CHLORATE REDUCTION IN WATER USING ADVANCED REDUCTION PROCESSES

A Thesis

by

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ABSTRACT

Chlorate is one of the disinfection byproducts when chlorine/chlorine dioxide is used as the primary disinfectant. Excess amounts of chlorate in drinking water above permissible limits are toxic. This study investigated chlorate removal from water by photochemical degradation using advanced reduction processes (ARP). This new class of treatment processes combines a reducing agent and an activation method to generate reducing radicals that can efficiently destroy persistent oxidized contaminants. The effectiveness of combinations of four reducing agents (sulfite, dithionite, sulfide, and ferrous iron) and three UV light sources (UV-L, UV-M, and UV-B) were evaluated for chlorate removal. Dithionite irradiated by broad-band UVB lamp having the output between 280 nm and 320 nm with peak energy at 312 nm (UV-B) showed the highest chlorate removal. In pursuit of finding the optimum ARP conditions, the process variables including pH, reducing agent dose, initial chlorate concentration and light intensity were investigated. Dithionite/UV-B ARP was effective at weakly acidic conditions less than pH 5, and chlorate removal occurred in two steps. The first was an initial rapid decrease in chlorate concentration that occurred before initiating UV irradiation and was attributed to reaction with dithionite decomposition products. Bisulfite or metabisulfite in equilibrium with bisulfite are believed to be the decomposition products responsible for chlorate reduction. The second step was a slow decrease during UV irradiation that is caused by radicals produced by photolysis of the products of dithionite decomposition. The major

product of chlorate destruction was chloride, with negligible amounts of chlorite produced.

DEDICATION

To my parents, sister and my uncle.

ACKNOWLEDGMENTS

NOMENCLATURE

ARP	Advanced Reduction Processes
UV-L	Low pressure mercury vapor irradiation
UV-M	Medium pressure mercury vapor irradiation
UV-B	Broad band mercury vapor irradiation
UV-B/ dithionite	the combination of dithionite and UV-B
IC	Ion Chromatography
H$^{\bullet}$	Hydrogen radical
e_{aq}^{-}	Aqueous electron
H^{+}	Hydrogen ion/ proton
C$_0$	Initial concentration
Conc.	Concentration
DDW	Deionized- deoxygenated water
MCL	Maximum contamination level
Sol.	Solution
Std.	Standard
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
Vol.	Volume

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1. INTRODUCTION

Disinfection is an integral process in seawater desalination systems and it is an essential process in most drinking water and wastewater treatment systems. Disinfection is a process of deactivating harmful and objectionable bacteria, viruses, cysts and other pathogenic microorganisms which spread waterborne diseases (Kumar and Pandit, 2012, Lenntech, 1998). Disinfection of water is of two types, chemical methods where chlorine, chlorine dioxide, chloramines, ozone, and hydrogen dioxide are employed and physical method of disinfection where heat, ultraviolet light and ultra- sonication could be employed to effect disinfection.

Chlorination involves the addition of chlorine or chlorine-based derivatives and is the most commonly used chemical method of disinfection because of its effectiveness against a wide spectrum of disease causing microorganisms, low cost and high reliability. According to the World Health Organization (WHO), chlorine based disinfectants are the only disinfectants that provide lasting residual protection to protect water from waterborne diseases throughout the distribution network, from the treatment plant to the consumer's tap (Kumar and Pandit, 2012). Advantages of chlorination comprise of reducing: (i) the levels of many disease causing microorganisms to safe concentration levels, (ii) disagreeable tastes and odors, (iii) sulfides and, (iv) foul smelling algae secretions. Chlorination also removes bacteria and molds which commonly grow in water supply tanks and on the walls of the storage tanks (Kumar and Pandit, 2012). Chlorine dioxide

and chlorine are the most common chlorinated compounds that are used for disinfection (Aieta and Berg, 1986, Atkin et al., 1982).

Although the use of chemical disinfectants is essential to water treatment, it is not trouble free. Each of the common disinfectants can produce disinfection byproducts (DBPs) that pose threats to human health or aquatic ecosystems. Ozonation and chlorine dioxide have become important alternatives to chlorine in water treatment because they avoid the production of chlorinated organic chemicals as byproducts. However, when ozone or chlorine dioxide is used, oxyhalide inorganic compounds such as bromate and chlorate are formed as disinfection byproducts (Bao et al., 1999, Lee et al., 2004).

Chlorate is a common by-product associated with chlorine dioxide treatment. Consumption of chlorate over the safe permissible limit contributes to toxicity. There have been studies which concluded that chlorate poisoning results in renal failure, abdominal pain and methemoglobinemia and reduction of antioxidants to the cells (Abdel-Rahman et al., 1979, Safe Drinking Water Commitee and National Research Council, 1987). The World Health Organization (WHO) regulates the maximum permissible limit of chlorate in drinking water to be 700 µg/L (WHO, 2004). The United States Environmental Protection Agency (USEPA) has not yet regulated a maximum contaminant level (MCL) for chlorate. However, Office of Health Hazard Assessment (OEHHA) stated the guideline value of chlorate to be at 500 µg/L (Howd, 2007) and the Canadian guideline is 1mg/L (Cotruvo, 2013, WHO, 2004). Hence there is a need to reduce chlorate to its innocuous products in drinking water in order to protect human health.

Oxidation-reduction reactions are the primary way in which water treatment processes destroy environmental contaminants such as chlorate. Advanced Oxidation Processes (AOP) is a class of treatment processes that have been employed to destroy contaminants by oxidizing them (Crittenden et al., 2005). They produce hydroxyl radicals ($OH^.$) that reacts rapidly with a wide range of contaminants (Tchobanoglous et al., 2003). Hydroxyl radical is a free radical that contains an unpaired electron which makes it very strong oxidant. It accepts an electron to form the hydroxide ion (OH^-). The hydroxyl radical can be produced by combining oxidizing agents (e.g. ozone or hydrogen peroxide) with an activating method (e.g. ultraviolet light, electron beam). However, there are also reductive free radicals that react by donating their unpaired electron to another compound.

A new class of treatment processes called Advanced Reduction Processes (ARP) that have mechanisms similar to AOP but differ in that they combine reducing reagents with activating methods to produce highly reactive reductant radicals to destroy oxidized contaminants. A number of halogenated organic compounds (PFOA, vinyl chloride, 1, 2-dichloroethane) (Liu et al., 2014a, Liu et al., 2013a, b, Qu et al., 2010, Song et al., 2013, Yoon et al., 2013) and oxidized inorganic anions (perchlorate, nitrate, and bromate) (Bensalah et al., 2013, Bensalah et al., 2014, Jung et al., 2013, Liu et al., 2014b, Vellanki and Batchelor, 2013) have been reported to have been degraded completely using ARP. This research focused on using ARP as a potential treatment method of reducing chlorate to chloride.

2. LITERATURE REVIEW

2.1. Chlorate

One of the primary sources of chlorate is chlorine dioxide (ClO_2) which is primarily used as disinfectant in water treatment plants. ClO_2 has replaced chlorine in many water treatment systems owing to its efficiency in deactivating bacteria and viruses over a broad pH range, controlling the taste and odor compounds and limiting the formation of trihalomethanes (THMs) (Gonce and Vudrias, 1993). At alkaline pH values (pH>10), chlorine dioxide undergoes disproportionation reaction to form chlorite (ClO_2^-) and chlorate ions (ClO_3^-) under conditions of low initial reactant concentrations or in the presence of excess chlorine or hypochlorous acid (Couri et al., 1982, Gonce and Vudrias, 1993, Gordon et al., 1990, Stevens, 1982).

Molecular ozone reacts with hypochlorite ion producing chlorite ion which is quickly oxidized to chlorate (Siddiqui, 1996). Another source of chlorate contamination is when sodium chlorate is used in the manufacturing of dyes, matches and explosives; for tanning and finishing leather. Sodium chlorate is also a popular herbicide, oxidizing agent, bleach (to make chlorine dioxide), and a defoliant (Safe Drinking Water Commitee et al., 1982, Safe Drinking Water Commitee and National Research Council, 1987, WHO, 2005). Additionally, chlorate and chlorite ions are formed when sodium hypochlorite and calcium hypochlorite solutions undergo degradation. Direct oxidation of chlorite, reaction of aqueous chlorine with chlorine dioxide or chlorite at neutral or alkaline pH also lead to chlorate. At acidic conditions, chlorine reacts with chlorite ions to form chlorate. But at neutral conditions, although chlorine exists as HClO and Cl^-, it did not affect the formation

of chlorate. Chlorate was also detected in hypochlorite solutions used for drinking water disinfection (Aieta and Berg, 1986, Black & Veatch Corporation, 2010, Bolyard et al., 1992, Taube and Dodgen, 1949) (Eqs. 2.1, and 2.2).

$$Cl_2 + NaClO_2 + OH^- \rightarrow NaClO_3 + Cl^- + HCl \qquad (2.1)$$

$$HOCl + 2ClO_2 + H_2O \rightarrow 2ClO_3^- + HCl + H^+ \qquad (2.2)$$
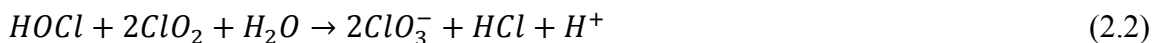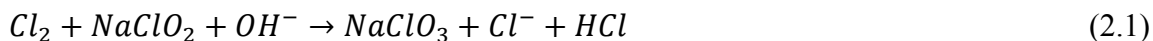
Oxidation of chlorine dioxide to chlorite by natural organic matter (NOM) and further oxidation of chlorite to chlorate by ozone, reaction of hypochlorite ions with ozone, photolytic decomposition of ClO_2 by sunlight or fluorescent lightning, dilute chlorite solutions at low pH (pH<3) also produce chlorate. Reaction of hypochlorous acid with the hypochlorite ion between pH 5.8- 6.5 and in the presence of sunlight forms the basis of commercial production of sodium chlorate in the pulp and paper industry.

$$2HOCl + OCl^- \rightarrow ClO_3^- + 2H^+ + 2Cl^- \qquad (2.3)$$

Base catalyzed disproportionation of chlorine dioxide at high pH values (pH>11), and excess of hypochlorous acid will also lead to the formation of chlorates (Aieta and Berg, 1986, Gonce and Vudrias, 1993, Griese et al., 1992, Haag and Hoigne, 1983, Nowack and Gunten, 1999, Praus, 2003, USEPA, 1999).

Toxicity associated with chlorate has not been studied to great extent but there are some articles published in this area. As it was found that chlorine dioxide (ClO_2) gives rise to un-wanted byproducts like chlorite and chlorate, this led to some investigations to study the ill- effects of chlorate and chlorite. Experiments conducted on rats led to the finding that chlorate could cause decrease in the count of red blood corpuscles (RBC), hemoglobin, hematocrit, glutathione (antioxidant that prevents damage to the cells) (Couri

et al., 1982), body weight due to decrease in organ weight, pituitary and thyroid cell depletion (Bio/dynamics, 1987, WHO, 2005). At tolerant levels, chlorate will be excreted as chloride and chlorite at small levels in the urine (Abdel-Rahman et al., 1982). One of the biggest issues associated with chlorate is the condition called Methemoglobinemia (Steffan and Wettzel, 1993). This is a condition of abnormal blood disorder where the formation of methemoglobin occurs. Methemoglobin is a form of hemoglobin. The only difference between the two is that while hemoglobin carries the oxygen in the blood to all the respiratory organs, methemoglobin has a decreased affinity to oxygen. Hence the formation of methemoglobin will reduce the amount of oxygen in the blood and consequently the body will be deprived of oxygen. This condition is called hypoxia. Abdel-Rahman et al., (1982) reported that the distribution of chlorate among the rats was the highest in the plasma followed by stomach, lung, kidney and bone marrow. No-observed-adverse-effect level (NOAEL) for chlorate i.e. the highest level of concentration of chlorate at which no adverse effects were found was found to be 30 mg/kg of body weight for rats (McCauley et al., 1995). The symptoms of consuming chlorate are predominantly Methemoglobinemia- lack of oxygen in blood, anuria- non passage of urine due to failure of kidneys, and abdominal pain (Safe Drinking Water Commitee et al., 1982). Toxicity of chlorate also extends to algal species where it has been found that chlorate is extremely toxic to macro brown algae species (Wijk et al., 1998). Although methemoglobinemia, is one of the most prominent problems of chlorate, hemolysis, anuria, abdominal pain, hemolysis, anoxia, nephron failure, anoxia, intravascular coagulation, and renal insufficiency determines the fate of the patients (Abdel-Rahman et

6

al., 1982, Couri et al., 1982, Safe Drinking Water Commitee et al., 1982, Safe Drinking Water Commitee and National Research Council, 1987, Steffan and Wettzel, 1993). Because of its use as a weed killer, chlorate toxicity severely attacked the cattle, resulting in several deaths. But it was successfully treated with methylene blue (Babjee et al., 1970).

Chlorate can be removed from water or reduced by biological, chemical, or physical methods. Chlorate was completely removed by microorganisms using a gas lift reactor at a constant pH of 7.7 and at a temperature of $36^{o}C$ (Kroom and Ginkel, 2004). Malmqvist and Welander, (1994) used a suspended biofilm carrier and obtained complete chlorate removal at pH 9.0. Under anaerobic conditions, chlorate was removed by using energy substrates and inocula (van Ginkel et al., 1995). Although biological method of removal was successful, there were certain limitations in that it took months to obtain complete removal of chlorate. Activated sludge was evaluated to remove chlorate from the soils with 75% of chlorate being recovered (Jiang et al., 2009). Among the chemical methods for chlorate removal is catalytic treatment using rhodium and palladium as catalysts in the presence of hydrogen which were found to be successful to reduce chlorate (Santen et al., 2001). Iridium was also reported to have successfully removed chlorate when it was supported with carbon in the presence of hydrogen. The removal of chlorate varied from partial removal (30%) to complete removal depending on water pH and temperature evaluated for removal (Kuznetsova et al., 2012). Chlorate was not removed using sulfite-sulfur dioxide in the presence of oxygen (Gordon et al., 1990). Removal of chlorate by electrolytic treatment was reported by few researchers. Srinivasan et al., (2009) investigated chlorate removal using nickel and carbon electrodes (chlorate removal

7

= 10 %), glassy carbon electrode and cobalt based electrodes (chlorate removal= 15% at pH 3.75), TiO$_2$- coated nickel electrodes (chlorate removal= 26% at pH 3.75). Reduction of chlorate with titanium electrode has been successful in the presence of H$^+$ ion produced from HCl acid (Brown, 1986). It has been reported that the presence of the hydrogen ion and electron reduced chlorate to chloride according to the following equation:

$$ClO_3^- + 6e^- + 6H^+ \rightarrow Cl^- + 3H_2O \hspace{3cm} (2.4)$$

It was also reported that 70% reduction of chlorate was achieved using iron fillings both in the presence and absence of dissolved oxygen (DO) (Srinivasan et al., 2009). Iron pentacarbonyl was also a good reductant for chlorate producing iron oxides as the iron by-product (Dieger Schlaefer et al., 1989). Addition of acids to the solution containing chlorate salts to decompose chlorate is yet another method to remove chlorate from the solution. Okajima et al., (1996) reported the removal of chlorate from aqueous alkali solution by adding HCl into the solution containing chlorate and keeping the reaction solution at an absolute pressure of less than 80 kPa and not lower than the saturated vapor pressure of the solution in a decomposition vessel. They have also reported an increase in chlorate removal when the reaction solution flows upward through the decomposition vessel under the same conditions. The main disadvantage of chemical method of removal is that most of the methods did not report complete reduction (100%) of chlorate within reasonable reaction time for practical application.

