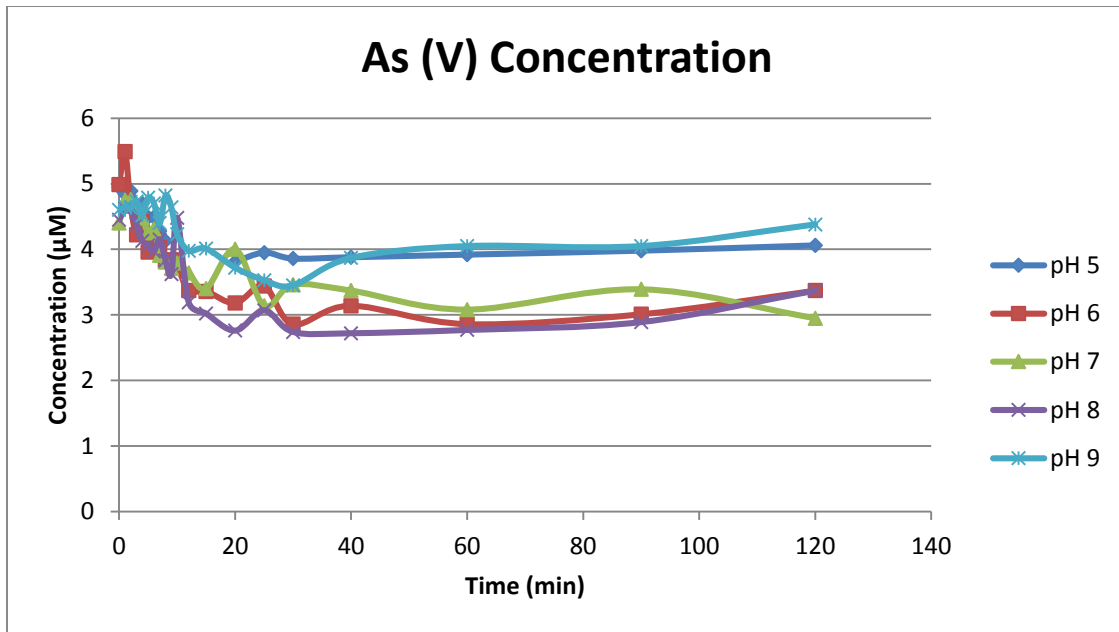


Figure 16. Effect of time on concentration of As (V) at different pH

Figure 16 indicates pH did not have a strong impact on precipitation of As (V), but that it was best at moderate pH (6, 7, 8).

Figure 17 shows how dithionite degradation was effected by pH during the kinetic experiments.

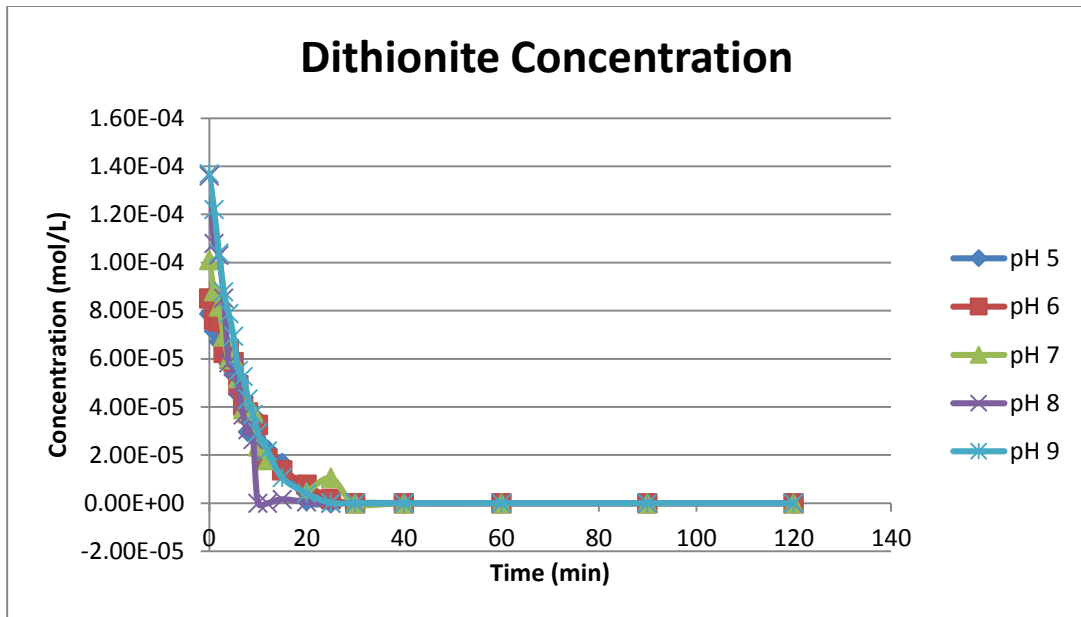


Figure 17. Dithionite Concentration Curve at different pH for As (V)

Figure 17 shows a steady decrease of dithionite at about the same rate for all pH. There appears to be some effect on the initial concentration of dithionite measured at different pH. The same amount of dithionite should have been added in each experiment, but more dithionite could have been degraded initially in solutions with lower pH. Low pH is known to promote anaerobic dithionite degradation (Leandro M de Carvalho, 2001).

4.3.2 Arsenite (As(III))

Additional experiments were performed to characterize the kinetics of As (III) precipitation at lower concentrations of As (III) and dithionite and at reduced UV-L irradiance (approximately 1 mW/cm²). Experiments were performed at pH 5, 6, 7, 8 and 9 using a 10-mM phosphate buffer with initial concentrations of dithionite and As (III) being 200 μ M and 5 μ M, respectively. Figure 18 shows the variation of concentration of As (III) with time at different pH.

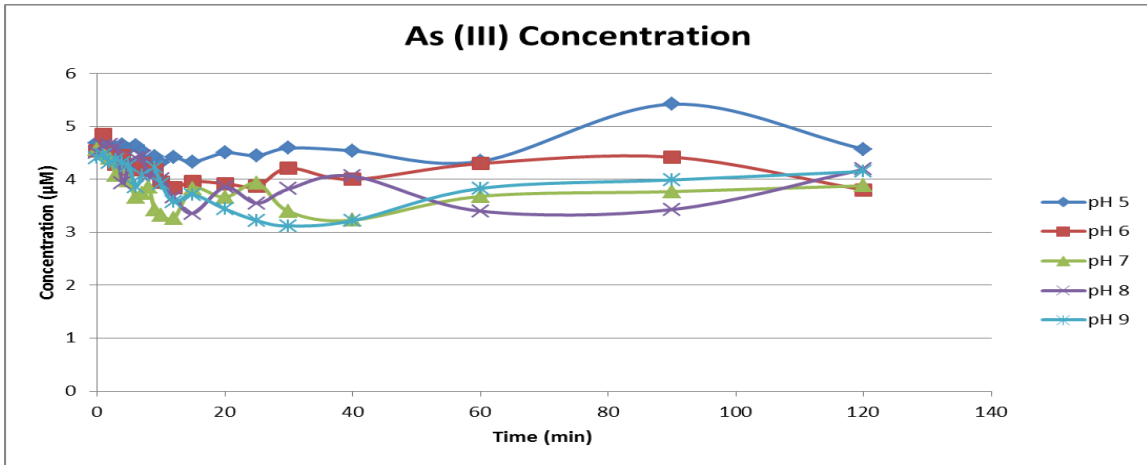


Figure 18. Effect of time on concentration of As (III) at different pH

Figure 18 indicates that reducing UV-L irradiance greatly slowed arsenic precipitation. The data also show that pH did not have a strong impact on precipitation of As (III). Figure 19 shows how dithionite degradation was effected by pH during the kinetic experiments.

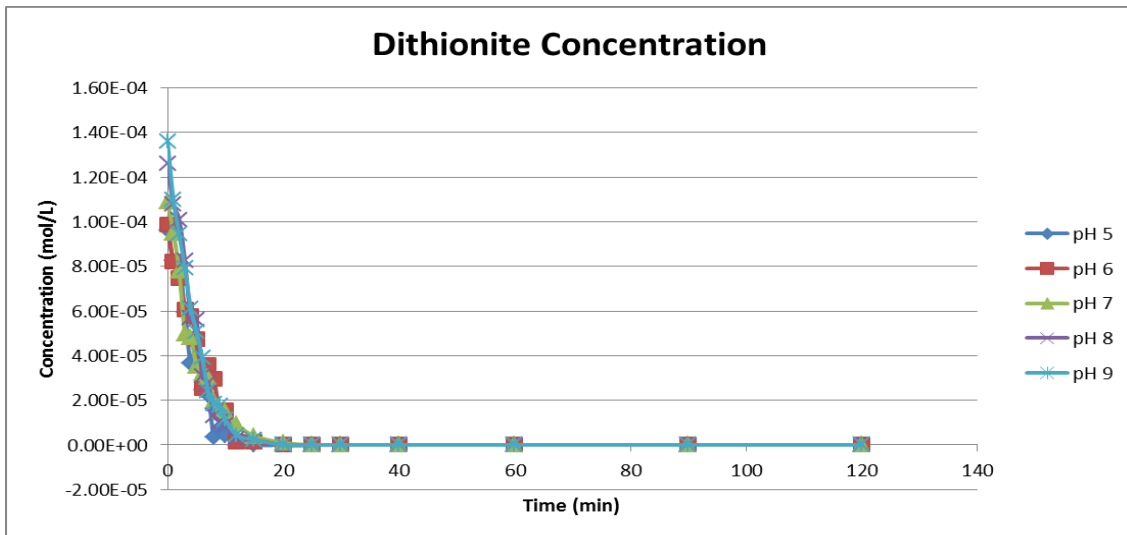


Figure 19. Dithionite Concentration Curve at different pH for As (III)

Figure 19 shows a steady decrease of dithionite at about the same rate for all pH. There appears to be some effect on the initial concentration of dithionite measured at different pH. The same amount of dithionite should have been added in each experiment, but more dithionite could have been degraded initially in solutions with lower pH. Low pH is known to promote anaerobic dithionite degradation.