Gonce and Vudrias, (1993) attempted to remove chlorate using granular activated carbon and found that chlorate was only reversibly sorbed and not completely removed. Chlorate was reduced to chloride in the presence of arsenic and the arsenic was

subsequently oxidized to arsenate (Sun et al., 2010). Removal of chlorate by photo degradation has been studied previously where powdered sodium chlorate was exposed to ^{60}Co gamma- rays (Herley and Levy, 1975). The samples showed the production of chloride ions indicating the decomposition of chlorate. However, no effort was made to elucidate the mechanism of the decomposition process. High flux of thermal neutrons was also used to irradiate sodium chlorate salt for a period of twenty- four weeks. The samples when analyzed after irradiation showed a decrease in the activity of Cl^{36} in the chlorate salt. This led to conclusion that sodium chlorate was considerably decomposed with a net loss of oxygen from the sample (Sharman and McCallum, 1955). Previously, removal of perchlorate (ClO_4^-), which has higher oxidation state than chlorate, has been investigated by ARP and it has been successfully reduced at high pH (pH>11) (Vellanki and Batchelor, 2013).

2.2. Advanced Reduction Process (ARP)

This research focused on employing Advanced Reduction Processes (ARP) to remove chlorate from water. ARP combines reducing agents with an activating method to produce highly reactive reductant radicals which can destroy oxidized contaminants such as chlorate. Free radicals are defined as any species that contain an unpaired electron. These free radicals have strong tendency to either donate their unpaired electron or accept an electron from another pair hence becoming either effective reductants (donating electrons) or oxidants (accepting electrons). The advantage of producing free radicals is that they are highly reactive, thus making the kinetics of the desired reactions viable when

9

the kinetics might be very slow with the common reductants. ARP can employ a variety of activating agents to produce the free radicals from the reducing agents. Some of the activating methods that can be used to produce free radicals from the reducing agents are ultraviolet light (UV), microwave, ultrasound and electron beam (Vellanki et al., 2013). Reducing agents proposed for ARP are dithionite, sulfite, sulfide and ferrous iron (Vellanki et al., 2013).

Previous researches have demonstrated that the theory of ARP is valid and that the combinations of dithionite, sulfite or ferrous iron with ultraviolet light (UV) have a high potential for being developed into commercial water treatment processes for destroying persistent oxidized contaminants and converting them to environmentally benign forms. ARPs have been successfully evaluated for destroying halogenated organic compounds (PFOA, vinyl chloride, 1,2- dichloroethane) (Liu et al., 2014a, Liu et al., 2013a, b, Liu et al., 2014b, Yoon et al., 2013), and oxidized inorganic anions (perchlorate, nitrate, and bromate) (Bensalah et al., 2013, Bensalah et al., 2014, Jung et al., 2013, Jung et al., 2014, Vellanki and Batchelor, 2013).

The objective of this study is to evaluate: (i) effectiveness of ARP to reduce chlorate, (ii) effects of the system variables (pH, initial chlorate concentration and reducing reagent dose) on degradation kinetics, (iii) chlorate degradation by- products, and (iv) mechanism of the photochemical degradation of chlorate. Different reducing agents have been reported to behave differently when the solution pH have been varied. The different reducing chemicals previously studied for ARP are listed in the following section.

10

2.2.1. Reducing agents used in ARP

Effective reducing agents for ARP can be different dependent on the conditions such as wavelength of irradiation, as different reducing agents absorb light at different wavelengths, and pH of the solution. Chemicals including dithionite, sulfite, sulfide, and ferrous iron were effective to produce reducing radicals like sulfur dioxide radical, sulfite radical, hydrated electrons, and hydrogen radical when activated (Liu et al., 2014a, Vellanki and Batchelor, 2013, Vellanki et al., 2013, Yoon et al., 2013).

Sulfite

The combination of UV/ sulfite has been employed previously for reduction of oxidized compounds using ARP. ARP that combines sulfite and low pressure UV-irradiation (UV-L) was able to destroy vinyl chloride where the largest rate constant was observed at pH 9 but complete dechlorination was not observed at this pH (Liu et al., 2013a, b). 1, 2- dichloroethane (1, 2- DCA) was also successfully reduced by the same combination (Liu et al., 2014a) and more than 90% of 1, 2- DCA was degraded in 20 minutes at alkaline conditions. UV-M and UV-B also removed 1, 2- DCA but with slower rate at acidic conditions (Yoon et al., 2013). Increase in sulfite dose increased the reduction of nitrate up to a certain extent after which further addition of sulfite did not affect nitrate reduction. The degradation rate also increased with increased pH and temperature (Vellanki et al., 2013). Bromate was reduced to bromide through direct photolysis using medium pressure UV- irradiation (UV-M) alone (Bensalah et al., 2013) and perchlorate

(ClO$_4^-$) has been found to be degraded completely by the combination of sulfite/ UV-L at alkaline pH (Vellanki and Batchelor, 2013).

Sulfite ion when irradiated in aqueous solutions, it produces sulfite radical anions and hydrated electrons as shown in Eqn. (2.6) (Dogliotti and Hayon, 1968, Liu et al., 2013b, Vellanki et al., 2013). The hydrated electron is a strong reducing agent with a reduction potential of -2.9 V and is widely used for degradation of many organic compounds (Buxton et al., 1988). Sulfite radicals also are effective reducing agents although they can recombine to form sulfite and sulfate.

$$SO_3^{2-} \xrightarrow{h\nu} SO_3^{\bullet-} + e_{aq}^- \qquad (2.5)$$

$$SO_3^{\bullet-} + SO_3^{\bullet-} + H_2O \rightarrow SO_4^{2-} + SO_3^{2-} + 2H^+ \qquad (2.6)$$
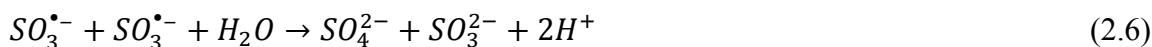
Eqn. 2.5 assumes that SO$_3^{2-}$ is the dominant sulfite species present in solution. However, depending on the solution pH, the dominant sulfite species could be sulfurous acid (H$_2$SO$_3$), bisulfite (HSO^{3-}) and sulfite (SO$_3^{2-}$) (Liu et al., 2014a, Vellanki et al., 2013). Aqueous solutions of sodium sulfite showed different absorption peaks at different pH (Getman, 1925, Vellanki and Batchelor, 2013) and different initial sulfite concentrations (Getman, 1925). At lower pH, the presence of sulfite species will not be of importance. Bisulfite (HSO$_3^-$), sulfurous acid (H$_2$SO$_3$), and metabisulfite (S$_2$O$_5^{2-}$) become more pronounced in acidic conditions (Horvath and Nagypal, 2006, Liu et al., 2014a, Yoon et al., 2013). Hence the reducing reactive species at very low pH conditions is not likely to be SO$_3^{2-}$ or e$_{aq}^-$ but could be HSO$_3^-$ or S$_2$O$_5^{2-}$. Bisulfite has already been reported to reduce chlorate to chloride under very low pH conditions in the absence of activating methods (Gleason et al., 1957, Nixon and Krauskopf, 1932, Szirovicza, 2009). Bisulfite undergoes

an ionic equilibrium with sulfurous acid when the pH is maintained constant (Eqn. 2.7) (Gleason et al., 1957), and sulfurous acid has also been reported to be very reactive with chlorate reducing it to chloride (Gleason et al., 1957, Szirovicza, 2009) without any activating methods. Sulfate has been the formed product of the reduction reaction.

$$H^+ + HSO_3^- \rightleftharpoons H_2SO_3 \tag{2.7}$$

Furthermore, bisulfite was not observed to produce any transients during photolysis at room temperature (Dogliotti and Hayon, 1968, Liu et al., 2014a). Bisulfite is known to have a thermodynamic equilibrium with metabisulfite ion, which could also be irradiated to form sulfite and sulfur dioxide radical, (Hayon et al., 1972) as shown in Eqn. (2.8):

$$2HSO_3^- \rightarrow S_2O_5^{2-} + H_2O \tag{2.8}$$

Dithionite

Sodium dithionite ($Na_2S_2O_4$) is a very powerful reducing agent because of its fast reaction rate, moderate cost and relatively low toxicity (Geoffroy and Demopoulos, 2009). It is being widely used in several industrial applications as a bleaching agent in the textile and paper industry, dyeing of cellulose fibers, biochemical and biological reductant, reducing agent in laboratory; and in the manufacture of various chemicals (de Carvalho and Schwedt, 2005, Dunitz, 1956, Lambeth and Palmer, 1973). Dithionite is known to have a long, weak S-S bond that can be broken to produce two sulfur dioxide radical anions ($SO_2^{\bullet-}$) (Amonette et al., 1994, Dunitz, 1956, Holman and Bennett, 1994, Lambeth and Palmer, 1973, Rinker, 1959, Rinker et al., 1964, Rinker et al., 1965). Hence the ion reversibly dissociates to form two highly reducing radicals. Mechanism of decomposition

of dithionite has been a subject of interest since the 1950's and has been vastly reported. Reduction reactions involving dithionite primarily undergo disproportionation reactions where the dithionate dissociates to yield two $SO_2^{\bullet-}$ radicals which undergo disproportionation reactions with the oxidized species to yield reduced products like sulfite (SO_3^{2-}), bisulfite (HSO_3^-) or thiosulfate ($S_2O_3^{2-}$) ions (Amonette et al., 1994, Holman and Bennett, 1994). This mechanism accelerates as the pH decreases. The formation of bisulfite and thiosulfate has also been reported by several researchers (Burlamacchi et al., 1968, Cermak and Smutek, 1975, de Carvalho and Schwedt, 2001, Greenwood and Earnshaw, 1984, Holman and Bennett, 1994, Lindholm, 1999, Rinker, 1959, Spencer, 1967) and is being depicted the following equation. Eqn. (2.9):

$$2\, S_2O_4^{2-} + H_2O \rightarrow 2\, HSO_3^- + S_2O_3^{2-} \tag{2.9}$$

The equilibrium established between bisulfite (HSO_3^-) and dithionite was further emphasized by Mayhew (Mayhew, 1978), who proposed that dithionite undergoes anaerobic oxidation to bisulfite as shown in Eqn. (2.10):

$$S_2O_4^{2-} + 2H_2O \rightleftharpoons 2HSO_3^- + 2H^+ + 2e^- \tag{2.10}$$

Holman and Bennett, (1994) were able to identify the presence of seven IR- active ions when they studied the decomposition of dithionite using attenuated total reflectance (ATR)-FTIR spectra. These ions were $S_2O_4^{2-}$ (dithionite), $S_2O_3^{2-}$ (thiosulfate), HSO_3^- (bisulfite), $S_3O_6^{2-}$ (trithionate), $S_2O_5^{2-}$ (metabisulfite), SO_3^{2-} (sulfite) and SO_4^{2-} (sulfate) at acidic pH. Literature suggests that pH plays a vital role in the mechanism of decomposition of dithionite. Cermak and Smutek, (1975) have studied the mechanism of decomposition of dithionite extensively and have found that its decomposition is greatly affected by the

acidity of the solution. At extremely acidic conditions, dithionite decomposes to form sulfur dioxide and sulfur as shown in Eqn. (2.11):

$$2H_2S_2O_4 \rightarrow 3SO_2 + S + H_2O \qquad\qquad (2.11)$$

They have suggested that thiosulfate, polythionates or hydrogen sulfide are the primary decomposition by-products that are produced from dithionite in the absence of oxidizing agents at different pH values. They have also showed that hydrogen sulfide formation is a very integral part of explaining the decomposition of dithionite (Cermak and Smutek, 1975). Although dithionite solutions are reported to absorb UV light with a maximum near 315 nm (McKenna et al., 1991), it was observed that there exists an equilibrium between the sulfoxyl radicals and the dithionite and hence the species giving rise to absorption band at 315 nm need not necessarily be dithionite as was believed (Amonette et al., 1994). The presence of sulfoxyl ions was also emphasized by Lambeth and Palmer, (1973) when they reduced proteins using dithionite and also by a few other researchers (Lynn et al., 1964, Rinker, 1959, Rinker et al., 1965). In both the cases, the pH was as high as 8.5. Dithionite has been employed previously in ARP studies and it was reported that 1, 2- DCA was reduced at faster rates in basic condition and at slower rates in acidic conditions. Regardless of the UV- irradiation source, the reduction of 1, 2- DCA in alkaline conditions was fast and complete (Liu et al., 2014a, Yoon et al., 2013). While the degradation at alkaline pH by dithionite was due to the formation of the sulfur dioxide radicals, the degradation at low pH was due to the formation of intermediate products from dithionite decomposition and not due to $SO_2^{\bullet-}$ (Yoon et al., 2013). Better removal of vinyl chloride by dithionite/ UV-L was observed at alkaline pH which led to the conclusion that

dithionite absorbed more light at high pH (Liu et al., 2013b). Dithionite/ UV-L and dithionite/ UV-B showed low removal efficiency of perchlorate, dichlorophenol (DCP), and perfluorooctanoic acid (PFOA) but dithionite/ UV-L showed higher removal of nitrate (Vellanki et al., 2013). Higher removal of nitrate was observed at alkaline and neutral pH but the reduction was negligible at low pH. Also, dithionite/UV-M showed higher efficiency to degrade nitrate than UV-L or UV-B (Bensalah et al., 2014).

Sulfide

Sulfide solutions undergo hydrolysis to produce bisulfide ions (HS^-) (Linkous et al., 2004) which can be irradiated by UV- irradiation to produce reactive bisulfide radicals ($HS^{\bullet-}$) (Eqn. 2.12). It has also been observed that aqueous solution of sodium sulfide absorbs UV light with wavelength at 230 nm (Dzhabiev and Tarasov, 1993, Linkous et al., 2004, Vellanki et al., 2013). It has been reported that photolysis of hydrogen sulfide produces bisulfide radicals and hydrogen atoms ($H^{\bullet}$) (Eqn. 2.13) (Khriachtchev and Pettersson, 1998, Mottley and Mason, 1988)

$$HS^- + h\nu \rightarrow HS^{\bullet-} \tag{2.12}$$

$$H_2S + h\nu \rightarrow HS + H^{\bullet} \tag{2.13}$$

Dzhabiev and Tarasov, (1993) have reported that the primary process of the photolysis of sulfide solution is a homolytic cleavage of the H-S bond resulting in H atom and $S^{\bullet-}$ anion radical formation. The above process can be explained by the following set of equations (2.14- 2.18):

$$HS^{\bullet-} \xrightarrow{h\nu} H + S^{\bullet-} \tag{2.14}$$

$$H + HS^- \rightarrow H_2 + S^{\bullet-} \tag{2.15}$$

16

$$H + H \rightarrow H_2 \tag{2.16}$$

$$H + S^{\bullet -} \rightarrow HS^- \tag{2.17}$$

$$S^{\bullet -} + S^{\bullet -} \rightarrow S_2^{2-} \tag{2.18}$$

In the context of ARP, Vellanki et al., (2013) observed that the combination of sulfide/ UV-L was very effective in removing nitrate and dichlorophenol (DCP). For both compounds, a removal percentage above 70% was reported. Yoon et al., observed that 1, 2- DCA was completely removed at high pH (pH 10.6) by sulfide/ UV-M and was attributed to the formation of free radicals by photochemistry (Yoon et al., 2013). Liu et al., (2014a) found that the highest rate of degradation of vinyl chloride was achieved at pH 7 by sulfide/ UV ARP. They also reported that the combination of both H_2S and HS^- would be active at this pH thus effecting the removal of vinyl chloride.

Ferrous iron

Ferrous iron absorbs light at a maximum of 220 nm and the UV- irradiation promotes the formation of hydrogen (Vellanki et al., 2013). Both Vellanki et al., (2013) and Liu et al., (2014a) have reported the formation of hydrated electrons when the solution of ferrous iron is irradiated with UV- light and it could be possible that the hydrated electrons would react with the hydrogen ions to form the reductive hydrogen atoms. The formation of aqueous electrons is given by the following equation (2.19):

$$Fe^{2+} + h\nu \rightarrow Fe^{3+} + e_{aq}^- \tag{2.19}$$

Liu et al., (2014a) explained that the mechanism of photolysis of the ferrous iron could be the result of two photolysis reactions, one of Fe^{2+} and the other by $Fe(OH)^+$. The production of hydrogen during photolysis is due to the absorption of lower wavelengths

by Fe^{2+} at low pH and the other due to the absorption of higher wavelengths by $Fe(OH)^+$ at high pH.

2.2.2. Ultraviolet light (UV) as activating agent

Ultraviolet light has been widely used in the advanced oxidation processes (AOP) for destruction of pollutants in water where they are used either in combination with the traditional methods of disinfection or as a stand-alone solution (Schalk et al., 2005). Hence UV is one of the most promising activation methods that can be used in ARP. UV region can be divided into UV-A, UV-B, and UV-C based on the wavelength of the light emitted (Lumen Dynamics, 2013). UV-A has a wavelength range of 315-400nm and is used in low energy UV polymerization reactions in the bonding and curing of various materials and also for non- destructive fluorescent methods. UV-B has a wavelength range of 280-315 nm and is used along with UV-A for polymerization reactions. UV-C has a wavelength region of 100- 280 nm and is the shortest and the most energetic of the wavelengths used in UV curing (Lumen Dynamics, 2013). It is widely used in the sterilization and germicidal processes and applications. UV radiation at 254 nm (UV-L) is well suited for disinfection process and it is currently being used in water and waste water treatment plants (Vellanki et al., 2013). Medium pressure lamps have a significantly higher electrical power input compared to low pressure mercury lamps (Emperor Aquatics, 1990). The disadvantage of medium pressure lamps is that they have a lower UV-C efficiency in the range of 5-15% and a shorter life time than UV-L (Schalk et al., 2005). Medium pressure lamps have a full spectrum output in the wavelength range of

18

185- 480 nm (Lenntech, 1998) and they have been used in some degradation and disinfection processes. Another type of UV- irradiation lamps are the UV-B lamps that emit light ranging from 290- 320nm. This spectrum is called the biological spectrum due to the human body's sensitivity to light of this region (International Agency for Research on Cancer, 2006). UV-B is composed of two kinds of lamps, narrowband ultraviolet (UV-N) that eliminates superfluous and harmful UV by emitting light at wavelengths of 311-313nm with a major peak wavelength at 312nm, and broadband ultraviolet (UV-B) that emits radiation from 290-320nm with a major peak at 306 nm. Although, UV-B lamps emit light at a broader wavelength, they can be dangerous as they emit light below 300nm. This spectrum can cause skin cancer. UV-N lamps do not emit light at this dangerous spectrum and limit the chances of burning the skin because of their narrow wavelength range. Hence, they have been used as an effective phototherapy option for skin treatment treating psoriasis, dermatitis, vitiligo, and pruritic disorders (Daavlin, 1999, van et al., 1988). Light emitted by UV-B lamp is effectively absorbed by reagents such as dithionite than lights emitted by UV-L and UV-M lamps (Vellanki et al., 2013, Yoon et al., 2013). UV-L, so far, has been reported to be the most effective activation method in ARP and it has been successful in the reduction of vinyl chloride (Liu et al., 2013a, b), 1, 2- DCA (Liu et al., 2014a, Yoon et al., 2013), perfluorooctanoic acid (Song et al., 2013, Vellanki et al., 2013), nitrate (Bensalah et al., 2014, Vellanki et al., 2013), dichlorophenol (DCP) (Vellanki et al., 2013). UV-B and UV-M were also investigated for the degradation of 1, 2- DCA and it was found that UV-M combined with sulfite, sulfide, or dithionite was very effective in the degradation of 1, 2- DCA but the efficiency of UV-B was slower and

was largely dependent on solution pH (Yoon et al., 2013). UV-B, alone or combined with sulfite, sulfide, and ferrous iron was effective in the degradation of DCP (Vellanki et al., 2013). UV-M was effective in degrading bromate even in the absence of any reducing agent (Bensalah et al., 2013) and it was very effective in reducing nitrate with the combination of dithionite (Bensalah et al., 2014).

2.3.   Research objectives

The objective of this research is to investigate the effectiveness of ARP to reduce chlorate to chloride in water using a combination of a reducing agent and UV light as an activating method. Three main tasks were performed to achieve the goal of this research. The first task was to develop the experimental and the analytical methods for laboratory experiments. The second task was to characterize the kinetics and equilibrium characteristics of chlorate reduction with ARP. This includes screening of different combinations of reducing agents and the UV light types in order to identify the optimum combination, which achieves efficient reduction of chlorate. Also, this task involves investigating the effects of operating conditions such as doses of reducing agents, solution pH, initial chlorate concentration and light intensity. The final task was to identify the degradation products and characterize the reaction mechanisms.

First, screening tests were conducted to evaluate the effectiveness of different combinations of activating methods and reducing agents on chlorate reduction. Experiments were conducted with combinations of five different reducing agents (dithionite, sulfite, sulfide, ferrous iron, and the combination of sulfite and ferrous iron)

and three different UV- light sources (UV-L, UV-M, and UV-B). In all these cases, the concentration of the reducing agent was hundred times the stoichiometric initial molar chlorate concentration. The combination of the reducing agent and the activating method that shows the maximum chlorate removal was used for further studies.

After the combination of reducing agent and activating method that achieves maximum chlorate removal was identified, the effects dose of reducing agent, initial chlorate concentration, pH, and light intensity on the kinetics and efficiency of chlorate reduction was evaluated. Reducing agent doses of 10, 50, 100, and 150 times the stoichiometric molar concentration of chlorate were evaluated.

The research plan is summarized in Table 1.

Table 1: Summary of the research plan

Task	Methodology	Expected benefits
Task 1: Develop experimental and analytical procedures	- Develop batch experimental procedure - Use Ion chromatography to analyze chlorate, chloride and chlorite - Perform standard calibration for chlorate, and measure method detection limit, accuracy, and precision	Ensure that the experimental procedures are reliable and the analytical methods are proven to be reproducible
Task 2: Characterize kinetics of chlorate reduction with ARP	Batch kinetic experiments with varying solution pH, reducing agent doses, chlorate initial concentration, and UV light intensity for UV-L, UV-M, and UV-B	Identify the best possible combinations of the reducing agents and the activation methods to reduce the target compound and hence validate the potential of ARP

Table 1: Continued

Task	Methodology	Expected benefits
Task 3: Characterize the reaction mechanism	• Identify the degradation products	• Check the effectiveness of ARP in producing non-hazardous products and elucidate the mechanism of chlorate reduction

3. MATERIALS AND METHODS

3.1. Materials

Sodium chlorate (NaClO$_3$, Fischer Scientific, Analytical reagent grade, conforms to EP and ACS, >80%) was used as a target component source. Sodium chlorite (NaClO$_2$, Fischer Scientific, Analytical reagent grade, conforms to EP and ACS, >80%), and sodium chloride (NaCl, Fischer Scientific, Analytical reagent grade, conforms to EP and ACS, >80%) were used for standard solutions of chlorite and chloride, respectively. Sodium sulfite (Na$_2$SO$_3$, Fischer Scientific, and anhydrous, Analytical reagent grade), Sodium dithionite (Na$_2$S$_2$O$_4$, Sigma Aldrich, ≥82%) Sodium sulfide (Na$_2$S, Fischer Scientific, and anhydrous, Analytical reagent grade), Sodium thiosulfate (Na$_2$S$_2$O$_3$, Fischer Scientific, anhydrous, Analytical reagent grade), Sodium metabisulfite (Na$_2$S$_2$O$_5$, Fischer Scientific, anhydrous, Analytical reagent grade) and Sodium bisulfite (NaHSO$_3$, Acros Organics, and containing small amounts of Na$_2$S$_2$O$_5$) were used as the source of reducing agents. Phosphate buffer of pH 7 was prepared by mixing 61 mL of 0.1 M monobasic sodium phosphate (NaH$_2$PO$_4$, Sigma Aldrich, ACS reagent 98-102%) and 39 mL of 0.1 M dibasic sodium phosphate (Na$_2$HPO$_4$, Mallinckrodt Chemicals, USP-GenAR). Solutions of 0.1M Sodium hydroxide (NaOH, Sigma Aldrich) or 0.1 M phosphoric acid (H$_3$PO$_4$, Sigma Aldrich) were used to adjust pH to the desired initial pH values.

The laboratory experiments were performed in an anaerobic chamber (Coy Laboratory Products Inc., Grass Lake, MI, USA). The chamber is filled with a gas mixture containing 99.995% nitrogen and remaining hydrogen. It contains detectors for measuring

24

Oxygen and Hydrogen concentrations, fan boxes and palladium catalyst STAK-PAK (Coy Laboratory Products Inc., Grass Lake, MI, USA). All the solutions were prepared using deionized deoxygenated water (DDW) from Milli-Q and purged with nitrogen gas (99.99% purity) for 2 hours before use. Chemicals and the aqueous solutions were deoxygenated in an air lock before moving to the anaerobic chamber.

3.2.   Experimental procedures

3.2.1. Preparation of stock solution and samples

Chlorate stock solution of 1000 ppm was prepared by dissolving 0.319 g of sodium chlorate solid in 250 mL DDW. The 1000 mg/L chlorate stock solution was diluted with DDW to prepare standard solutions with initial chlorate concentrations of 2, 5, 10 and 20 mg/L. Standard solutions of chlorite and chloride were prepared using the same procedure.

Stock solutions of the reducing agents were prepared based on the stoichiometric molar initial chlorate solutions. The solution containing chlorate and the reducing agent was prepared in a 500 mL beaker for all the experiments. The beaker is initially filled with 250 mL of DDW. The required amount of chlorate stock solution is calculated and this amount of water is taken out. The initial stock solution of the reducing agents is prepared with concentration equal twice the required dose of the reducing agent. 250 mL of the reducing agent stock solution is added to the beaker containing water to obtain the required dose of the reducing agent. The desired volume of chlorate stock solution is then added to

achieve the required initial chlorate concentration in solution. pH of the mixture is then adjusted to the desired values. The mixture is stirred using a magnetic stirrer (VWR model hot plate stirrer) and then transferred to quartz cells which are then taken to UV chamber with the specified light intensity. At the desired sampling time, 3mL of the solution is taken in an IC vial for analysis.

Effect of pH was evaluated using pH values of 7, 9, 11, and with no pH control. First, 0.1 M phosphate buffer solution was prepared to control the solution pH value at pH 7. Then certain values of concentrated NaOH or HCl solutions were used to adjust pH at the desired values. The preparation of 0.1 M phosphate buffer solution is described in the following steps:

1. Preparation of 0.2 M monobasic sodium phosphate: 27.6 g of monobasic sodium phosphate is dissolved in 1 L of deionized water.

2. Preparation of 0.2 M dibasic sodium phosphate: 28.4 g of dibasic sodium phosphate is dissolved in 1 L of deionized water.

3. 39 mL of 0.2M monobasic sodium phosphate is mixed with 61 mL of dibasic sodium phosphate.

4. 100 mL of deionized water is added to the solution resulting in 0.1 M phosphate buffer solution with pH 7

5. NaOH or HCl will be added to adjust pH to the desired.

Batch experiments were performed by diluting the solution to 5 mM buffer solution.

Effect of initial chlorate concentration was evaluated using four different initial chlorate concentrations (2, 5, 10, and 20 mg/L). Additionally, the effect of UV light intensity was investigated. Light intensity of the UV- lamp was changed by increasing or decreasing the number of lamps installed in the reactor system. The range of light intensities was measured to be 2000- 5000 $\mu W/cm^2$ for UV-L, 1100- 1300 $\mu W/cm^2$ for UV-M and 110- 640 $\mu W/cm^2$ for UV-B.

The extent of degradation was characterized by measuring final concentrations of chlorate, chlorite, and chloride in the solution. Chlorite and chloride are the most probable by- products of chlorate reduction. However, other products such as hypochlorite or chlorine radicals can also be formed. Final concentrations of chlorite and chloride were determined using Ion Chromatograph (IC). Formation of other degradation products was determined using material balance. Hypotheses of reaction mechanisms and pathways were made and these hypotheses were tested and validated using experimental results and data reported by previous researchers.

3.2.2. Reactor systems

The reactor system consisted of 17-mL quartz cells (Starna 32/Q/10, Spectrosil ® Quartz) (Atascadero, CA, USA) with 10 mm path length and fitted with a PTFE stopper. Three different UV- lamps, broad band UV lamps (UV-B), low pressure UV lamps (UV-L), and the medium pressure UV lamps (UV-M) were used in this research. T-8 lamps (BioLink, Vilber Lourmat, USA) were used as a source of UV light to reduce chlorate.