4.3.3 *Effect of pH on Initial Dithionite Concentration*

The above similarities in the behavior of dithionite lead to a study of the relationship of initial concentration of dithionite and pH and the results are shown in Figures 20 and 21.

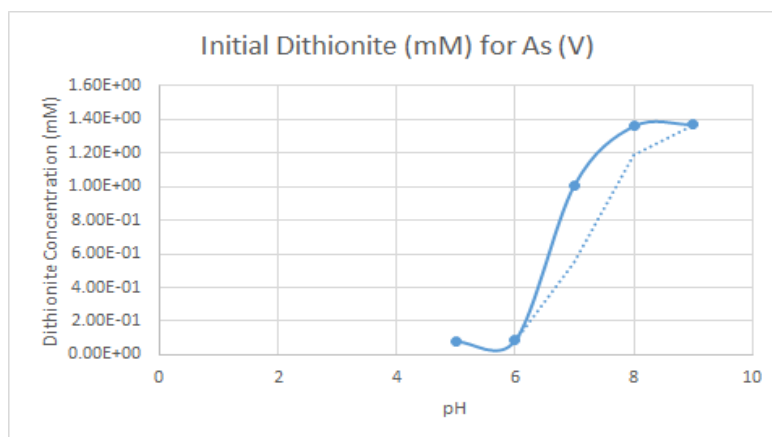


Figure 20. Initial dithionite present with As (V) with varying pH

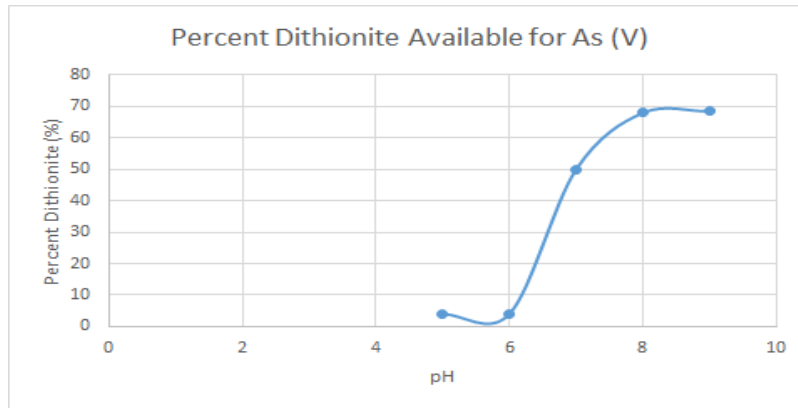


Figure 21. Percent of added dithionite available at different pH

The initial dithionite concentration increases with an increase in the pH, for the same amount of sodium dithionite salt added per volume of solution. This is consistent with the studies that say that low pH is promotes anaerobic dithionite degradation (Leandro M de Carvalho, 2001). The above figures represent the initial dithionite measured by an ultraviolet-visible spectrophotometer at time zero. The solution was prepared to achieve an initial dithionite concentration of 0.2 mM if the sodium dithionite solid was pure and none degraded after dissolving.

4.4 Approach to Model Development

A design model for target removal by the dithionite/UV-L ARP was developed using a simple second-order kinetic model of the process in which As (III) and As (V) are removed from solution. Although it is known that dithionite photolyzes under UV light to form the highly reactive sulfur dioxide radicals that are responsible for arsenic reduction, the rate equation for removal of arsenic from solution was assumed to be proportional to the concentrations of arsenic and dithionite. This approach is based on the assumption that the rate of production of radicals is proportional to the concentration of

dithionite. This is reasonable, since the rate of radical production should be equal to the product of a quantum yield, molar extinction coefficient and concentration of dithionite. The rate of photolysis of dithionite is proportional to the rate of radical production, so the model is able to independently describe how the concentration of dithionite changes over time and use that to describe the change in the concentration of soluble arsenic.

4.4.1 Modelling Dithionite Concentration

A model for the concentration of dithionite was developed as a function of time in a batch, completely mixed reactor. The model assumes that the rate of loss of dithionite at any point in the reactor is proportional to the product of a quantum yield (ϕ , mol/einstein), the molar extinction coefficient (ϵ' , base e, L/mol/cm), the molar concentration of dithionite (C , mol/L) and the photon flux (I' , einstein/m²/sec).

$$r_{loss} = \phi \epsilon' I' C$$

Equation 7

The reactor is assumed to be well mixed, so the concentration of dithionite is the same throughout the reactor. However, the photon flux decreases through the reactor as it is absorbed by dithionite. Therefore, an average rate for the reactor (r_{loss} , mol/L/sec) is calculated using Equation 7 with an average photon flux (I_{avg} , einstein/m²/sec), which is calculated by integrating the photon flux across the reactor using the reactor depth (L , cm), which is the path length of light through the reactor.

$$I_{avg} = \frac{I'_0}{\varepsilon'CL} (1 - \exp(-\varepsilon'CL))$$

$$r_{loss} = \frac{\varphi I'_0}{L} (1 - \exp(-\varepsilon'CL))$$

Equation 8

This average rate of dithionite loss is applied in a material balance equation for a batch system with the assumption that photolysis was the only reaction that would affect dithionite.

$$\frac{dC}{dt} = -\frac{\varphi I'_0}{L} (1 - \exp(-\varepsilon'CL))$$

Equation 9

The material balance can be solved by integration to obtain a relationship for the concentration of dithionite as a function of irradiation time.

$$C = \frac{\text{Ln} \left(\frac{\exp(\varphi I'_0 \varepsilon' t) + \exp(\varepsilon' C_0 L) - 1}{\exp(\varphi I'_0 \varepsilon' t)} \right)}{\varepsilon' L}$$

Equation 10

where, C_0 (mol/L) is the initial concentration of dithionite and other variables as described above. This model was used in a non-linear regression on measured concentrations of dithionite during photolysis to obtain values of the quantum yield. It can also be used with those values of quantum yield to predict dithionite concentrations that are used in the kinetic model describing how soluble arsenic concentrations change with time. (Appendix C)

4.4.2 Modelling Arsenic Concentration

A second-order rate equation was used to describe the effects of the concentration of dithionite (C, mol/L) and arsenic (A, mole/L) on the rate of loss of arsenic from solution by the dithionite/UV-L ARP.

$$r_{loss} = kCA$$

Equation 11

In the above equation, k is the second order rate constant (L/mol/min). The relationship for the concentration of dithionite as a function of time (Equation 10) can be substituted into this rate equation and combined with a material balance equation to obtain:

$$\frac{dA}{dt} = k \frac{\text{Ln} \left(\frac{\exp(\phi I_0' \varepsilon' t) + \exp(\varepsilon' C_0 L) - 1}{\exp(\phi I_0' \varepsilon' t)} \right)}{\varepsilon' L} A$$

Equation 12

This differential equation can be solved numerically to calculate concentrations of soluble arsenic as a function of time during treatment by the dithionite/UV-L ARP. This was done with the MATLAB function ode45 in combination with the MATLAB function nlinfit (Appendix C) to conduct non-linear regressions with measured data for soluble arsenic to obtain second-order rate constants and initial concentrations of arsenic with the regression. Arsenic concentrations were used only when they occurred at a time when dithionite was still present in the system (25 minutes) and Equation 12 would describe behavior of arsenic. The results of these regressions are shown in Table 5.

No.	Element/ pH	Rate Constant (K) (L/mol/min)	Confidence Interval	Sum of Squared Errors (Experimental value – Model value) ²	Coefficient of Variation (Root mean square / Mean)
1	As(V) pH 5	348	310 to 386	3.02E-07	0.020
2	As(V) pH 6	616	567 to 666	9.24E-07	0.054
3	As(V) pH 7	436	358 to 514	9.80E-07	0.062
4	As(V) pH 8	520	396 to 645	1.56E-06	0.103
5	As(V) pH 9	210	144 to 277	1.16E-06	0.068
6	As(III) pH 5	174	141 to 207	3.34E-07	0.019
7	As(III) pH 6	348	304 to 392	4.80E-07	0.029
8	As(III) pH 7	534	451 to 617	8.05E-07	0.053
9	As(III) pH 8	383	299 to 468	1.03E-06	0.064
10	As(III) pH 9	368	285 to 451	9.32E-07	0.062

Table 5. Value of rate constants for Arsenic at different pH as computed from MATLAB modelling and their goodness of fit

Figures 22-31 show model predictions (line) and experimental values (points) for arsenic concentrations at various pH. The figures show the modeled and experimental values for all the 120 minutes of the experiment.

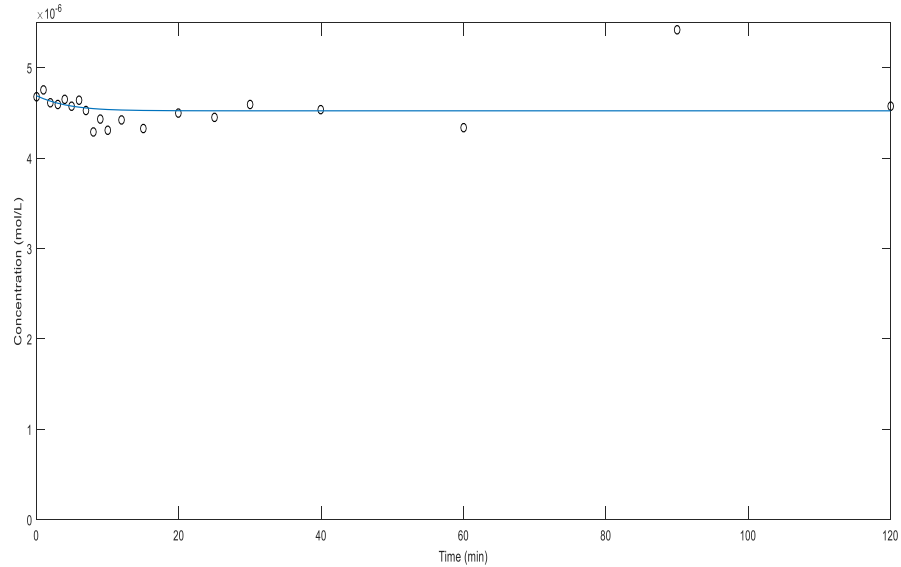


Figure 22. Measured and modeled concentrations of soluble As (III) at pH 5 as functions of time

Figure 22 shows the measured soluble As (III) concentrations as dots (°) and the line is a model developed using the kinetic model discussed above. This graph shows results at pH 5 for the first 30 minutes of the experiment, which is the time period when dithionite was present in the system, as can be seen from Figure 19. A goodness of fit parameter was calculated for all of the kinetic experiments as the coefficient of variation, i.e. the ratio of the root mean squared error to the mean of all values. The coefficient of variation for pH 5 (0.019) shows that the model is a good fit to the experimental values. Although results at pH 5 do not show much As (III) removal, the model describes all the data points well.