Five T-8 lamps of 8W were located at the top of the UV chamber (BioLink, Vilber Lourmat, USA) which has dimensions of 14.5 cm (H) × 33 cm (D) × 26 cm (W). The UV lamps were warmed up for 10 min before the experiments began and the light intensity during experiments was measured using actinometers (ST- 513, General Tools, NY, USA) for UV-B, and UV-M and (ST- 512, General Tools, NY, USA) for UV-L. During the experiments, quartz cells containing the samples were placed at the bottom of the chamber, approximately 15 cm in vertical distance away from the lamps, so that the UV falls perpendicular to the cells. The three different T-8 lamp sources were (i) T-8M lamps, which was used as a source of broad band UV-B light emitting wavelengths from 280nm to 320nm with a major peak at 312nm (ii) T-8C lamps, were used as a source of low pressure lamps and they emit a monochromatic light at 254 nm (UV-254), and (iii) T-8L lamps were the source of medium pressure lamps emitting UV light primarily in the range 320 - 380 nm with a major peak at 365 nm. The details of the lamps are illustrated in Table 2.

Table 2: UV lamps and their specifications

Name	UV type	Lamp	Manufacturer	Wavelength
Low pressure lamp	UV-L	T-8C (8W)	Vilber Lourmat, France	Monochromatic at 254 nm
Medium pressure lamp	UV-M	T-8L (8W)	Vilber Lourmat, France	320 – 380 nm with peak irradiance at 365 nm
Broad band lamp	UV-B	T-8M (8W)	Vilber Lourmat, France	280 – 320 nm with peak irradiance at 312 nm

3.3. Analytical methods

Chlorate, chlorite and chloride concentrations were measured using Dionex ICS-2000 ion chromatograph (IC). The instrument contains an AS auto sampler, Ion Pac AG19 guard column (4x50 mm), Ion Pac AS19 separation column (4x250 mm), ASRS 300-4 mm suppressor, DS6 conductivity cell and an eluent generator (EGC). The mobile phase in the system is aqueous solution of Potassium Hydroxide, KOH (20 mM, prepared manually) and it flows at a constant flow rate of 1 mL/min. Standard solutions of chlorate, chlorite and chloride were prepared and used for the calibration curves. The equation generated from the calibration curves were used for the calculation of analyte concentrations. The range of concentrations used for calibration for all the three anions were 10, 50, 100, 500, 1000, 5000, and 10,000 µg/L.

Method detection limits of analyte quantification were obtained. The U.S. Environmental Protection Agency (USEPA) defines Method (Minimum) Detection Limit

as the minimum concentration of a substance that can be reported with 99- percent confidence that the analyte concentration is greater than zero (U.S. Environmental Protection Agency 1997). It is calculated by Eqn. (3.1) (United States Geological Survey, 2013).

$$MDL = s \times t_{(n-1, 1-\alpha=0.99)} \qquad (3.1)$$

Where, n: the number of replicate spike determinations at 1 to 5 times the estimated MDL,

s: standard deviation of measured concentrations of n spike determinations,

t: student's t value at n-1 degrees of freedom and 1-α (99 percent) confidence level.

At α= 0.01 and n=6, t= 3.365.

α: level of confidence.

Accuracy refers to the closeness of the measured value to a standard (known) value. It was obtained by calculating the percentage recovery for each of the prepared samples and taking the average. The percentage recovery is calculated by dividing the measured chlorate concentration by the desired concentration. Precision is referred to as the closeness of two or more measurements to each other and was calculated as the relative standard deviation.

$$Precision = Relative\ standard\ deviation = \frac{Standard\ deviation}{average} \times 100 \qquad (3.2)$$

The method detection limit (MDL) of chlorate using IC analysis was calculated to be 5.26 μg/L and precision ("standard deviation") and accuracy ("recovery") for six samples with known amounts (10 μg/L) were 1.56 and 104% respectively.

The pH of the solution was measured using pH-meter (Orion, Thermo Scientific, U.S.A). The pH meter probe (Orion 8107UWMMD, (ROSS Ultra pH/ ATC Triode, USA)) was calibrated before pH measurements using buffer solutions of pH 4 (Orion Application solution 910104, Thermo Scientific), pH 7 (Orion Application solution 910107, Thermo Scientific) and pH 10 (Orion Application solution 910110, Thermo Scientific). UV- Vis absorbance was measured by Perkin Elmer (Lambda 25) UV- Vis spectrophotometer or (Lambda 950) UV/ VIS/ NIR spectrometer using a quartz cell with 1cm optical path length.

4. RESULTS AND DISCUSSION

4.1. Screening experiments for chlorate removal

Screening tests were conducted to evaluate the effectiveness of the reducing agents and the activation methods for chlorate reduction. Five different reducing agents (sulfite, sulfide, dithionite, ferrous iron and the mixture of sulfite and ferrous iron) and three different UV-light sources (UV-L, UV-M, and UV-B) were combined and tested for chlorate removal. The solution pH was not buffered during these experiments. The initial pH of aqueous dithionite, sulfite, sulfide, ferrous iron and a mixture of ferrous iron and sulfite was pH 5.2, 7.1, 10.8, 4.1, and 6.9 at given conditions, respectively (Table 3). The applied irradiation time was 7 h. As shown in Figure 1, dithionite solutions were observed to be the most effective in reduction of chlorate. The chlorate reduction by dithionite solutions was generally high with all UV sources showing the chlorate removal percentage of 60.5% by UV-L, 47.2% by UV-M, and 78.4% by UV-B. It has been reported that dithionite decomposes into various products such as bisulfite (HSO_3^-), sulfite (SO_3^{2-}), sulfate (SO_4^{2-}), thiosulfate ($S_2O_3^{2-}$), metabisulfite ($S_2O_5^{2-}$), and trithionate ($S_3O_6^-$) and that decomposition is accelerated at lower pH (Holman and Bennett, 1994). Because of the potential for dithionite decomposition, concentrations of dithionite presented here should be considered as the concentrations in the solution as it was prepared, not necessarily the actual concentration of dithionite in solution at the start of the experiment. The distribution of species from dithionite decomposition will change with pH and the light absorption rate also will change with UV sources, so both of these factors should affect chlorate reduction

kinetics. This will be discussed further in the next section along with a discussion of dithionite chemistry. Sulfite/UV-L ARP and sulfite/UV-M ARP resulted in 26% and 18% chlorate removal, respectively. Sulfide, ferrous iron and the mixture of ferrous iron and sulfite showed less than 10% reduction of chlorate, regardless of UV light sources and hence, they were not considered for further investigation.

Table 3: Screening experimental conditions and chlorate removal percentages

| No. | Initial chlorate conc. (mM) | Reducing agent | Reducing agent conc. (mM) | Initial pH | UV irradiation | | Removal (%) |
					UV	Peak wavelength (nm)	
1	0.12	Sulfide	3	10.8*	UV-L	254	8.3
2	0.12	Sulfide	3	10.8*	UV-M	365	0
3	0.12	Sulfide	3	10.8*	UV-B	315	2.7
4	0.12	Fe^{2+}	3	4.1*	UV-L	254	5.6
5	0.12	Fe^{2+}	3	4.1*	UV-M	365	1.4
6	0.12	Fe^{2+}	3	4.1*	UV-B	315	0
7	0.12	Sulfite	3	7.1*	UV-L	254	26.1
8	0.12	Sulfite	3	7.1*	UV-M	365	18.4
9	0.12	Sulfite	3	7.1*	UV-B	315	2.9
10	0.12	Dithionite	3	5.2*	UV-L	254	60.5
11	0.12	Dithionite	3	5.2*	UV-M	365	47.2
12	0.12	Dithionite	3	5.2*	UV-B	315	78.4

Table 3: Continued

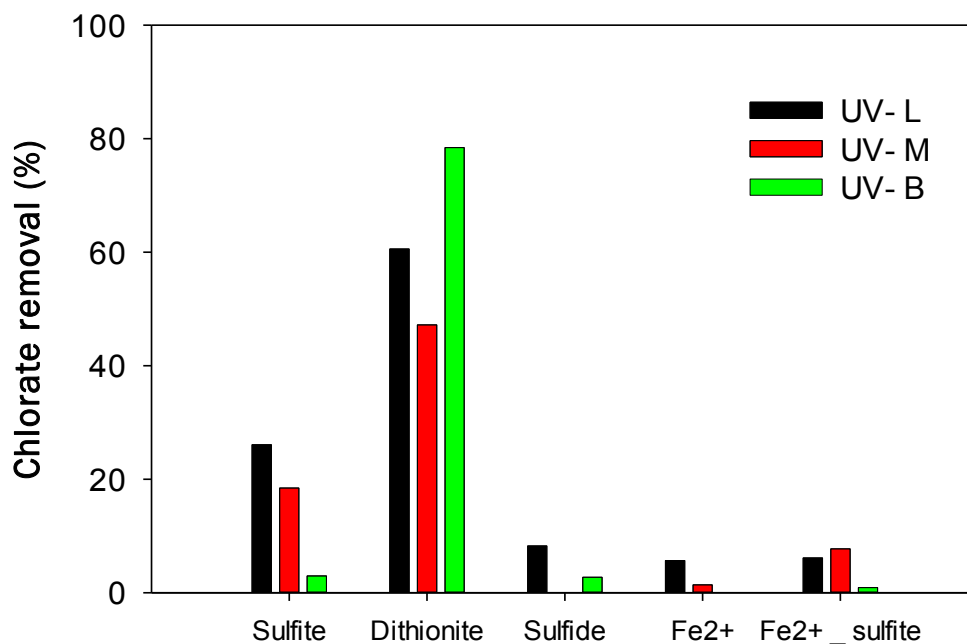| No. | Initial chlorate conc. (mM) | Reducing agent | Reducing agent conc. (mM) | Initial pH | UV irradiation | | Removal (%) |
					UV	Peak wavelength (nm)	
13	0.12	Fe^{2+} + sulfite	3	6.9*	UV-L	254	6.1
14	0.12	Fe^{2+} + sulfite	3	6.9*	UV-M	365	7.7
15	0.12	Fe^{2+} + sulfite	3	6.9*	UV-B	315	0.9

Figure 1: Chlorate removal by different reducing agents and UV light sources. Conditions: $[ClO_3^-]_0 = 0.12$ mM, concentration of reducing agents = 3 mM

34

4.2. Chlorate removal by dithionite/UV-B ARP

From screening test results, dithionite/UV-B ARP was chosen for a further study to investigate the effect of the process variables on chlorate reduction kinetics. The initial chlorate concentration was 0.12 mM in these experiments, unless otherwise specified. In addition to dithionite, its potential disassociation products were also evaluated as reducing agents individually. More detailed experimental conditions are shown in Table 4.

Table 4: Experimental conditions of chlorate reduction batch tests

Exp. No.	Chlorate (mM)	Reducing agent (mM)		UV-B	pH_0	pH_f
1	0.12		0	No	5.8*	N/A
2	0.12		0	Yes	5.8*	N/A
3	0.12	Dithionite	12	No	5.6*	4.0
4	0.06	Dithionite	6	Yes	5.6*	4.9
5	0.12	Dithionite	12	Yes	5.6*	5.0
6	0.12	Dithionite	12	Yes	3.5	3.5
7	0.12	Bisulfite	12	No	4.5*	3.6
8	0.12	Bisulfite	12	Yes	4.5*	N/A
9	0.12	Thiosulfate	12	Yes	4.2*	5.3
10	0.12	Bisulfite	12	No	6.9	7.0
11	0.12	Bisulfite	0.6	Yes	4.5*	N/A
12	0.24	Dithionite	24	Yes	4.6	4.3
13	0.24	Dithionite	12	Yes	4.1	3.8
14	0.024	Dithionite	1.2	Yes	3.8	3.6
15	0.12	Dithionite	6	Yes	4.4	3.8

Table 4: Continued

Exp. No.	Chlorate (mM)	Reducing agent (mM)		UV-B	pH$_0$	pH$_f$
16	0.12	Dithionite	1.2	Yes	4.2	4.0
17	0.12	Dithionite	18	Yes	4.3	3.8
18	0.12	Dithionite	12	Yes (360 µW/cm^2)	3.9	3.7
19	0.12	Dithionite	12	Yes (113 µW/cm^2)	3.9	3.9
20	0.12	Dithionite	12	Yes (660 µ W/cm^2)	4.5	2.8
21	0.12	Dithionite	12	Yes	4.7	N/A
22	0.12	Sulfite	12	Yes	4.0	3.8

*The pH was not buffered

4.3. Chlorate photolysis

Figure 2a shows the results of control tests prior to characterizing chlorate removal by ARP. Three control tests were conducted: one includes only chlorate (●), the second test includes chlorate and UV irradiation (■), and the third one includes chlorate and dithionite without UV irradiation (▲). The data points at zero time are for samples taken right after mixing all reagents, but before any irradiation. The dashed line represents the concentration of chlorate that would have been measured in the solution if no reaction occurred. In the absence of dithionite, direct photolysis of chlorate by UV-B did not result in appreciable removal of chlorate. However, in the presence of dithionite, chlorate was rapidly reduced to about 33% of its initial concentration and then no further removal was observed. Figure 2b shows concentrations of chloride formed as a result of chlorate

reduction. In the absence of dithionite, chloride formation was negligible, but in the presence of dithionite, 17% of initial chlorate concentration was converted to chloride.
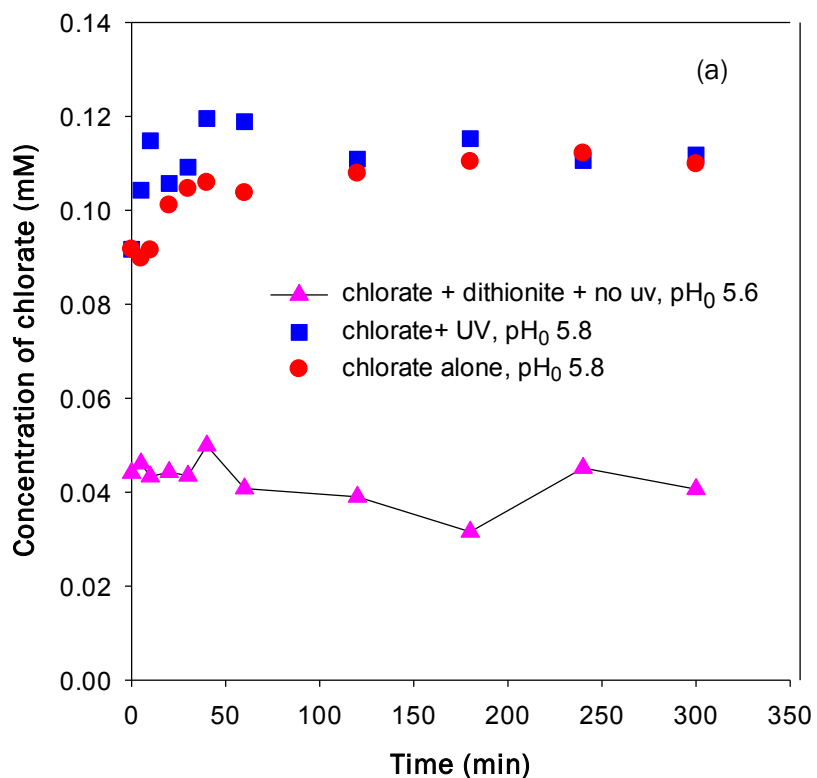