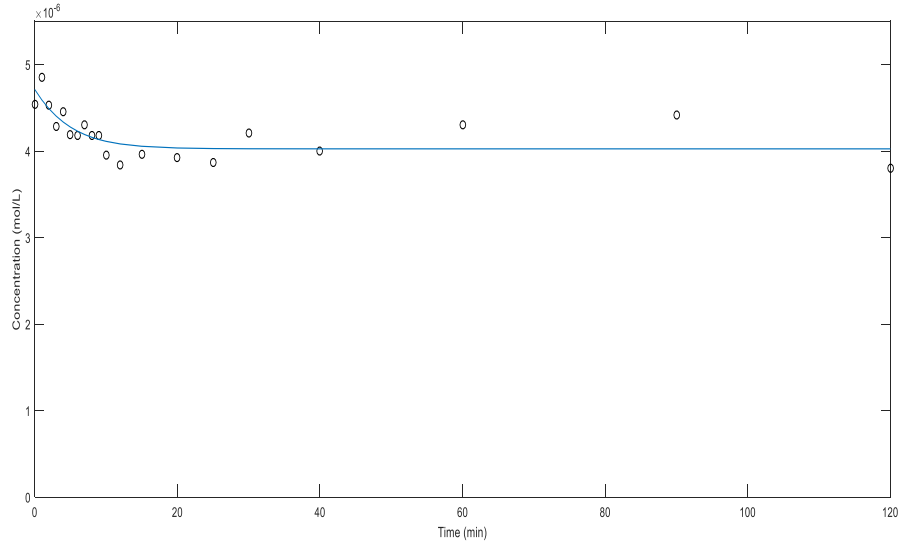


Figure 23. Measured and modeled concentrations of soluble As (III) at pH 6 as functions of time

Figure 23 shows variation in soluble As (III) concentration with time for pH 6. The low value of the goodness of fit parameter (0.029) suggests that the model provides a fairly good fit to the experimental values. The model and data both show better As (III) removal at pH 6 than at pH 5. The model agrees with the experimental data points and appears to average the random variations in the data due to experimental errors.

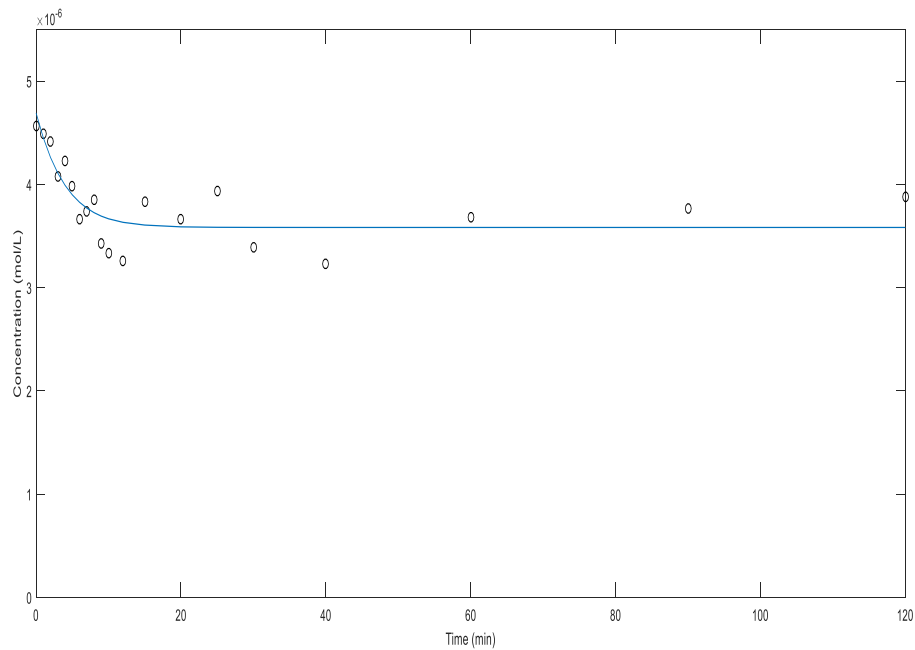


Figure 24. Measured and modeled concentrations of soluble As (III) at pH 7 as functions of time

Figure 24 is a graph showing variation of soluble As (III) with dithionite at pH 7. The experimental values are scattered on both sides of the modeled concentration. The experimental values initially show a decrease in the concentration of arsenic and then an increase indicating resolubilization of arsenic after about 15 minutes from the start of the experiment. The data show a better As (III) removal at pH 7 than what was observed at pH 5 and 6.

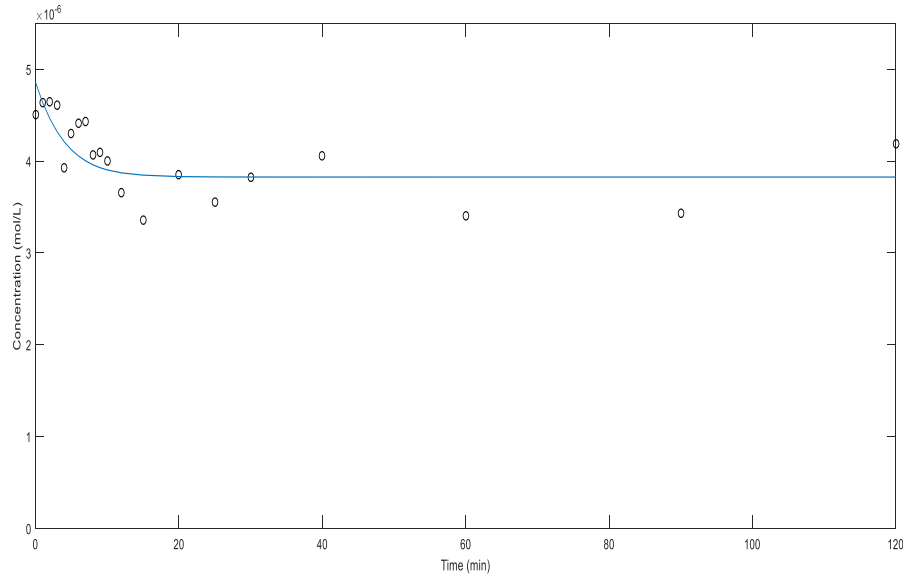


Figure 25. Measured and modeled concentrations of soluble As (III) at pH 8 as functions of time

Figure 25 shows a significant decrease in the initial soluble concentration of As (III) at pH 8, when reacted with dithionite under UV light. The experimental data suggests that the removal of As (III) is almost the same at pH 7 and pH 8, which both show greater removal that was observed at pH 5 and 6. The experimental data shows more removal than predicted by the model.

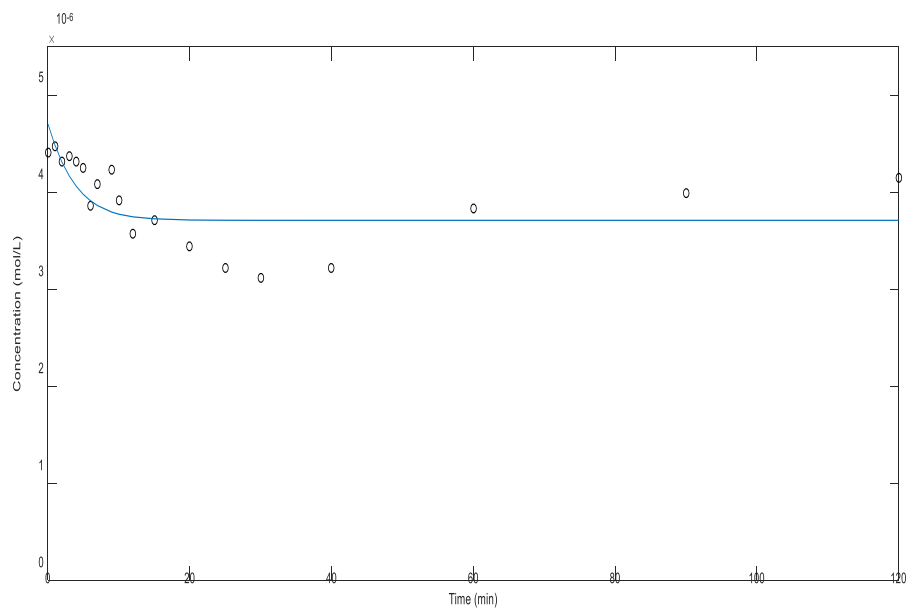


Figure 26. Measured and modeled concentrations of soluble As (III) at pH 9 as functions of time

Figure 26 shows variation of soluble As (III) concentration with time at pH 9. The experimental values show a relatively slower reduction of arsenic than seen at pH 8. The experiments show an initial decrease in arsenic concentration and then an increase, indicating resolubilization after 30 minutes. As (III) removal was greater at pH 9 than was observed at pH 5, 6, 7 or 8. The model does not show as high As (III) removal as observed after about 30 min.

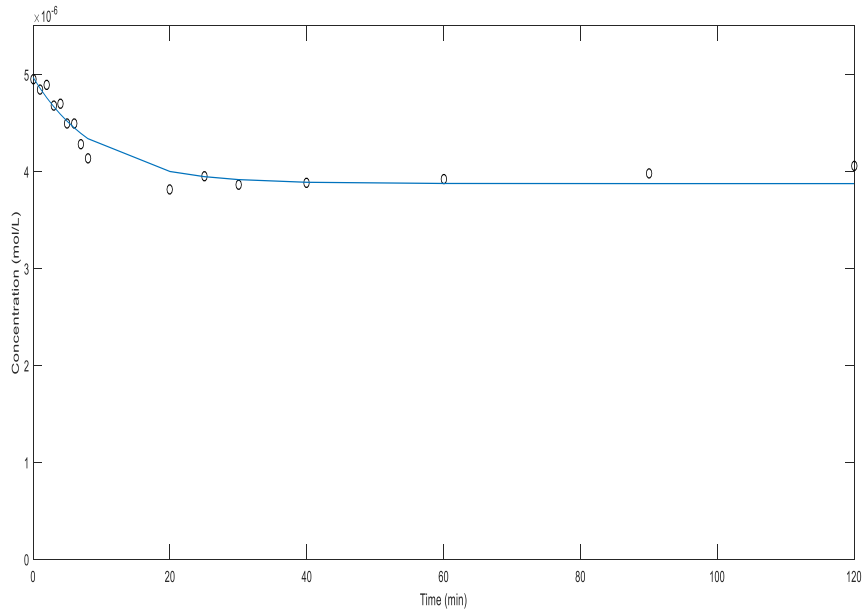


Figure 27. Measured and modeled concentrations of soluble As (V) at pH 5 as functions of time

Figure 27 shows soluble As (V) concentrations varying with time at pH 5 with dithionite as the reducing reagent. The model is a very good fit to the experimental results. The model and data show As (V) removal continued until a little after 20 minutes, after which the As (V) concentration becomes constant and no further removal is observed. Removal of As (V) is higher than removal of As (III) at this pH.

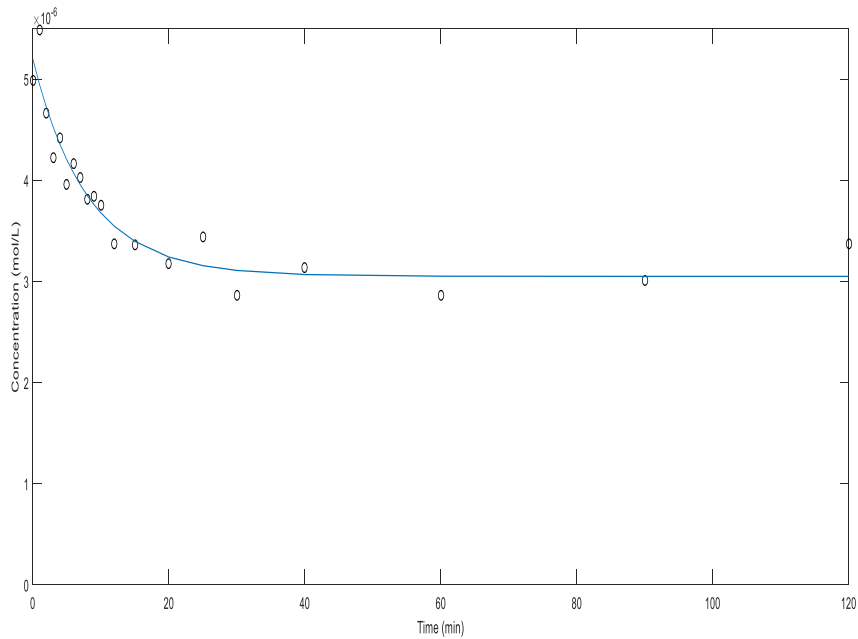


Figure 28. Measured and modeled concentrations of soluble As (V) at pH 6 as functions of time

Figure 28 shows soluble As (V) concentration at pH 6 and the model shows a good fit to the experimental data. As (V) removal is a much greater than As (III) removal at this pH and also greater than the maximum removal of As (III) that was observed at pH 9. The model and data show As (V) removal until about 30 minutes, after which no further removal is observed.

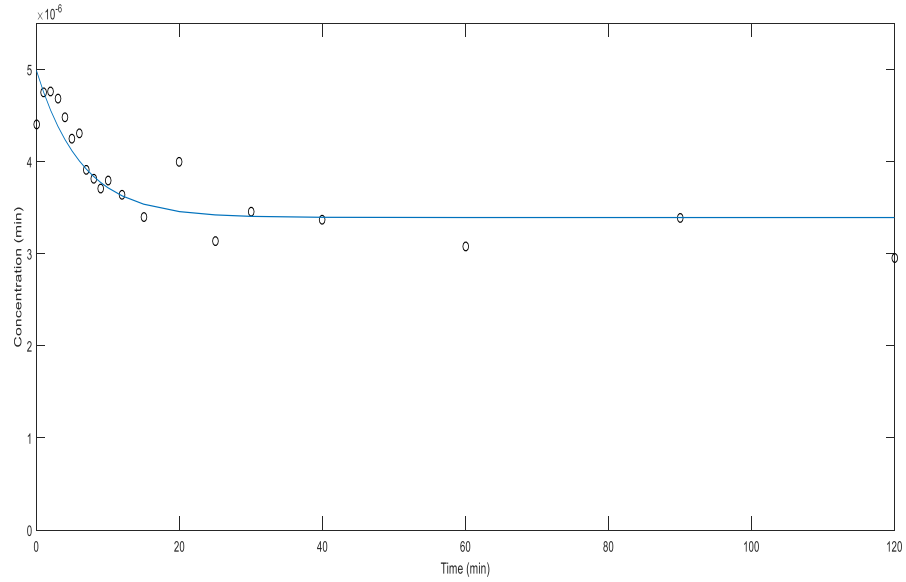


Figure 29. Measured and modeled concentrations of soluble As (V) at pH 7 as functions of time

Figure 29 depicts concentrations of soluble As (V) at pH 7. As (V) removal at pH 7 is good and is similar to As (III) removal achieved at this pH. The model is a good fit for this data.

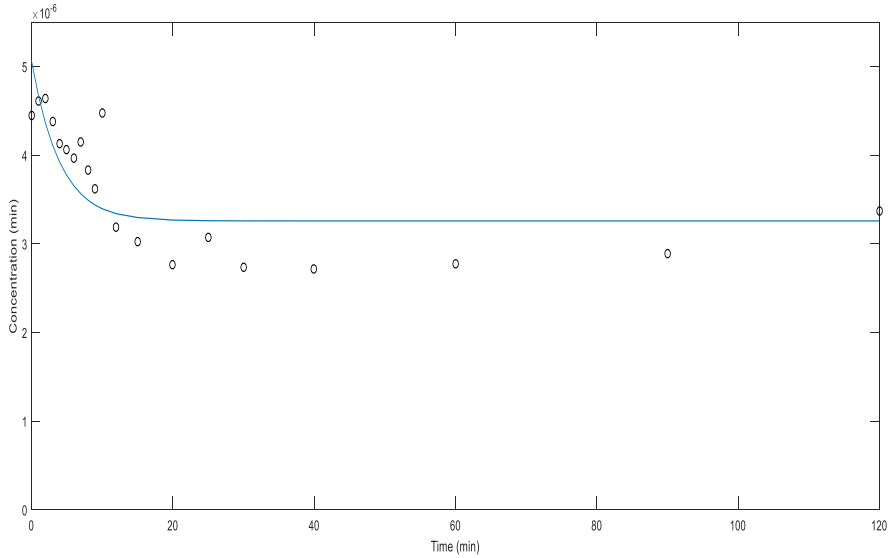


Figure 30. Measured and modeled concentrations of soluble As (V) at pH 8 as functions of time

Figure 30 shows measured and modeled concentrations of soluble As (V) at pH 8. The experimental values show much As (V) removal in a short span of time (about 20 minutes) after which no further removal is observed. Arsenic removal at this pH is higher than observed at any pH, including As (III) removals. The model does not fit the experimental data well and predicts less As (V) removal than observed.

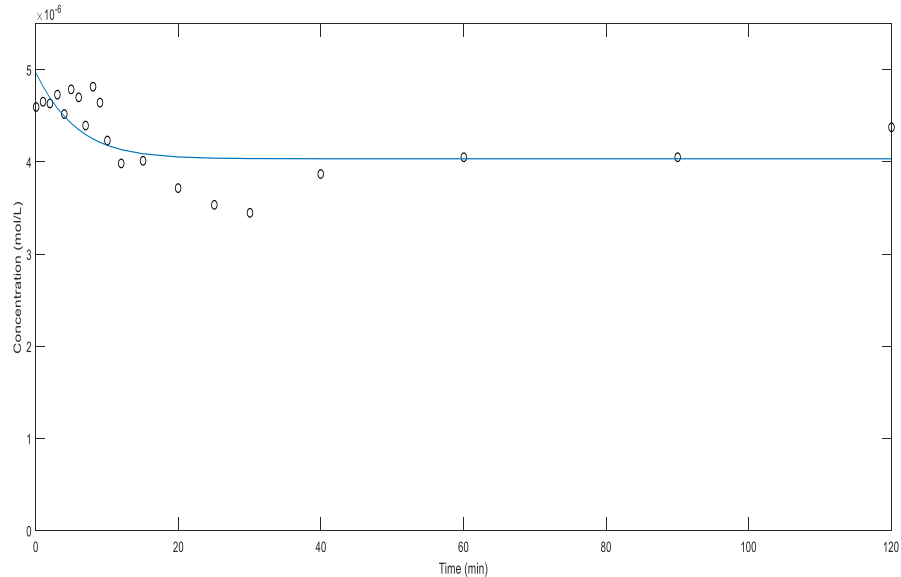


Figure 31. Measured and modeled concentrations of soluble As (V) at pH 9 as functions of time

Figure 31 shows variation of the concentration of soluble As (V) with time at pH 9. The graph indicates clear resolubilization of arsenic after about 30 minutes. The model is not a good fit for the data and predicts less removal of As (V) than observed. However, As (V) removal at pH 9 was good relative to removals at other pH values.