Figure 2: Chlorate concentrations (a) and chloride concentrations (b) in solutions of chlorate and a mixture of chlorate and dithionite with and without UV-B irradiation. Conditions: $[ClO_3^-] = 0.12$ mM, and the solution pH was not buffered. The above data belong to experiments 1, 2, and 3 in Table. 4
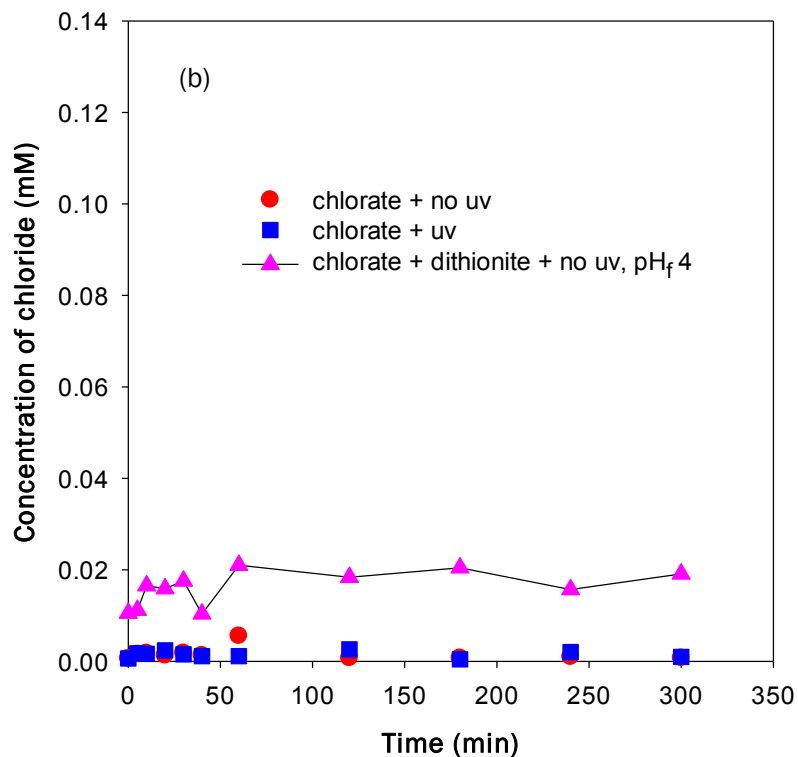
Figure 2: Continued

To better understand the extent of chlorate photolysis, the UV absorbance of chlorate at different concentrations was measured. Chlorate absorbance increased at low wavelengths below 230 nm, as shown in Figure 3. It has been reported that it is degraded by direct photolysis at 222 nm. The absorption spectra of chlorate showing no light absorption between 280 nm and 320 nm in Figure 3 supports the observation that chlorate was not reduced by UV-B irradiation as shown in Figure 2a.
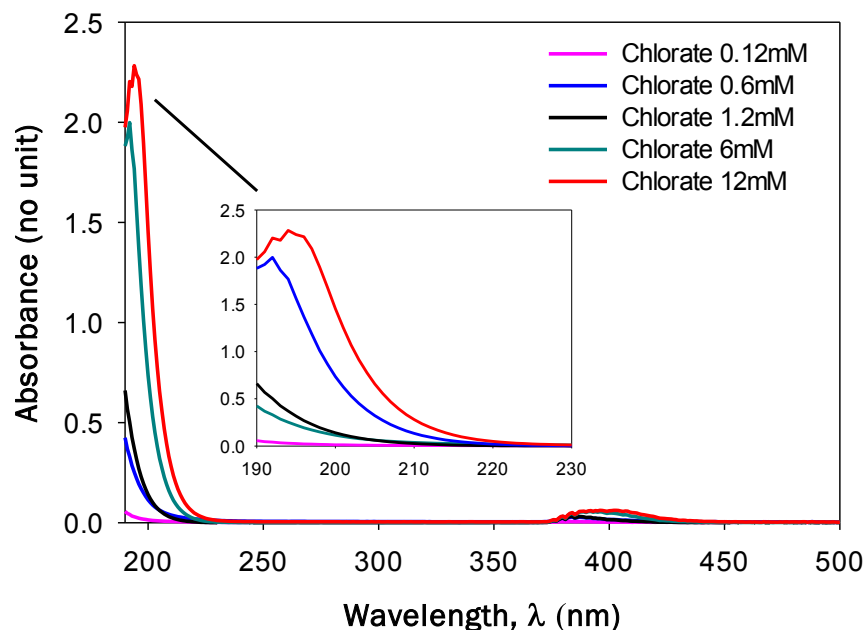
Figure 3: Absorption spectra of aqueous chlorate (ClO_3^-) at different concentrations

4.4. Effect of pH

Kinetics of chlorate reduction by the dithionite/UV-B ARP was studied at different pH values (Figure 4). The nominal initial pH values were measured before starting irradiation as pH 3.5, 4.7, and 5.6. The solution prepared at nominal pH 5.6 was not buffered. The solutions prepared at nominal pH 3.5, and 4.7 were buffered using 0.1M phosphoric acid (H_3PO_4). The final pH values are presented in Table 4. At pH 5.6, the final pH of the solution decreased to pH 5, whereas the final pH of the solution which was buffered at pH. 3.5, and pH 4.7 was not found to decrease. However, the presence of phosphate buffer at low pH did not affect the reduction of chlorate. In the presence of dithionite at all pH values, chlorate was reduced by about 80% at before irradiation. This

39

indicates that chlorate can be rapidly reduced by dithionite alone at acidic pH. Chlorate concentration was not reduced over time with UV irradiation in the experiment with nominal pH 5.6. At pH 3.5, chlorate concentration did decrease with irradiation time until its concentration becomes negligible at t = 150 min. At pH 4.7, chlorate concentration decreased over time, but more slowly than at pH 3.5. Chlorate was partially converted to chloride in all experiments, but more strongly at low pH (Figure 4b). At pH 3.5, 67% of the initial chlorate concentration was converted to chloride in 150 min. Figure 4 indicates that chlorate can be effectively converted to chloride by combining dithionite and UV-B irradiation at acidic conditions. In all experiments, no chlorite was detected by IC (Figure 5). Without UV- irradiation chlorate did not reduce to chloride immediately. Hence chlorate could have been reduced to other intermediates like hypochlorite ions (OCl^-). With UV irradiation, chloride formation was gradually increased and it was more discernable at lower pH. Also, incomplete chloride recovery can be explained by the formation of hypochlorous acid (HOCl), which is a volatile intermediate. Other possibility of lower chloride recovery could be explained by the formation of radicals (e.g. $ClO_3^{2-\bullet}$, or $SO_3ClO_3^{4-\bullet}$) which is discussed in the later sections. IC results shown in Figure 5 identify the presence of chloride from the reduction of chlorate.
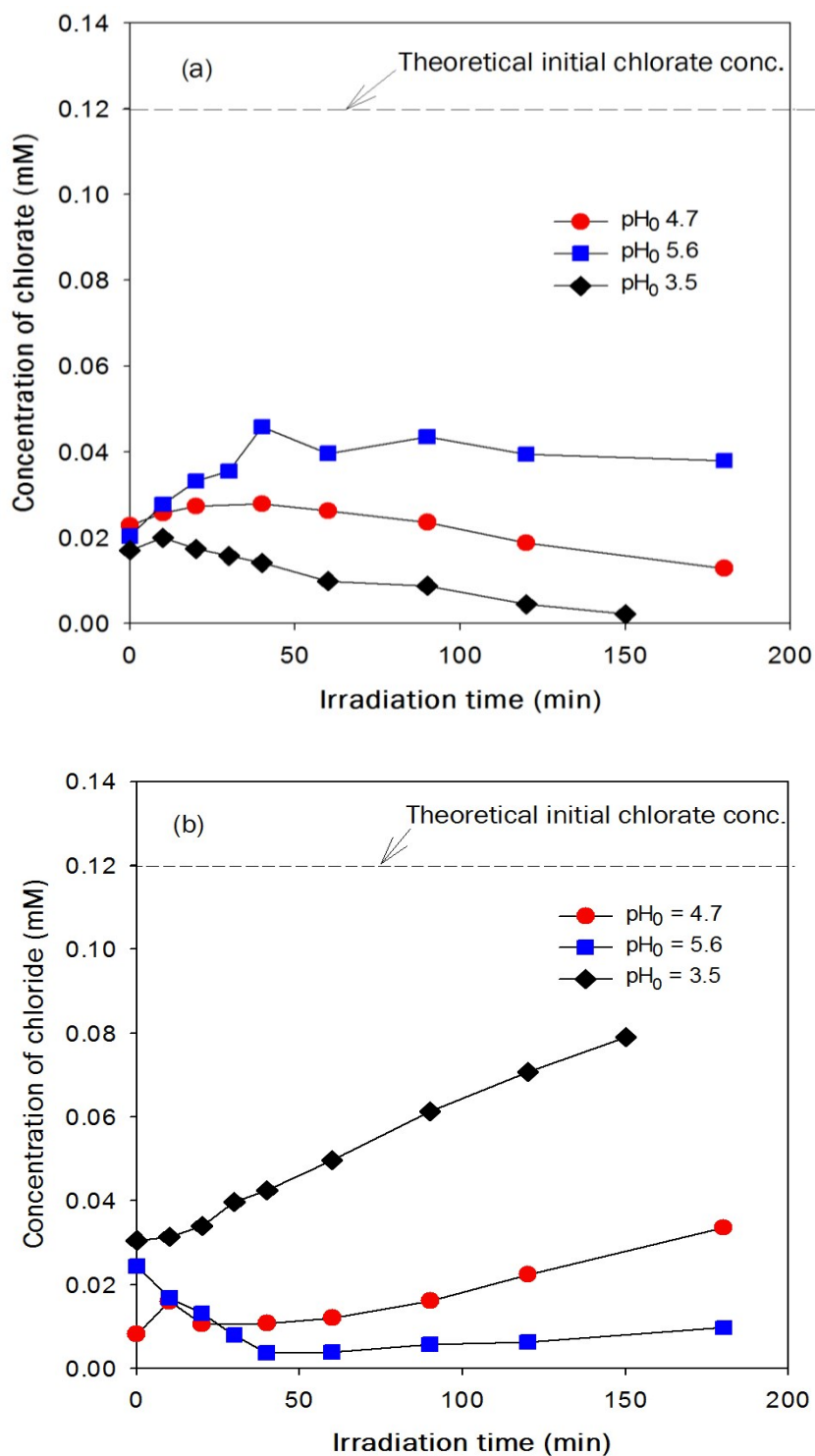
Figure 4: Effect of pH in the dithionite/UV-B ARP on (a) chlorate concentrations and (b) chloride concentrations. Conditions: $[ClO_3^-]$ = 0.12 mM, $[S_2O_4^{2-}]$ = 12 mM, and the solution pH was buffered by H_3PO_4. The data belong to experiments 5, 6, and 21

Dithionite undergoes various reduction reactions (Lindholm, 1999):

$$S_2O_4^{2-} + 2H_2O \rightarrow 2HSO_3^- + 2H^+ + 2e^- \tag{4.1}$$

$$S_2O_4^{2-} + 2H_2O \rightarrow S_2O_6^{2-} + 4H^+ + 4e^- \tag{4.2}$$

$$S_2O_4^{2-} + 4H_2O \rightarrow 2HSO_4^- + 6H^+ + 6e^- \tag{4.3}$$

The reactions (4.1- 4.3) produce electrons and bisulfite, dithionate, bisulfate, and protons, and are known as bleaching reactions in pulp and paper production (Lindholm, 1999).

It is known that a decrease of pH accelerates anaerobic decomposition reactions that produce thiosulfate and bisulfite (Equation 2.9) and that the reaction is rapid at pH less than 5.5 (Burlamacchi et al., 1968, Cermak and Smutek, 1975, de Carvalho and Schwedt, 2005, Holman and Bennett, 1994, Rinker, 1959).

$$2S_2O_4^{2-} + 2H_2O \rightarrow S_2O_3^{2-} + 2HSO_3^- \tag{2.9}$$

All sulfur containing species (dithionite, sulfite, sulfate, bisulfite, and metabisulfite) were found to have the same retention time near to 4.9 min (Figure 5) at the current IC conditions. Therefore, it was difficult to separate these dithionite decomposition products with simultaneous measurements of chlorate, chlorite and chloride at given IC condition.

The solution prepared using thiosulfate alone was measured by IC and its retention time was 6.7 minutes. When the solution including chlorate and dithionite at pH 3.5 (Experiment 6) was measured, the peak found at retention time= 6.7 minutes was identified as thiosulfate. Chlorate reduction showed major peaks at retention times 4.9 min

and 6.7 min along with the peak of chloride. It is expected that the peak at 4.9 min. is one

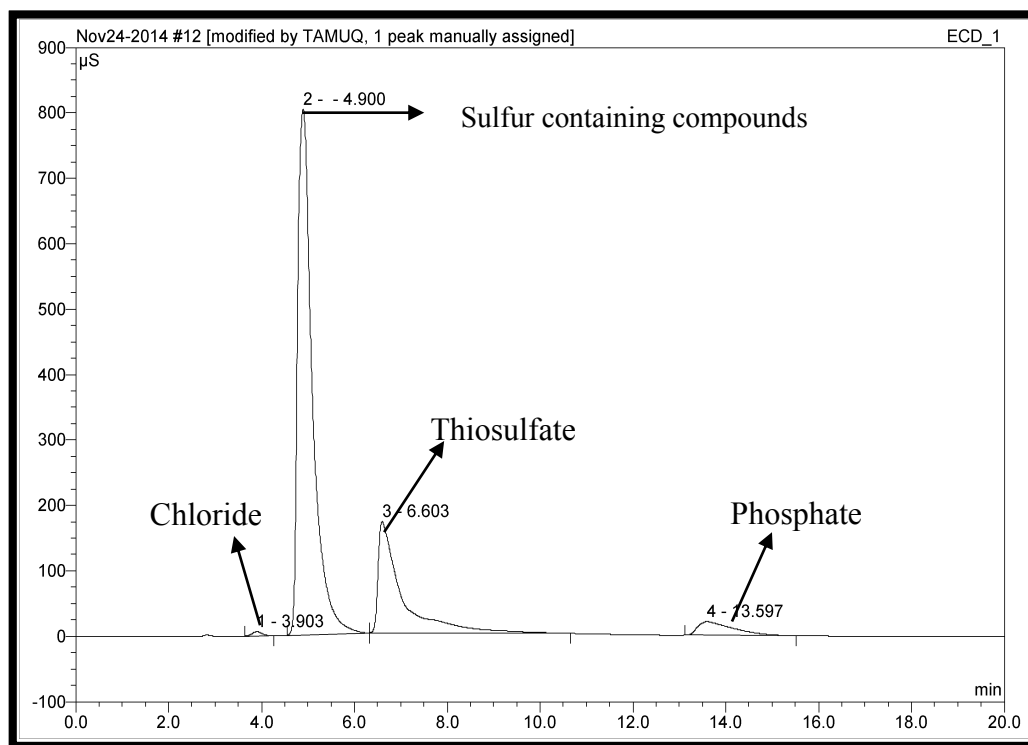of sulfur- containing species (bisulfite), whose formation is shown in Equation 2.9.