To summarize, the model fits the data well for As (III) and As (V) at pH 5 and 6. For the rest of the pH values, removal of arsenic was a greater than predicted by the model. At pH 9, significant resolubilization was observed for As (III) and As (V), which, cannot be explained using the current model. Maximum arsenic removal was experimentally observed with the combination of As (V) at pH 8 using dithionite/UV-L ARP.

5. SUMMARY

5.1 Conclusion

The advanced reduction processes are known to be successful in removing many oxidized contaminants and this work shows that it is useful in removing arsenic. Generally, application of UV-L alone or a reagent by itself was unable to remove target compounds, although low levels of removal of As (III) and As (V) were observed with only UV-L. Reagents without activation were generally unable to remove target compounds; however, dithionite by itself was able to remove arsenic. This is because dithionite can produce SO_2^\cdot (sulfur dioxide radical) without the need of activation energy (Housecroft & Sharpe, 2008).

A series of screening experiments conducted in our laboratory, identified dithionite as the most effective reagent for treating arsenic in water. Experience in our laboratory and a review of the literature indicated that dilute solutions of dithionite are unstable, so additional work was conducted to investigate dithionite stability. Batch kinetic tests were conducted to evaluate arsenic removal using dithionite.

The experiments indicated initial removal of arsenic followed by resolubilization of arsenic at later sampling times. These results indicated more complex reaction mechanisms than were anticipated, so additional experiments were conducted to better understand the behavior of arsenic during ARP treatment. The reaction mechanism and intermediates should be determined and the results presented in this work will be useful in doing that, which will help make this ARP viable for industrial wastewaters that contain

arsenic. Experiments conducted by our research group have shown arsenic removal as high as 80% with UV- dithionite ARP.

It was determined that As(V) removal is much slower than that observed for As(III) removal, which should be expected because As(V) requires more electrons to be reduced to elemental arsenic. Experimental results indicate that the presence of dithionite is needed for precipitation of As (V) and its absence results in resolubilization during irradiation. The results also show that UV irradiation is required for resolubilization

A potential mechanism for resolubilization during UV-L irradiation is that a product of dithionite photolysis is photolyzed and its photolysis products react with solid phase arsenic to solubilize it.

A product of dithionite decomposition that could have been responsible for resolubilization was thiosulfate and additional experiments were conducted to evaluate the effect of additions of thiosulfate. These experiments showed that thiosulfate was not responsible for resolubilization of arsenic.

The data showed that pH strongly impacts the extent and kinetics of arsenic removal. pH also determines the behavior of dithionite.

The absorbance of dithionite at 315 nm decreased with UV irradiation time and eventually, the absorbance peak at 315 nm was not found. Therefore, experiments should be quickly done to avoid oxidation of dithionite solution.

A design model was developed for arsenic removal by the dithionite/UV-L ARP and kinetics were identified by doing a non-linear regression using Matlab on a simple second-order kinetic equation.

A hypothesis for arsenic removal using ARP proposed that ARP is reducing As (III) to the elemental form rapidly and then slowly reducing As (0) to arsine (As (-III)), which is dissolved in the solution. Levy et al. investigated TiO₂-photocatalytic reduction of As (V) and As (III) and they showed that elemental arsenic (As (0)) and AsH₃ were produced as reaction products in an anoxic environment (Levy IK, 2012). If As(0) is produced from As(III) reduction by dithionite in the dithionite/UV-L ARP system, any As(0) that is formed could proceed to be further reduced to produce AsH₃. Identifying the reducing radicals that are responsible for reducing As (0) to AsH₃ would be investigated in further research at our lab.

5.2 Recommendations

1. After determining the intermediates and solving the resolubilizing issue of arsenic, a cost analysis of the commercial viability of dithionite/ UV-L ARP for removal of arsenic from wastewater can be done.
2. The effects of actual wastewater conditions and interference of co-ions could be studied.
3. Pilot scale laboratory testing could be done to test flow variation and mixing effects.
4. The kinetic model can be improved once the reaction intermediates and products are known.

REFERENCES

- A. Gomez-Camirero, P. H. (2001). Arsenic and Arsenic Compounds. Geneva: International Programme on Chemical Safety (IPCS).
- Abdel-Fattah, K. B. (2005). Adsorption of Arsenate and Arsenite by Iron-Treated Activated Carbon and Zeolites: Effects of pH, Temperature, and Ionic Strength. *Journal of Environmental Science and Health*, 40, 723–749. doi:10.1081/ESE-200048254
- Abdel-Wahab, N. B. (2014). Nitrate removal from water using UV-M/S2O4²⁻ advanced reduction process. *International Journal of Environmental Science and Technology*, 11(6). doi:10.1007/s13762-013-0375-0
- Amonette JE, S. J. (1994). Abiotic reduction of aquifer materials by dithionite: a promising in-situ remediation technology. *Thirty-Third Symposium on Health and the Environment In Situ Remediation: Scientific Basis for Current and Future Technologies*. US Department of Energy.
- Appelo, C. V. (2002). Surface complexation of ferrous iron and carbonate on ferrihydrite and the mobilization of arsenic. *Environmental Science and Technology*, 36(14), 3096–103.
- ATSDR, A. f. (2007). *CERCLA Priority List of Hazardous Substances for 2007*. U.S. Department of Health and Human Services. Retrieved from <http://www.atsdr.cdc.gov/cercla/07list.html>

- Barlow, D. S. (2015, 2 21). *Arsenic*. Retrieved 3 20, 2015, from Green Facts - Facts on Health and the Environment: <http://www.greenfacts.org/en/arsenic>
- Bentor, Y. (2012). *Periodic Table: Arsenic*. Retrieved 10 14, 2015, from <http://www.chemicalelements.com>:
<http://www.chemicalelements.com/elements/as.html>
- Bisceglia, K. R. (2005). Iron(II)-catalyzed oxidation of arsenic(III) in a sediment column. *Environmental Science and Technology*, 39(23), 9217–22.
- Buxton, A. G. (1988). Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\bullet\text{OH}/\bullet\text{O}^-$) in aqueous solution. *J. Phys. Chem*, 17(2), 513-886.
- Chemicool Periodic Table*. (2012, October 15). Retrieved February 14, 2015, from Chemicool: <http://www.chemicool.com/elements/arsenic.html>
- Deliyanni, E. B. (2003). Sorption of As(V) ions by akagane'ite-type nanocrystals. *Chemosphere*, 50(1), 155–63.
- Devaney, T. (2015). *EPA drops water pollution rules*. The Hill. Retrieved from <http://thehill.com/regulation/energy-environment/255492-epa-drops-water-pollution-rules>
- Dodd, M. V. (2006). Kinetics and mechanistic aspects of As(III) oxidation by aqueous chlorine, chloramines, and ozone: relevance to drinking water treatment. *Environmental Science and Technology*, 40(10), 3285–92.
- Duffus, J. (2002). "'Heavy Metals"—A Meaningless Term?'. *Pure and Applied Chemistry*, vol. 74, no. 5, 793–807.

- E.V., P. S. (2005). A new procedure for the spectrophotometric determination of nitrogen(II) oxide in solutions. *J. Anal. Chem.*, 60, 21.
- El-Safty, S. A. (2012). Development Of Material For Quick, Simple Removal Of Toxic Arsenic In Drinking Water. *Water Online*. Retrieved from <http://www.wateronline.com/doc/development-of-material-for-quick-simple-0001>
- EPA. (2009). *ARSENIC TRIOXIDE*. Retrieved 10 14, 2015, from [http://www2.epa.gov/](http://www2.epa.gov/http://www2.epa.gov/sites/production/files/2014-09/documents/arsenictrioxide_interim_nd_dec2008_c.pdf): http://www2.epa.gov/sites/production/files/2014-09/documents/arsenictrioxide_interim_nd_dec2008_c.pdf
- EPA. (2013, September 17). *Arsenic in Drinking Water*. Retrieved March 20, 2015, from Lawa and Regulations: <http://water.epa.gov/lawsregs/rulesregs/sdwa/arsenic/index.cfm>
- EPA US, U. E. (2002). *Proven Alternatives for Aboveground Treatment of Arsenic in Groundwater*. Office of Solid Wastes and Emergency.
- F.H., G. (1926). The ultra-violet absorption spectra of aqueous solutions of sulfur dioxide and some of its derivatives. *J. Phys. Chem.*, 30, 266.
- Focazio MJ, W. A. (1999). *A Retrospective Analysis on the Occurrence of Arsenic in Ground-Water Resources of the United States and Limitations in Drinking Water Supply Characterizations*. USGS Water-Resources Investigations Report. Retrieved from <http://pubs.usgs.gov/wri/wri994279/pdf/wri994279.pdf>
- Garcia, M. D. (2004). Solar light induced removal of arsenic from contaminated groundwater:. *Solar Energy*, 77(5), 601–13.

- GLOBAL, H. H.-T. (2016). Description of ICP Mass Spectrometry (ICP-MS). Retrieved from <http://www.hitachi-hightech.com/global/products/science/tech/ana/icp/descriptions/icp-ms.html/>
- Hayat, B. (2015, September 30). *New Power Plant Rules Will Reduce Toxic Pollution and Save Water*. Retrieved from Natural Resources Defense Council Staff Blog: http://switchboard.nrdc.org/blogs/bhayat/new_power_plant_rules_will_red.html
- Helmenstine, A. M. (2015). *Arsenic Facts - Chemical and Physical Properties of Arsenic*. Retrieved 3 20, 2015, from About Education: <http://chemistry.about.com/od/elementfacts/a/arsenic.htm>
- Henke, K. R. (2009). Waste Treatment and Remediation Technologies for Arsenic. In *Arsenic: Environmental Chemistry, Health Threats and Waste Treatment*. John Wiley & Sons, Ltd. Retrieved from <http://onlinelibrary.wiley.com.ezproxy.library.tamu.edu/doi/10.1002/9780470741122.ch7/pdf>
- Holleman, A. F., Wiberg, E., & Wiberg, N. (1985). *Lehrbuch der Anorganischen Chemie (in German); "Arsen"* (91–100 ed. ed.). Germany: Walter de Gruyter.
- Housecroft, C. E., & Sharpe, A. G. (2008). Chapter 16: The group 16 elements. In *Inorganic Chemistry* (3rd ed., p. 520). Pearson.
- Hug, S. C. (2001). Solar oxidation and removal of arsenic at circumneutral pH in iron containing waters. *Environmental Science and Technology*, 35(10), 2114–21.
- J.J., D. R. (1968). Nature of the transient species in the photochemistry of negative ions in aqueous solution. *J. Phys. Chem.*, 72, 3815.

- Kowalski, W. (2009). *Ultraviolet Germicidal Irradiation Handbook: UVGI for Air and Surface Disinfection*. New York: Springer. Retrieved from https://books.google.com/books?id=ReqUM_XNGjoC&pg=PA87&lpg=PA87&dq=uv+low+pressure+medium+pressure+narrowband&source=bl&ots=2JOaczSQ7a&sig=WUCd0aLBLqcAJXx2ILFLuqO3nCE&hl=en&sa=X&ved=0ahUKEwiZtq3VwZjKAhUIRiYKHQT4CB0Q6AEIHDA#v=onepage&q=uv%20low%20pressure
- Leandro M de Carvalho, G. S. (2001). Polarographic determination of dithionite and its decomposition products: kinetic aspects, stabilizers, and analytical application. *Analytica Chimica Acta.*, 436(2), 293-300. doi:10.1016/S0003-2670(01)00921-7
- Levy IK, M. M. (2012). TiO₂-photocatalytic reduction of pentavalent and trivalent arsenic: production of elemental arsenic and arsine. *Environmental Science and Technology*, 46, 2299-308.
- Liu, X., Yoon, S., Batchelor, B., & Abdel-Wahab, A. (2013). Photochemical degradation of vinyl chloride with an Advanced Reduction Process (ARP) – Effects of reagents and pH. *Chemical Engineering Journal*, 215-216, 868–875.
- Live Science Staff. (2013, May 10). *Facts about Arsenic*. Retrieved February 2, 2015, from Live Science: <http://www.livescience.com/29522-arsenic.html>
- Mahzuz, H. (2014, December 22). Arsenic Problem In Bangladesh. Sylhet, Bangladesh.
- Makarov, S. (2001). Novel trends in chemistry of sulfur-containing reductants. *Uspekhi Khimii*.

- Mckenna CE, G. W. (1991). A method for preparing analytically pure sodium dithionite. Dithionite quality and observed nitrogenase-specific activities. *Biochimica et Biophysica Acta.*, 109-17.
- Michael F. Hughes, B. D. (2011). Arsenic Exposure and Toxicology: A Historical Perspective. *Toxicological Sciences*, 123(2), 305-332. doi:10.1093/toxsci/kfr184
- Mollehuara, R. B. (September 2012). *Arsenic - Sources, Pathways And Treatment Of Mining And Metallurgical Effluents* . Output SEAP.
- Norman, N. C. (1998). *Chemistry of Arsenic, Antimony and Bismuth*. Springer.
- NRC, N. R. (2001). *Arsenic in Drinking Water. Update to the 1999 Arsenic in Drinking Water Report*. Washington, DC: National Academy Press.
- R.W., J. A. (1989). ESR studies of solvated electron in liquid solution using photolytic production. *J. Phys. Chem.*, 93, 3511.
- Reinsel, M. (2015). Arsenic Removal Technologies: A Review. *Water Online*. Retrieved from <http://www.wateronline.com/doc/arsenic-removal-technologies-a-review-0001>
- Rubidge, G. (2004). Thesis faculty of Applied Science . *Evaluation and optimisation of selected methods of arsenic removal from industrial effluent* . Port Elizabeth Technikon.
- S.G., M. (1978). The redox potential of dithionite and sulfur dioxide(1-) from equilibrium reactions with flavodoxins, methyl viologen and hydrogen plus hydrogenase. *Eur. J. Biochem.*, 85(2), 535-547. Retrieved from <http://www.ncbi.nlm.nih.gov/pubmed/648533>

- Sanderson, R. T. (2014, 10 19). *Arsenic*. Retrieved 02 14, 2015, from Encyclopedia Britannica: <http://www.britannica.com/EBchecked/topic/36266/arsenic-As>
- Smedley, D. K. (2001). *Arsenic Contamination of Groundwater in Bangladesh*.
Keyworth: British Geological Survey.
- Steinmaus C, Y. Y. (2003). Case-control study of bladder cancer and drinking water arsenic in the western United States. *Am. J. Epidemiol*, 1193-2001.
- Sunhee Yoon, D. S.-W. (2014). Degradation of 1,2-dichloroethane using advanced reduction processes. *Journal of Environmental Chemical Engineering*, 2(1), 731-37. Retrieved from <http://www.sciencedirect.com.ezproxy.library.tamu.edu/science/article/pii/S2213343713002285>
- Tanaka, T. (1988). Distribution of arsenic in the natural. In *Appl. Organomet. Chem.* (pp. 283-295).
- Training, P. E. (2014). Inductively coupled plasma mass spectrometry (ICP- MS) at Department of Chemistry, Texas A&M University.
- USDept.ofLabor. (1978, 10 10). *Safety and Health topics*. Retrieved March 20, 2015, from Occupational Safety and Health Administration: https://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=DIRECTIVES&p_id=1537
- US-Food&DrugAdmin. (2015, January 2). *Metals*. Retrieved March 20, 2015, from FDA: <http://www.fda.gov/Food/FoodborneIllnessContaminants/Metals/default.htm>

- Valentine, K. (2015). *EPA Rule Aims To Curb Toxic Coal Plant Pollution In Waterways*. Think Progress. Retrieved from <http://thinkprogress.org/climate/2015/09/30/3707481/epa-stream-pollution-rule/>
- Van_der_Meer, T. (2011). *Arsenic removal from effluents*. Outotec reports.
- Vellanki BP, B. B.-W. (2013). Advanced Reduction Processes: A New Class of Treatment Processes. *Environmental Engineering Science*, 264-271.
- Welch, A. W. (2000). Arsenic in ground water of the United States-- occurrence and geochemistry. *Ground Water*, 38(4), 589-604.
- Yue LI, M. X. (2009). Experimental Study on the Removal of Arsenic in Waste Water from Semiconductor manufacturing. *Journal of Water Resource and Protection*, 1, 1-57. Retrieved from file:///C:/Users/user/Desktop/JWARP20090100008_28023626.pdf

APPENDIX A

Time (min)	Reagent Control		Light Control		ARP		Blank	
	Concentration (μM)	pH	Concentration (μM)	pH	Concentration (μM)	pH	Concentration (μM)	pH
0	4.70	7.91	4.72	7.93	4.70	7.91	4.72	7.93
3	4.53	7.91	4.68	8.02	3.43	7.98		
30	4.47	7.84	4.69	8.03	3.69	7.81		
300	4.90	7.94	4.77	8.00	4.61	7.85	4.47	7.98

Table 6A. Soluble concentrations of As (V) at various times when reacted with 500 μM Dithionite at nominal pH 8. (Highlighted concentration is minimum value observed)

Time (min)	Reagent Control		Light Control		ARP		Blank	
	Concentration (μM)	pH	Concentration (μM)	pH	Concentration (μM)	pH	Concentration (μM)	pH
0	5.00	7.72	4.95	7.83	5.00	7.80	4.95	7.83
3	4.65	7.81	5.00	7.92	4.64	7.81		
30	4.64	7.79	4.81	7.94	4.56	7.80		
300	4.59	7.71	5.00	7.97	3.40	7.78	4.77	7.86

Table 7A. Soluble concentrations of As (V) at various times when reacted with 500 μM ferrous ion solution at nominal pH 8. (Highlighted concentration is minimum value observed)

Time (min)	Reagent Control		Light Control		ARP		Blank	
	Concentration (μM)	pH	Concentration (μM)	pH	Concentration (μM)	pH	Concentration (μM)	pH
0	4.92	7.90	4.69	7.88	4.92	7.90	4.69	7.88
3	4.91	8.00	4.83	7.92	4.89	7.99		
30	4.89	7.97	4.71	7.94	4.80	7.93		
300	5.05	7.91	4.64	8.04	4.71	8.03	4.63	7.91

Table 8A. Soluble concentrations of As (V) at various times when reacted with 500 μM Sulfite ion solution at nominal pH 8. (Highlighted concentration is minimum value observed)

Time (min)	Reagent Control		Light Control		ARP		Blank	
	Concentration (μM)	pH	Concentration (μM)	pH	Concentration (μM)	pH	Concentration (μM)	pH
0	4.88	7.93	4.83	7.94	4.88	7.93	4.83	7.94
3	4.75	7.93	4.73	7.93	4.88	7.93		
30	4.73	7.97	4.74	8.04	4.95	7.97		
300	4.80	7.93	4.70	8.07	4.64	8.00	4.67	8.04

Table 9A. Soluble concentrations of As (V) at various times when reacted with 100 μM ferrous ion solution at nominal pH 8. (Highlighted concentration is minimum value observed)

Time (min)	Reagent Control		Light Control		ARP		Blank	
	Concentration (μM)	pH	Concentration (μM)	pH	Concentration (μM)	pH	Concentration (μM)	pH
0	10.07	7.81	10.00	7.94	10.07	7.81	10.00	7.94
3	10.20	7.83	10.01	8.01	9.72	7.88		
30	10.20	7.87	9.90	7.97	9.34	7.84		
300	10.46	7.81	9.91	8.00	5.66	7.87	8.39	8.00

Table 10A. Soluble concentrations of As (III) at various times when reacted with 500 μM ferrous ion solution at nominal pH 8. (Highlighted concentration is minimum value observed)

APPENDIX B

PART a. Kinetic Experiment results – As(V) and corresponding dithionite concentration values

pH 5

Phosphate buffer 10 mM

Initial dithionite = 0.2 mM

Initial As (V) = 5 micro-molar

Irradiance = 1 mW/cm²

S.no	Time (min)	Concentration (μ M)	pH
1	0	4.95	5.27
2	1	4.84	5.10
3	2	4.89	5.15
4	3	4.68	5.16
5	4	4.70	5.10
6	5	4.49	5.10
7	6	4.49	5.08
8	7	4.28	5.10
9	8	4.13	5.08
10	20	3.81	5.12
11	25	3.95	5.10
12	30	3.86	5.10
13	40	3.88	5.10
14	60	3.92	5.20
15	90	3.98	5.24
16	120	4.06	5.17