Figure 5: Major dithionite decomposition byproducts obtained from chlorate reduction by dithionite/ UV- ARP. Conditions: $[ClO_3^-]= 0.12mM$, $[S_2O_4^{2-}]= 12mM$, and the solution pH was buffered to pH 3.5 by H_3PO_4. This sample was analyzed after the final irradiation time of 150 minutes

Experiments were conducted to measure pH changes in solutions of chlorate, dithionite, and a mixture of chlorate and dithionite in the absence and presence of UV irradiation (Figure 6). The concentrations used in these experiments were the same as those shown in Figure 4. When chlorate is present alone with and without UV irradiation,

there was no significant pH changes during the reaction time of 5.0 hours. For solutions prepared with dithionite without chlorate or UV irradiation, the solution pH slowly decreased with time which indicates that disassociation of dithionite in water resulted in production of hydrogen ion (H^+). This is consistent with reactions (4.1 – 4.3). In solutions that have dithionite and chlorate without UV light irradiation, the decrease of pH was more significant than in the absence of chlorate. This confirms that chlorate reacts with dithionite disassociation products in the absence of UV light. The rapid decrease of pH could be caused by reactions of chlorate with dithionite products such as bisulfite or sulfurous acid resulting in formation of hydrogen ion according to the following reactions (Szirovicza, 2009),

$$ClO_3^- + HSO_3^- \rightarrow SO_4^{2-} + ClO_2^- + H^+ \qquad (4.4)$$

$$ClO_2^- + HSO_3^- \rightarrow SO_4^{2-} + HClO \qquad (4.5)$$

$$HClO + HSO_3^- \rightarrow SO_4^{2-} + Cl^- + 2H^+ \qquad (4.6)$$

In a mixture of chlorate and dithionite with UV irradiation, the behavior of pH was similar to that with dithionite alone. However, comparing pH values of experiments with and without UV-B showed that pH decreased more significantly than corresponding values without UV-B.
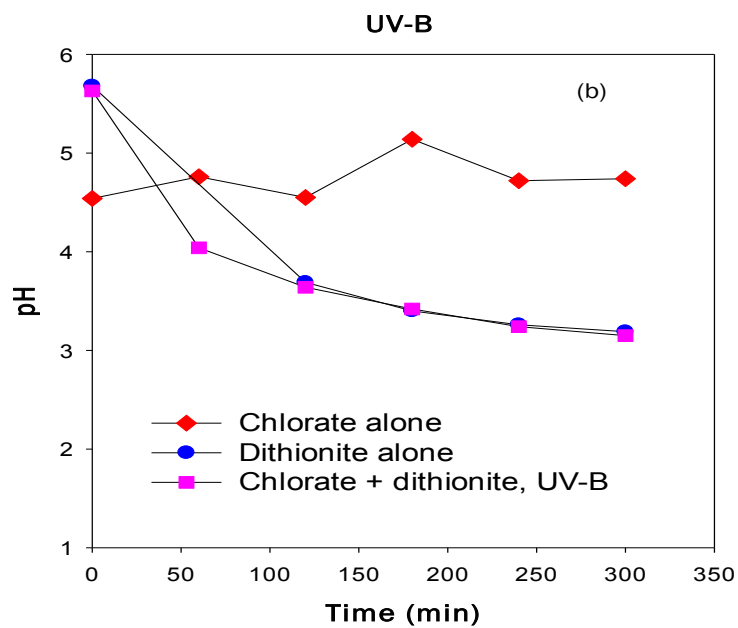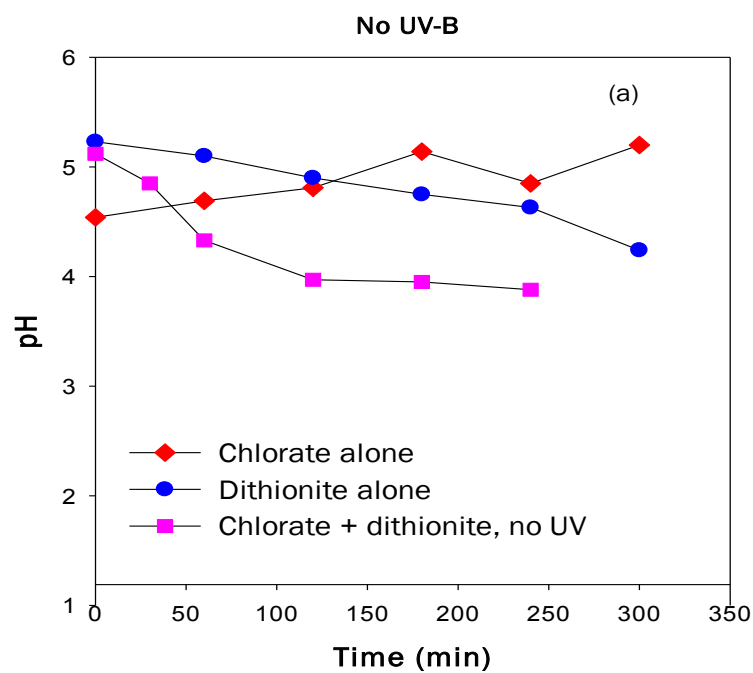
Figure 6: The pH changes in solutions of chlorate, dithionite, and a mixture of chlorate and dithionite (a) without and (b) with UV-B irradiation

Figure 4 shows that most of the reduction in chlorate by dithionite solutions occurred rapidly without UV. The initial rapid reduction was followed by a gradual decrease in chlorate concentration during UV irradiation that was affected by pH. The pH is important in dithionite/UV-B ARP because the pH influences dithionite decomposition and its products, which are converted to reactive radicals by UV irradiation. These potential photochemical agents that are responsible for chlorate reduction will be discussed in a later section.

4.5. Effect of dithionite dose

Figures 7a and 7b show the effect of initial dithionite concentration on chlorate reduction by dithionite/UV-B ARP and the formation of chloride ion. The extent of chlorate reduction and chloride production after reagent mixing but before irradiation (i.e. at t = 0) increased with increasing dithionite concentration. Chlorate removal efficiencies of 16%, 26%, 86%, and 100% were obtained at dithionite doses of 1.2, 6, 12, and 18 mM, respectively, before irradiation when initial chlorate concentration was 0.12 mM. The pH during these experiments was in the range of pH 3.5 - 4.5. Although significant chlorate removal efficiency was obtained at high dithionite doses, chloride formation before irradiation was not significant. This indicate that intermediate byproducts other than chloride were formed. Additional chlorate removal and chloride production was observed after UV-B irradiation. The percentages of chlorate removal of 100%, 98%, 58%, and 22%, and chloride formation of 100%, 66%, 44%, and 16% after irradiation time of 180 min were obtained at dithionite doses of 18 mM, 12 mM, 6 mM, and 1.2 mM, respectively

(Figure 7c). This additional removal is believed to be due to conversion of the dithionite decomposition products by UV-B into highly reactive species such as free radicals. Higher dithionite doses will produce more decomposition products such as bisulfite, and these compounds appear to accelerate chlorate reduction rates after being activated by UV-B light.
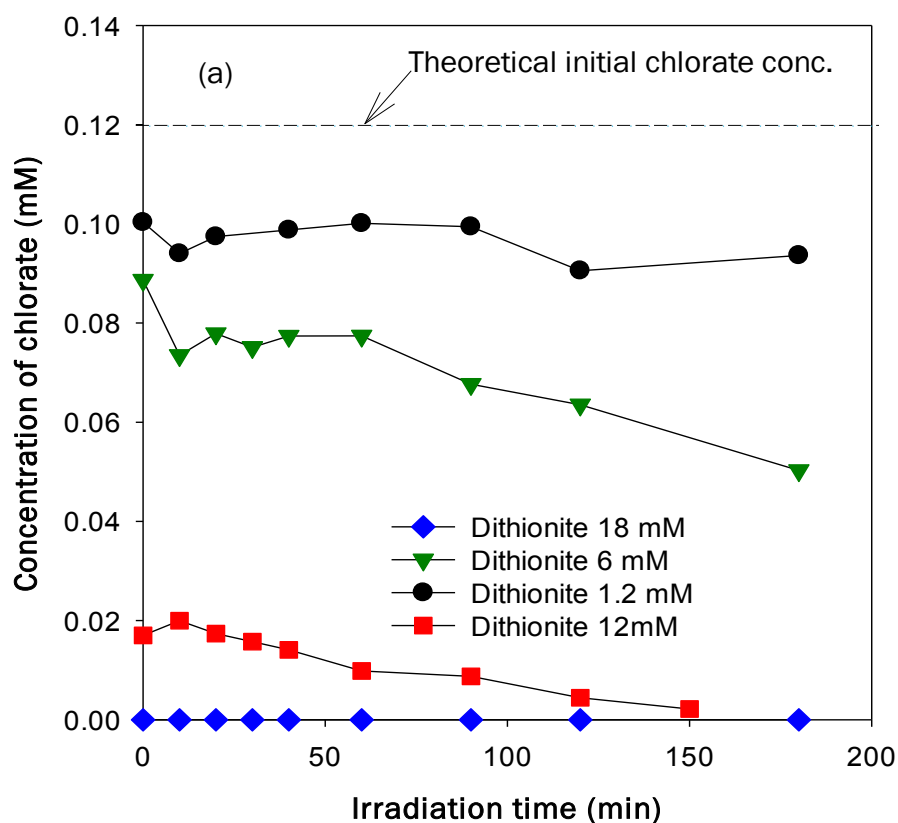

Figure 7: Effect of dithionite dose in the dithionite/UV-B ARP on (a) chlorate concentrations, (b) chloride concentrations, and (c) the percentage of chlorate removal or chloride formation with dithionite concentration. Condition: $[ClO_3^-]$ = 0.12 mM, light intensity = 570 $\mu W/cm^2$, and the solution pH was buffered at between pH 3.5 and pH 4.5. The data belong to experiments 6, and 15-17
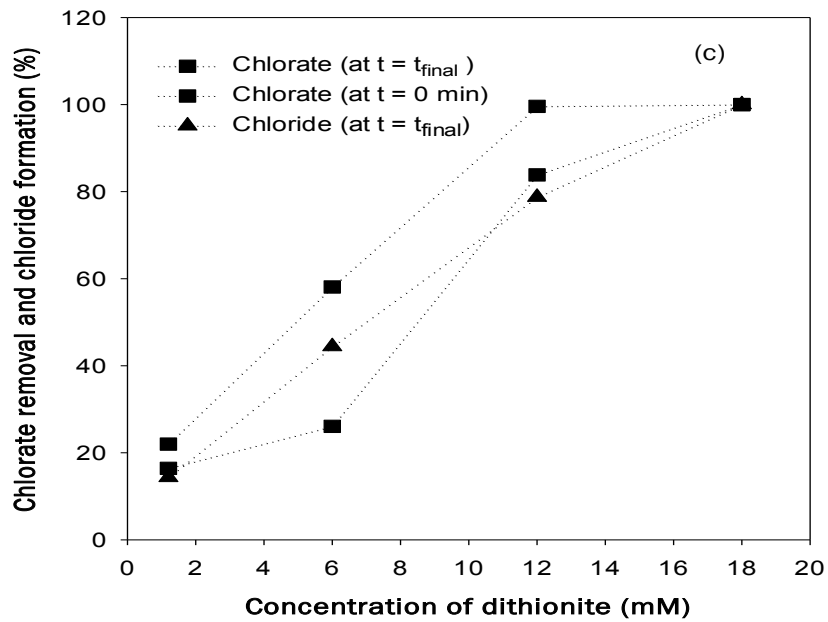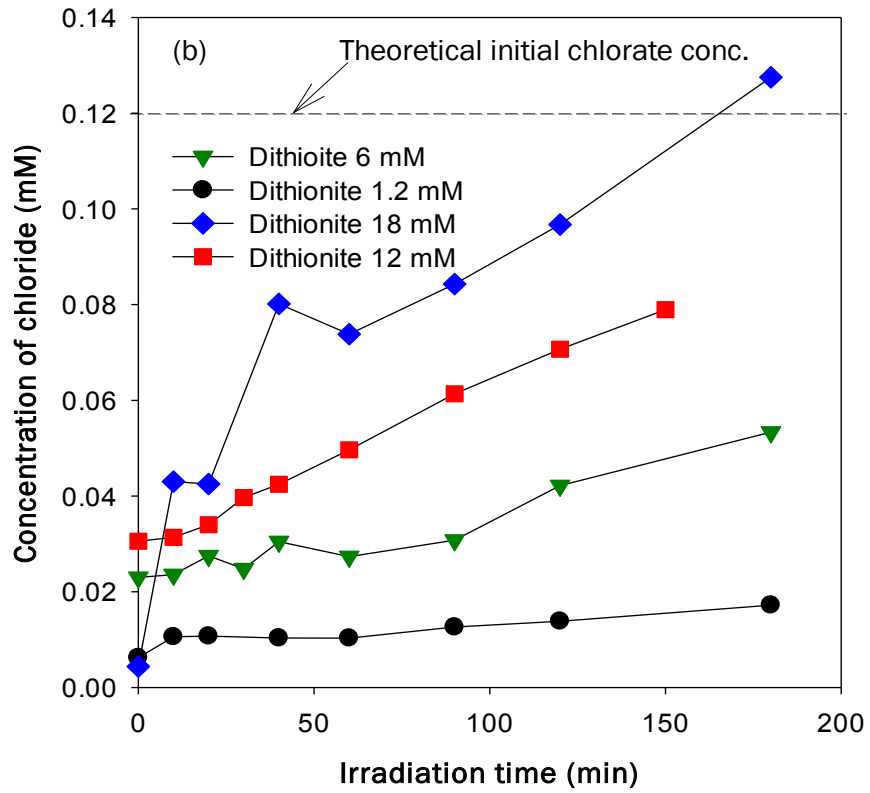
Figure 7: Continued