Dithionite absorbance at 316 nm was analysed as follows:

S.no	Time (min)	ABS	Concentration (mol/L)
1	0	0.63289	7.86883E-05
2	1	0.57477	7.14621E-05
3	2	0.54018	6.71615E-05
4	3	0.49190	6.11588E-05
5	4	0.46498	5.78118E-05
6	5	0.43043	5.35161E-05
7	6	0.36411	4.52704E-05
8	7	0.30598	3.8043E-05
9	8	0.23859	2.96643E-05
10	10	0.27766	3.45219E-05
11	12	0.17893	2.22467E-05
12	15	0.13440	1.67102E-05
13	20	0.0074813	9.30163E-07
14	25	0	0
15	30	0.0017014*	2.11538E-07
18	40	0	0
19	60	0	0
20	90	0	0
21	120	0	0

*At 314nm

pH 6
Phosphate buffer 10 mM
Initial dithionite = 0.2 mM
Initial As (V) = 5 micro-molar
Irradiance = 1 mW/cm²

S.no	Time (min)	Concentration (μM)	pH
1	0	4.99	6.10
2	1	5.49	6.08
3	2	4.66	6.06
4	3	4.22	6.07
5	4	4.42	6.07
6	5	3.96	6.08
7	6	4.16	6.08
8	7	4.03	6.09
9	8	3.81	6.06
10	9	3.84	6.08
11	10	3.75	6.06
12	12	3.37	6.08
13	15	3.36	6.07
14	20	3.18	6.06
15	25	3.44	6.08
16	30	2.86	6.06
17	40	3.14	6.08
18	60	2.86	6.07
19	90	3.01	6.07
20	120	3.37	6.08

Dithionite absorbance at 316 nm was analysed as follows:

S.no	Time (min)	ABS	Concentration (mol/L)
1	0	0.68478	8.51399E-05
2	1	0.61336	7.62601E-05
3	2	0.60751	7.55328E-05
4	3	0.50259	6.24879E-05
5	4	0.51564	6.41104E-05
6	5	0.47122	5.85876E-05
7	6	0.39420	4.90116E-05
8	7	0.32668	4.06167E-05
9	8	0.30399	3.77956E-05
10	9	0.26436	3.28683E-05
11	10	0.26188	3.256E-05
12	12	0.14880	1.85006E-05
13	15	0.11039	1.3725E-05
14	20	0.06148*	7.64391E-06
15	25	0.014966*	1.86075E-06
16	30	0	0
17	40	0	0
18	60	0	0
19	90	0	0
20	120	0	0

*At 317nm

pH 7
Phosphate buffer 10 mM
Initial dithionite = 0.2 mM
Initial As (V) = 5 micro-molar
Irradiance = 1 mW/cm²

S.no	Time (min)	Concentration (μ M)	pH
1	0	4.40	7.08
2	1	4.75	7.13
3	2	4.76	7.15
4	3	4.68	7.11
5	4	4.48	7.11
6	5	4.25	7.12
7	6	4.31	7.09
8	7	3.91	7.12
9	8	3.81	7.13
10	9	3.71	7.11
11	10	3.79	7.12
12	12	3.64	7.12
13	15	3.40	7.10
14	20	4.00	7.10
15	25	3.14	7.11
16	30	3.46	7.09
17	40	3.37	7.13
18	60	3.08	7.07
19	90	3.39	7.11
20	120	2.95	7.06

Dithionite absorbance at 316 nm was analysed as follows:

S.no	Time (min)	ABS	Concentration (mol/L)
1	0	0.81610	0.000101
2	1	0.70853	8.81E-05
3	2	0.65773	8.18E-05
4	3	0.55708	6.93E-05
5	4	0.48267	6E-05
6	5	0.48155	5.99E-05
7	6	0.41750	5.19E-05
8	7	0.31464	3.91E-05
9	8	0.30035	3.73E-05
10	9	0.30563	3.8E-05
11	10	0.18989	2.36E-05
12	12	0.14385	1.79E-05
13	15	No data	No data
14	20	0.03447	4.29E-06
15	25	0.08550	1.06E-05
16	30	0	0
17	40	0	0
18	60	0	0
19	90	0	0
20	120	0	0

pH 8
Phosphate buffer 10 mM
Initial dithionite = 0.2 mM
Initial As (V) = 5 micro-molar
Irradiance = 1 mW/cm²

S.no	Time (min)	Concentration (μM)	pH
1	0	4.45	7.89
2	1	4.61	7.93
3	2	4.64	7.94
4	3	4.38	7.93
5	4	4.13	7.92
6	5	4.06	7.90
7	6	3.97	7.89
8	7	4.15	7.89
9	8	3.83	7.95
10	9	3.62	7.90
11	10	4.48	7.87
12	12	3.19	7.88
13	15	3.02	7.90
14	20	2.76	7.88
15	25	3.07	7.89
16	30	2.74	7.91
17	40	2.72	7.87
18	60	2.77	7.88
19	90	2.89	7.81
20	120	3.37	7.88

Dithionite absorbance at 316 nm was analysed as follows:

S.no	Time (min)	ABS	Concentration (mol/L)
1	0	1.094	0.000136
2	1	0.866	0.000108
3	2	0.827	0.000103
4	3	0.685	8.52E-05
5	4	0.470	5.84E-05
6	5	0.457	5.68E-05
7	6	0.393	4.89E-05
8	7	0.295	3.67E-05
9	8	0.245	3.05E-05
10	9	0.212	2.64E-05
11	10	0	0
12	12	0	0
13	15	0.013	1.62E-06
14	20	0.004	4.97E-07
15	25	0	0
16	30	0	0
17	40	0	0
18	60	0	0
19	90	0	0
20	120	0	0

pH 9

Phosphate buffer 10 mM

Initial dithionite = 0.2 mM

Initial As (V) = 5 micro-molar

Irradiance = 1 mW/cm²

I obtained the following results:

S.no	Time (min)	Concentration (μM)	pH
1	0	4.60	8.61
2	1	4.65	8.69
3	2	4.63	8.74
4	3	4.73	8.65
5	4	4.52	8.59
6	5	4.79	8.58
7	6	4.70	8.58
8	7	4.40	8.57
9	8	4.82	8.54
10	9	4.64	8.56
11	10	4.23	8.44
12	12	3.98	8.49
13	15	4.01	8.44
14	20	3.72	8.44
15	25	3.53	8.42
16	30	3.45	8.44
17	40	3.87	8.45
18	60	4.05	8.45
19	90	4.05	8.47
20	120	4.38	8.46

Dithionite absorbance at 316 nm was analysed as follows:

S.no	Time (min)	ABS	Concentration (mol/L)
1	0	1.10420	0.000137
2	1	0.97940	0.000122
3	2	0.83569	0.000104
4	3	0.70738	8.79E-05
5	4	0.63373	7.88E-05
6	5	0.55800	6.94E-05
7	6	0.44298	5.51E-05
8	7	0.42340	5.26E-05
9	8	0.34790	4.33E-05
10	9	0.29777	3.7E-05
11	10	0.23555	2.93E-05
12	12	0.17533	2.18E-05
13	15	0.085357	1.06E-05
14	20	0.032557	4.05E-06
15	25	0.0014801	1.84E-07
16	30	0	0
17	40	0	0
18	60	0	0
19	90	0	0
20	120	0	0

PART b. Kinetic Experiment results – As(III) and corresponding dithionite concentration values

pH 5

Phosphate buffer 10 mM

Initial dithionite = 0.2 mM

Initial As (III) = 5 micro-molar

Irradiance = 1 mW/cm²

I obtained the following results:

S.no	Time (min)	Concentration (μM)	pH
1	0	4.68	4.90
2	1	4.75	4.85
3	2	4.61	4.85
4	3	4.59	4.91
5	4	4.65	4.89
6	5	4.57	4.91
7	6	4.64	4.78
8	7	4.53	4.80
9	8	4.29	4.93
10	9	4.43	4.89
11	10	4.31	4.95
12	12	4.42	4.81
13	15	4.33	4.92
14	20	4.50	4.84
15	25	4.45	5.01
16	30	4.59	4.93
17	40	4.54	4.92
18	60	4.34	4.94
19	90	5.42	5.01
20	120	4.57	5.05

Dithionite absorbance at 316 nm was analysed as follows:

S.no	Time (min)	ABS	Concentration (mol/L)
1	0	0.77363	9.61867E-05
2	1	0.66438	8.26035E-05
3	2	0.65886	8.19172E-05
4	3	0.47914	5.95723E-05
5	4	0.29586	3.67848E-05
6	5	0.37378	4.64727E-05
7	6	0.19831	2.46562E-05
8	7	0.18032	2.24195E-05
9	8	0.02992	3.72E-06
10	9	0.054761	6.80853E-06
11	10	0.033448	4.15865E-06
12	12	0.020532	2.55278E-06
13	15	0	0
14	20	0	0
15	25	0	0
16	30	0	0
17	40	0	0
18	60	0	0
19	90	0	0
20	120	0	0

pH 6
Phosphate buffer 10 mM
Initial dithionite = 0.2 mM
Initial As (III) = 5 micro-molar
Irradiance = 1 mW/cm²

S.no	Time (min)	Concentration (μM)	pH
1	0	4.54	6.04
2	1	4.85	6.05
3	2	4.53	5.99
4	3	4.28	6.05
5	4	4.45	6.00
6	5	4.19	5.97
7	6	4.18	6.05
8	7	4.30	6.02
9	8	4.18	5.99
10	9	4.18	6.00
11	10	3.95	5.96
12	12	3.84	6.00
13	15	3.96	6.03
14	20	3.92	5.99
15	25	3.87	5.99
16	30	4.21	5.97
17	40	4.00	6.03
18	60	4.30	6.05
19	90	4.42	6.10
20	120	3.80	6.02

Dithionite absorbance at 316 nm was analysed as follows:

S.no	Time (min)	ABS	Concentration (mol/L)
1	0	0.79539	9.88922E-05
2	1	0.65970	8.20216E-05
3	2	0.60117	7.47445E-05
4	3	0.48908	6.08082E-05
5	4	0.46388	5.7675E-05
6	5	0.38048	4.73057E-05
7	6	0.20348	2.5299E-05
8	7	0.28864	3.58871E-05
9	8	0.23722	2.9494E-05
10	9	0.12530	1.55788E-05
11	10	0.12566	1.56235E-05
12	12	0.01221	1.51809E-06
13	15	0.011333	1.40905E-06
14	20	0	0
15	25	0	0
16	30	0	0
17	40	0	0
18	60	0	0
19	90	0	0
20	120	0	0

pH 7
Phosphate buffer 10 mM
Initial dithionite = 0.2 mM
Initial As (III) = 5 micro-molar
Irradiance = 1 mW/cm²

S.no	Time (min)	Concentration (μ M)	pH
1	0	4.56	6.93
2	1	4.49	6.89
3	2	4.41	6.82
4	3	4.08	6.98
5	4	4.23	6.89
6	5	3.98	6.86
7	6	3.66	6.83
8	7	3.74	6.86
9	8	3.85	6.88
10	9	3.43	6.91
11	10	3.33	6.97
12	12	3.26	6.91
13	15	3.83	6.97
14	20	3.66	6.93
15	25	3.93	6.96
16	30	3.39	6.94
17	40	3.23	6.94
18	60	3.68	6.89
19	90	3.77	6.96
20	120	3.88	6.92

Dithionite absorbance at 316 nm was analysed as follows:

S.no	Time (min)	ABS	Concentration (mol/L)
1	0	0.87499	0.000109
2	1	0.76546	9.52E-05
3	2	0.62630	7.79E-05
4	3	0.40262	5.01E-05
5	4	0.38783	4.82E-05
6	5	0.28294	3.52E-05
7	6	0.25857	3.21E-05
8	7	0.24589	3.06E-05
9	8	0.15804	1.96E-05
10	9	0.12071	1.5E-05
11	10	0.12306	1.53E-05
12	12	0.074541	9.27E-06
13	15	0.032438	4.03E-06
14	20	0.0087113	1.08E-06
15	25	0	0
16	30	0	0
17	40	0	0
18	60	0	0
19	90	0	0
20	120	0	0

pH 8
Phosphate buffer 10 mM
Initial dithionite = 0.2 mM
Initial As (III) = 5 micro-molar
Irradiance = 1 mW/cm²

S.no	Time (min)	Concentration (μM)	pH
1	0	4.51	7.88
2	1	4.64	7.91
3	2	4.65	7.89
4	3	4.61	7.91
5	4	3.93	7.88
6	5	4.30	7.88
7	6	4.41	7.89
8	7	4.43	7.87
9	8	4.07	7.85
10	9	4.09	7.88
11	10	4.00	7.85
12	12	3.66	7.83
13	15	3.36	7.87
14	20	3.85	7.85
15	25	3.55	7.89
16	30	3.82	7.85
17	40	4.06	7.85
18	60	3.40	7.87
19	90	3.43	7.89
20	120	4.19	7.88

Dithionite absorbance at 316 nm was analysed as follows:

S.no	Time (min)	ABS	Concentration (mol/L)
1	0	1.01290	0.000126
2	1	0.86496	0.000108
3	2	0.81058	0.000101
4	3	0.66346	8.25E-05
5	4	0.45770	5.69E-05
6	5	0.45145	5.61E-05
7	6	0.24928	3.1E-05
8	7	0.22190	2.76E-05
9	8	0.10575	1.31E-05
10	9	0.085717	1.07E-05
11	10	0.071429	8.88E-06
12	12	0.021681*	2.7E-06
13	15	0.01869**	2.32E-06
14	20	0	0
15	25	0	0
16	30	0	0
17	40	0	0
18	60	0	0
19	90	0	0
20	120	0	0

*At 315nm **At 317nm

pH 9
Phosphate buffer 10 mM
Initial dithionite = 0.2 mM
Initial As (III) = 5 micro-molar
Irradiance = 1 mW/cm²

S.no	Time (min)	Concentration (μ M)	pH
1	0	4.41	8.62
2	1	4.47	8.55
3	2	4.32	8.54
4	3	4.37	8.53
5	4	4.32	8.49
6	5	4.25	8.48
7	6	3.86	8.47
8	7	4.08	8.46
9	8	7.94	8.41
10	9	4.23	8.41
11	10	3.92	8.40
12	12	3.57	8.42
13	15	3.71	8.42
14	20	3.44	8.41
15	25	3.22	8.42
16	30	3.12	8.41
17	40	3.22	8.40
18	60	3.83	8.41
19	90	3.99	8.46
20	120	4.15	8.52

Dithionite absorbance at 316 nm was analysed as follows:

S.no	Time (min)	ABS	Concentration (mol/L)
1	0	1.09700	0.000136
2	1	0.88209	0.00011
3	2	0.76017	9.45E-05
4	3	0.63640	7.91E-05
5	4	0.49225	6.12E-05
6	5	0.40885	5.08E-05
7	6	0.31366	3.9E-05
8	7	0.19355	2.41E-05
9	8	0.14894	1.85E-05
10	9	0.14012	1.74E-05
11	10	0.090650	1.13E-05
12	12	0.035431	4.41E-06
13	15	0.018664*	2.32E-06
14	20	0	0
15	25	0	0
16	30	0	0
17	40	0	0
18	60	0	0
19	90	0	0
20	120	0	0

*At 315nm

APPENDIX C

Differential equation 12 was solved numerically to calculate concentrations of soluble arsenic as a function of time during treatment by the dithionite/UV-L ARP using the MATLAB code provided in this appendix. Two m-files were created as follows:

M-file 1: deriv_ode.m

```
function output = deriv_ode(pars,t)

function dcmddt = ode(t,cmod)
    % this is the ODE we are fitting to
    k= pars(1);
    L=0.01; % path length in meter
    e=3677; % molar absorbtivity in l/mol/cm
    e_1=2.303*e; % base e molar absorbtivity
    I_0=1; % light intensity in unit mW/cm^2
    w=254*10^-9; % wavelength of UV light in meter
    Na=6.02*10^23; % avogadro's number in mol^-1
    h=6.626*10^-34; % planck's number in J-s
    c_1=3*10^8; % speed of light in m/s
    I=I_0*w*10/Na/h/c_1; % convert unit for light intensity to
    einstein/m^2/s

    Q=0.273; %Quantum yield in mol/Einstein (depends on arsenic
    and ambient pH)
    D_o=0.000136; %Initial concentration of Dithionite in mol/L
    (depends on arsenic and ambient pH)

    dcmddt = k*cmod*
    (log(exp(e_1*L*100*Q*I*t*60/(1000*L)))/(exp(e_1*L*100*Q*I*t*
    60/(1000*L))+exp(e_1*L*100*D_o)-1))/(L*e_1*100));

end
data = load ('AsIIIpH9.txt');
t = data(:,1); % measured values of time
cmeas_data = data(:,2); % measured values of concentration

    cmod0 = pars(2);
```

```

        [t, cmod] = ode45(@ode, t, cmod0);
        output = cmod;
end

```

* As (III) pH9 was the name of a text file that had time and measured arsenic concentrations of As (III) at pH 9 arranged in two columns. Similarly each pH and arsenic species combination was modeled.

M-file 2: main.m

```

% This script m-file inputs data and calls nlinfit_ode.m to
conduct non-linear least squares regression

```

```

clear all
%Load and Plot data
data = load ('AsIIIpH9.txt');
% AsIIIpH9.txt is the name of a text file that contains the
data used in the regression.
% It is a matrix with the first column holding the values
of the independent variable (i.e.time)
% The subsequent column holds the value of the dependent
variable (i.e. concentration)
t = data(:,1); % measured values of time
cmeas_data = data(:,2); % measured values of concentration
plot(t, cmeas_data, 'ko ')
xlabel('t')
ylabel('cmeas_data')

%Non linear regression
parguess = [1.3;1]; % initial guesses for parameter
[pars, resid, J] =
nlinfit(t, cmeas_data, @deriv_ode, parguess);

%parameter confidence intervals
alpha = 0.05; % this is for 95% confidence intervals
pars_ci =
nlparci(pars(1), resid, 'jacobian', J(:,1), 'alpha', alpha);

sprintf('The true value of k is between %1.2f and %1.2f at
the 95% confidence level', pars_ci)

%plot output

```

```

hold on
fit = deriv_ode(pars(:,1),t);

hold all
plot(t,fit(:,1))

%Sum of squared Errors
SSE = norm(fit(:,1) - cmeas_data)

% Print k (l/mol/sec)s
pars

%Print Confidence interval
pars_ci

% Coeffiient of variation - Cv
(fit - cmeas_data); % Errors
(fit - cmeas_data).^2 ; % Squared Error
mean((fit - cmeas_data).^2); % Mean Squared Error
RMSE = sqrt(mean((fit - cmeas_data).^2)); % Root Mean
Squared Error
Cv = RMSE/mean(cmeas_data)

```

Following is a table for the "Q" and "D_o" values of various arsenic species and pH combination:

	Q (mol/einstein)	D_o (mol/L)
AsIII pH5	0.244	9.62E-05
AsIII pH6	0.204	9.89E-05
AsIII pH7	0.249	0.00011
AsIII pH8	0.255	0.00013
AsIII pH9	0.273	0.00014
AsV pH5	0.103	7.87E-05
AsV pH6	0.109	8.51E-05
AsV pH7	0.151	0.0001
AsV pH8	0.247	0.00014
AsV pH9	0.19	0.00014

Table 11C. Values of quantum yield (Q) and initial concentration of dithionite (D_o) for arsenic at various pH. The Q values were calculated using nonlinear regression on measured concentrations of dithionite.