48

4.6. **Effect of initial chlorate concentration**

The effect of the initial chlorate concentration on the reduction rate of chlorate was investigated. Dithionite concentration was set at 50 times (Figures 8a and b) the initial chlorate concentration. Figure 8 shows that chlorate reduction efficiency and chloride concentration increased with increasing initial chlorate concentration although the ratio of dithionite dose to initial chlorate concentration remains constant at 50:1. When the reaction was terminated, the percentages of chlorate reduction at the dithionite/chlorate molar ratio of 50 were 100%, 58%, and 53% for initial chlorate concentrations of 0.24 mM, 0.12 mM, and 0.024 mM, respectively. The extent of chlorate removal before initiation of UV irradiation increased with increasing initial chlorate and dithionite concentrations.
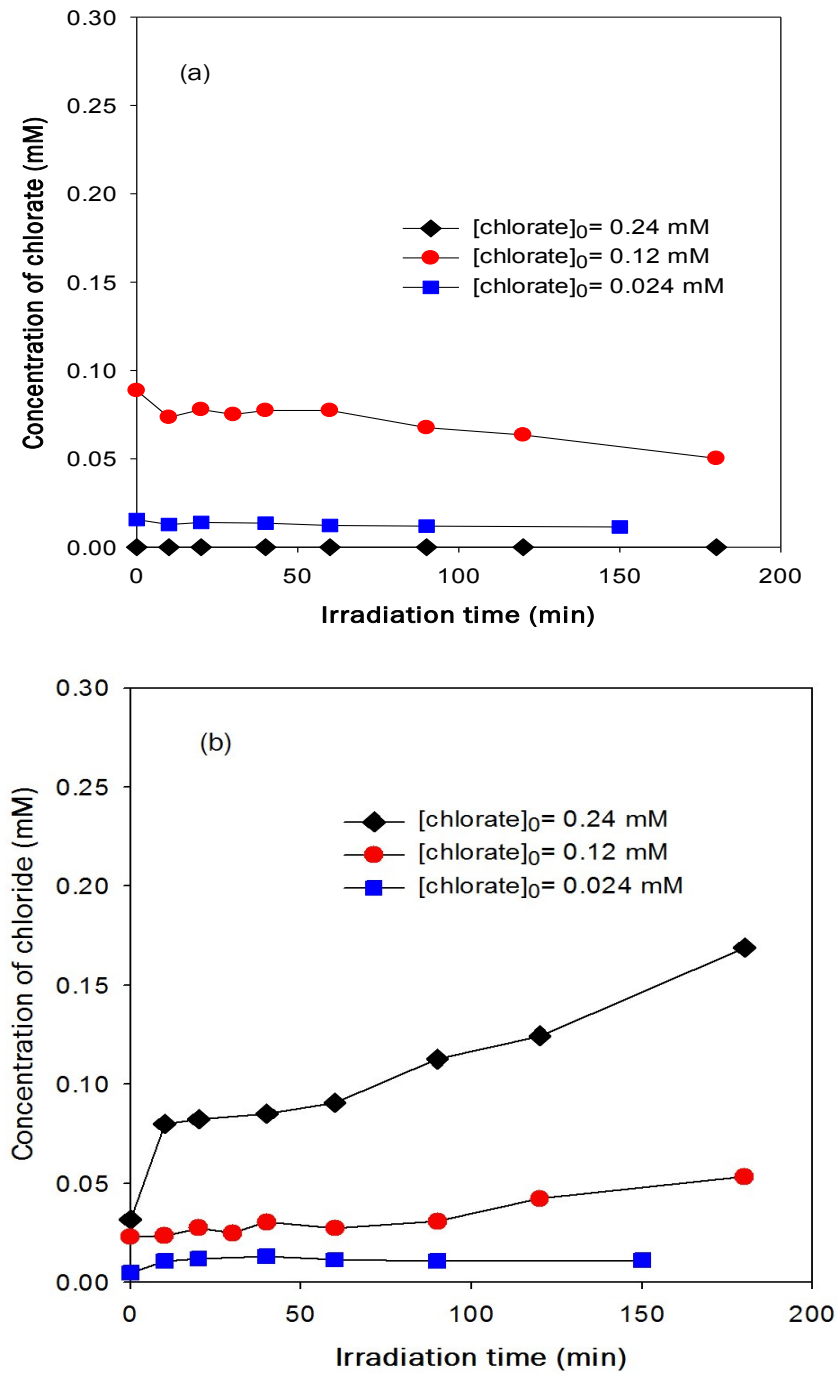
Figure 8: Effect of initial chlorate concentration in the dithionite/UV-B ARP on (a) chlorate concentrations and (b) chloride concentrations. Conditions: dithionite was added by 50 times (a and b) of an initial molar chlorate concentration and the pH was buffered between 3.5 and 4.5. The data belong to experiments 13-15

4.7. Effect of light intensity

The influence of UV light intensity on chlorate reduction was also studied. Figure 9 shows that chlorate reduction and chloride production increased with increasing light intensity. However, most of the chlorate was removed before initiation of irradiation. Dithionite, or the decomposition products from dithionite, will absorb more light at higher light intensity and produce more reactive radicals able to reduce chlorate. At a reaction time of 180 min, the percentages of chlorate removal were 99%, 98%, 93%, and 90% for UV light intensities of 660 $\mu W/cm^2$, 573 $\mu W/cm^2$, 360 $\mu W/cm^2$, and 113 $\mu W/cm^2$, respectively. Chloride formation was 83% (at t = 300 min) of an initial chlorate concentration at the highest light intensity. The results shown in Figure 9 suggest that even at the same concentration of the reducing agent, higher light intensity is required to produce sufficient reactive radicals to effectively reduce chlorate to chloride during irradiation.
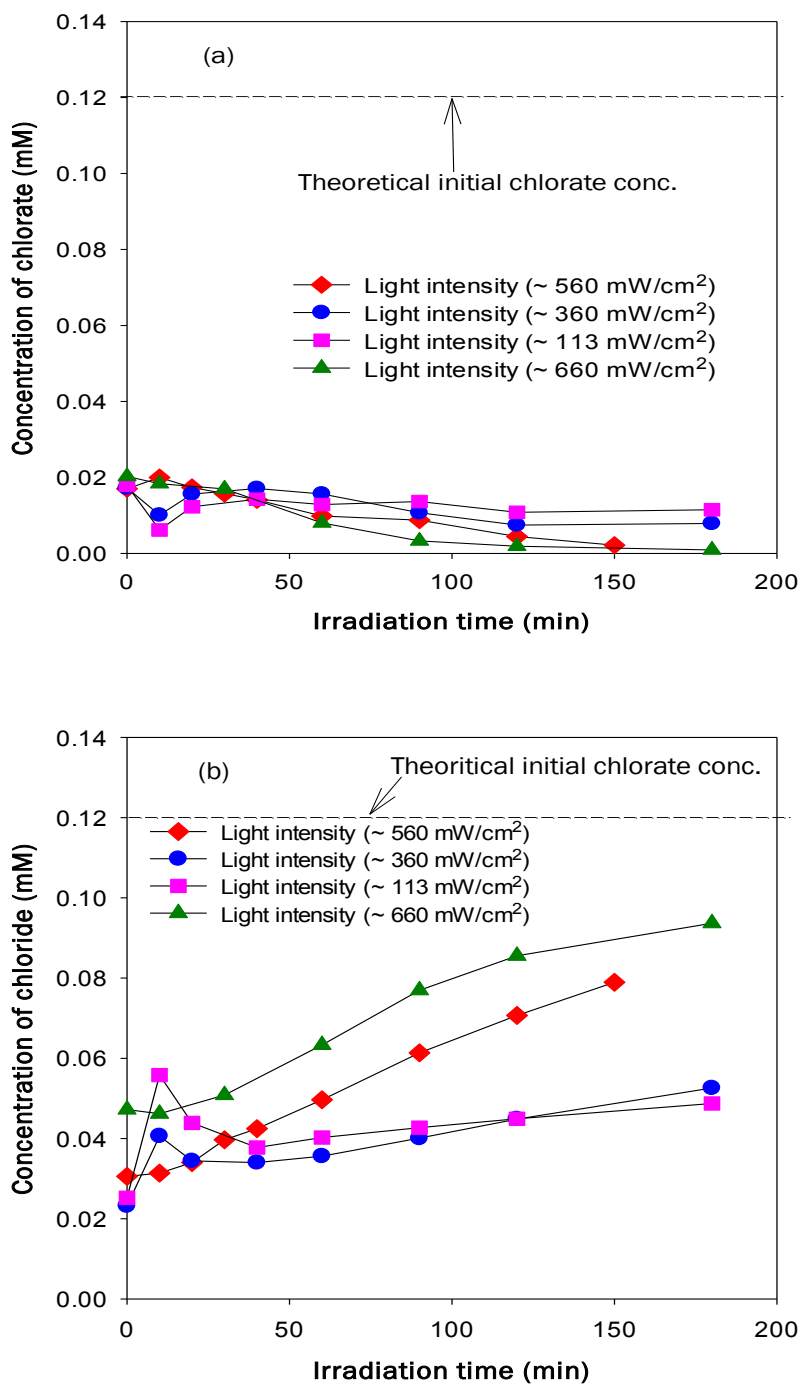
Figure 9: Effect of light intensity in the dithionite/UV-B ARP on (a) chlorate concentrations and (b) chloride concentrations. Conditions: $[ClO_3^-]$ = 0.12 mM, $[S_2O_4^{2-}]$ = 12 mM, and pH was buffered at between pH 3.5 and pH 4.5. The data belong to experiments 6, and 18-20

4.8. Reaction mechanism and byproducts of chlorate reduction

Most of the chlorate was rapidly removed at low pH in dithionite/UV-B ARP before irradiation began and this is believed to be the result of reaction of chlorate with dithionite decomposition products. In pursuit of finding the effective species that is responsible for chlorate reduction in ARP among dithionite decomposition products, chlorate reduction kinetic tests were conducted using three reducing reagents (dithionite, thiosulfate, and sulfite). The results are shown in Figure 10.

At pH 5.6, UV irradiation did not decrease chlorate concentration (Figure 4a), so values of solution pH ranged between pH 3.5 and pH 4.5 in these experiments. In exp. 8 (Figure 10), bisulfite was added as a reducing agent. However, solutions prepared with bisulfite quickly equilibrate among dissolved sulfur dioxide, sulfurous acid, bisulfite ion, sulfite ion, and metabisulfite ion. Such solutions will be described as being total sulfite solutions. At equilibrium, the relative amounts of sulfite ion and bisulfite ion will depend on pH; equal amounts will exist at $pH = pK_a$ (= 7.2), more bisulfite ion will exist at $pH < pK_a$, more sulfite ion will exist at $pH > pK_a$.

Total sulfite solutions at initial pH 4 and pH 4.5 showed complete or nearly complete chlorate reduction even at the first sampling point ($t = 0$), which was after mixing reagent and chlorate but before initiating UV-B irradiation (Figure 10a). Chloride concentration at $t = 0$ for initial pH 4.5 (exp. 8) was approximately 83% of the initial chlorate concentration and remained relatively constant during irradiation (Figure 10b). The experiment with a total sulfite solution at initial pH 4 (exp. 22) showed chloride production of about 75% of an initial chlorate concentration after 60 min. Experiments

using thiosulfate and dithionite showed approximately 14% and 92% decrease of the initial

chlorate concentration after 60 min irradiation, respectively. Chloride formation was

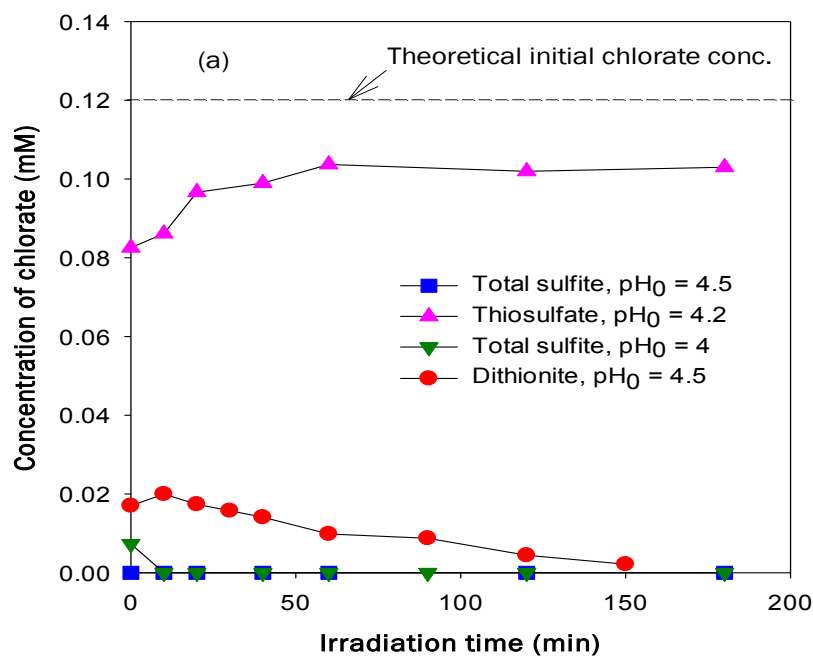negligible with thiosulfate and about 66% with dithionite after 180 min.

Figure 10: Effect of various reducing agents with UV-B irradiation on (a) chlorate concentrations, and (b) chloride concentrations. Conditions: $[ClO_3^-]_0$= 0.12mM, reducing agents conc. = 12mM, and pH was buffered between pH 3.5 and pH 4.5. The data belong to experiments 6, 8, 9, and 22
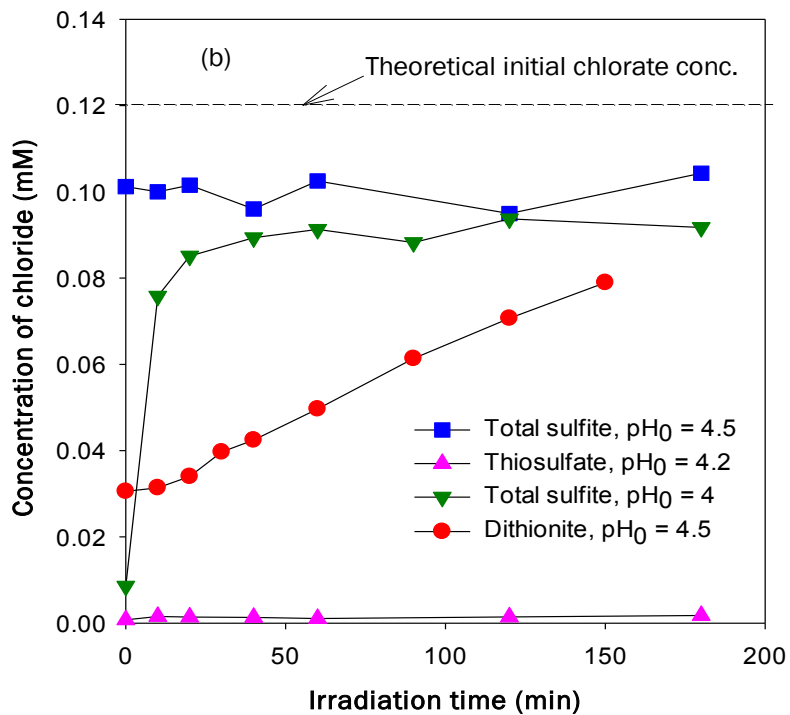
Figure 10: Continued

The reducing ability of total sulfite solutions for chlorate reduction without UV irradiation was also tested. An experiment was conducted using a total sulfite solution of 12 mM that was prepared by addition of sodium metabisulfite. The results showed that chlorate was completely removed in 240 min (Figure 11).
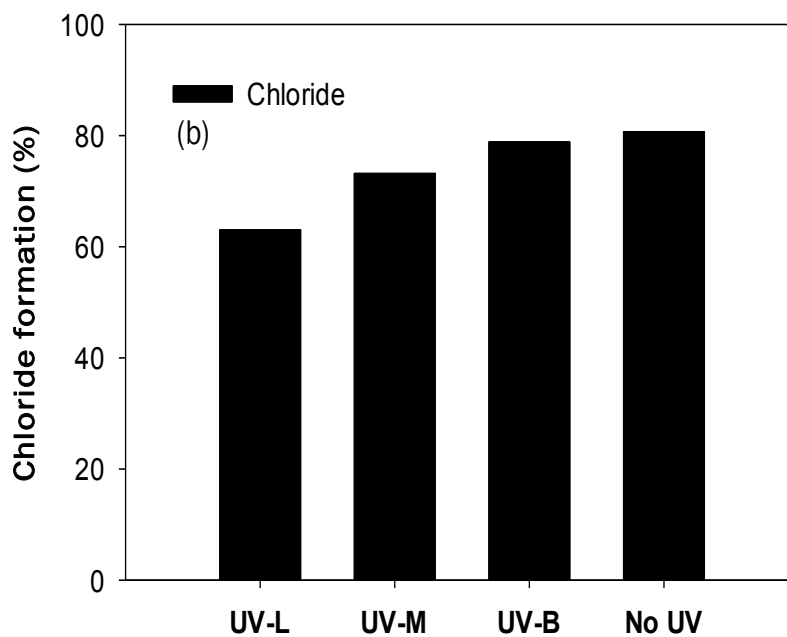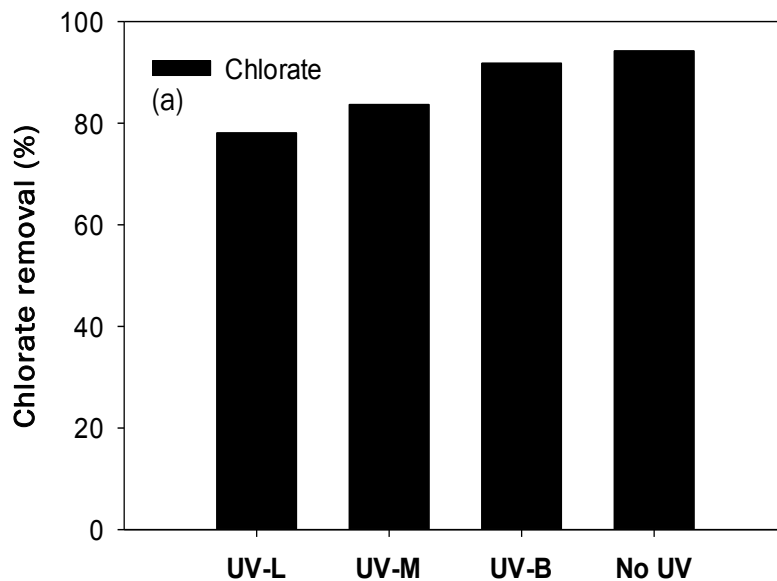
Figure 11: Percentage of (a) chlorate removal and (b) chloride formation dependent on UV light source. Reducing agent was prepared by metabisulfite solution and the total sulfite concentration was 12mM. Solution pH was not buffered and it was measured at pH 4.5. Initial chlorate conc. =12mM, irradiation time= 240 min

Chlorate reduction by total sulfite was characterized at different pH and total sulfite concentrations as shown in Figure 12. At initial pH 4.5 without pH control, 12 mM total sulfite prepared by bisulfite solution resulted in complete chlorate removal and more than 80% conversion to chloride before UV irradiation began. At the same total sulfite concentration but at pH 7, more than 90% chlorate removal occurred before irradiation and nearly 100% removal occurred after irradiation for 180 min. However, chloride production represented only 1.3% of the initial chlorate concentration. To confirm the effectiveness of sulfite solutions at lower concentrations, an experiment was conducted in which total sulfite concentration (0.6 mM) was only 5 times the initial chlorate concentration (0.12 mM). Chlorate reduction was limited to 41% and chloride formation was approximately 10%.

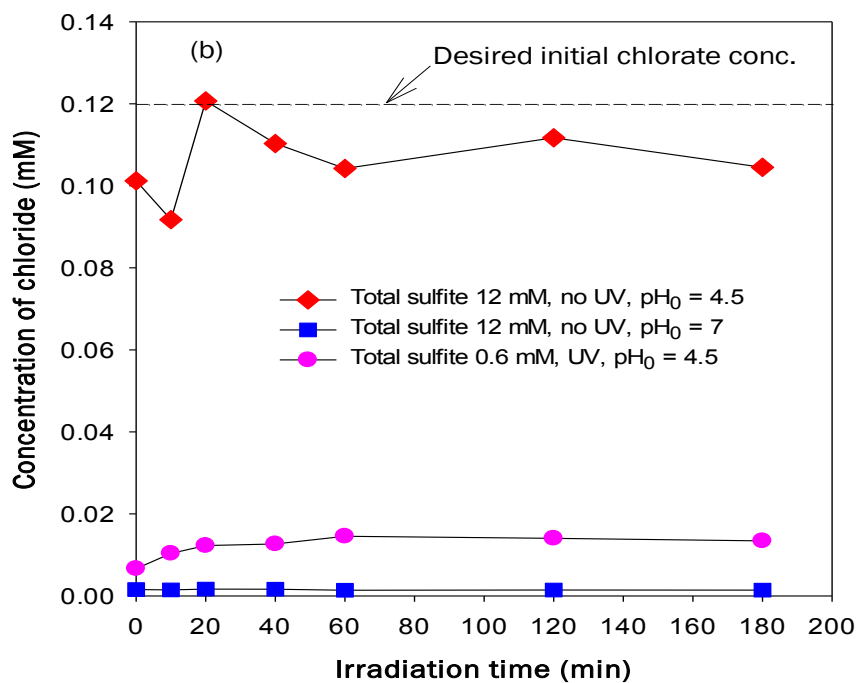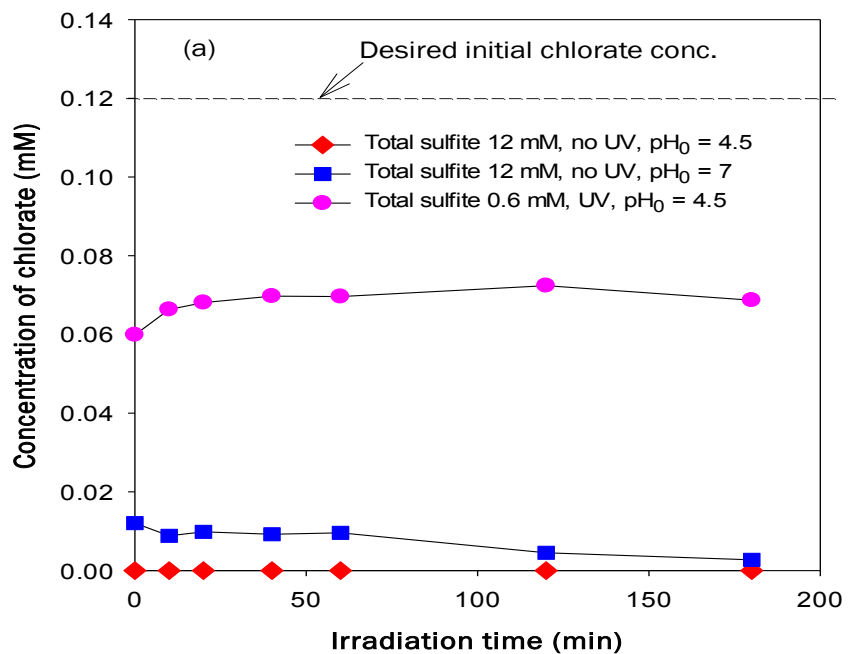**Figure 12:** Chlorate (a) and chloride (b) concentrations by total sulfite with and without UV-B irradiation. Conditions: $[ClO_3^-]_0 = 0.12mM$, total sulfite conc. = 12mM, pH was buffered only ay pH 7. The data belong to experiments 7, 10, and 11

Also, the effect of thiosulfate on chlorate reduction was investigated at pH 4.5 and pH 7 (Figure 13). Thiosulfate reduced chlorate but its effect was less than that of total sulfite solutions.
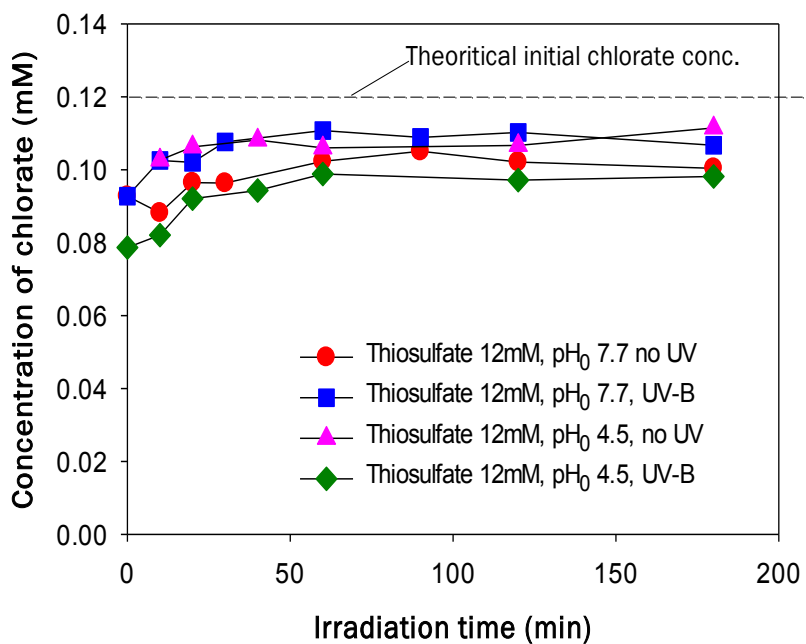
Figure 13: Chlorate removal by thiosulfate alone or thiosulfate/UV-B ARP at different pH

It was reported that bisulfite and sulfurous acid can reduce chlorate to chloride without any activating method (Nixon and Krauskopf, 1932, Szirovicza, 2009). However, the kinetics is slower than observed in these experiments. The results shown in Figures 10, 11, and 12, and published works indicate that a component in total sulfite solutions (bisulfite, metabisulfite, sulfurous acid) is responsible for chlorate reduction at acidic

conditions without UV irradiation. The effectiveness of bisulfite, and sulfurous acid in the reduction of chlorate without any activating method has already been well documented before (Equations 4.7- 4.8) and metabisulfite forms an equilibrium with bisulfite according to Eqn. 4.10 which reduces chlorate in the absence of activation method. In all the cases sulfate has been the oxidized product of the reduced reaction. Since, it was difficult to independently estimate the amounts of these reducing agents present in total sulfite, it cannot be ascertained, which of these reactions will be dominant although it is believed that all the three reactions will take place.

$$ClO_3^- + 3HSO_3^- \rightarrow Cl^- + 3SO_4^{2-} + 3H^+ \tag{4.7}$$

$$ClO_3^- + 3H_2SO_3 \rightarrow Cl^- + 3SO_4^{2-} + 6H^+ \tag{4.8}$$

$$2ClO_3^- + 3S_2O_5^{2-} + 3H_2O \rightarrow 2Cl^- + 6SO_4^{2-} + 6H^+ \tag{4.9}$$
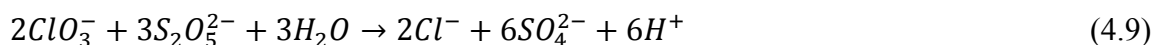
At pH less than 5, dithionite solutions continued to degrade chlorate gradually with UV irradiation, as shown in Figure 4. Published data shows that dithionite rapidly decomposes at acidic conditions and forms various products including bisulfite and thiosulfate (Holman and Bennett, 1994). Therefore, a decomposition product that is being activated by UV could be responsible for degrading chlorate during UV irradiation. Bisulfite is the dominant species in sulfite solutions at pH 3-5, but it absorbs little light in the wavelength ranges of UV-B lamp that was used (Fischer and Warneck, 1996), so it is unlikely to be responsible for chlorate degradation during irradiation.

To better understand photochemical degradation of chlorate in ARP, the UV absorbance of aqueous solutions made from dithionite, sulfite, thiosulfate, and metabisulfite were studied at different pH or concentrations (Figure 14). The absorbance

of a dithionite solution prepared at pH 9 (Figure 14a), where decomposition is slow, shows the typical dithionite peak at 315 nm, which has been attributed to the sulfur dioxide radical ($SO_2^{\bullet-}$) (Amonette et al., 1994, McKenna et al., 1991). Figure 14b shows that this peak decreases in dithionite solutions at lower pH, where decomposition is more rapid. When the characteristic dithionite peak at 315 nm is absent, a broader peak near 220 nm is present (Figure 14a), which is where the absorbance peak for thiosulfate is found, as reported by Awtrey and Connick, (1951). This is also the region where sulfite ion absorbs and sulfite is another product of dithionite decomposition. However, the spectra in Figure 14c and 14d at low pH show a weak absorption peak centered around 260-270 nm, which overlaps the range of UV-B light production. This peak increases with increasing concentration (Figure 14d) and the increase is more than proportional to the increase in total sulfite concentration. Several researchers (Golding, 1960, Hayon et al., 1972) have identified this peak as being caused by the metabisulfite ion, which is formed by reaction of bisulfite ions.

$$2HSO_3^- \rightleftarrows S_2O_5^{2-} + H_2O \tag{4.10}$$
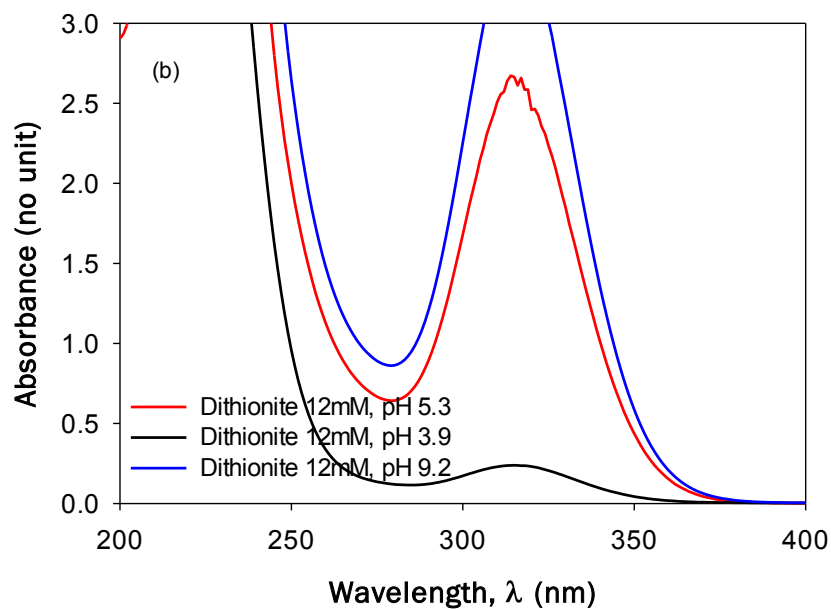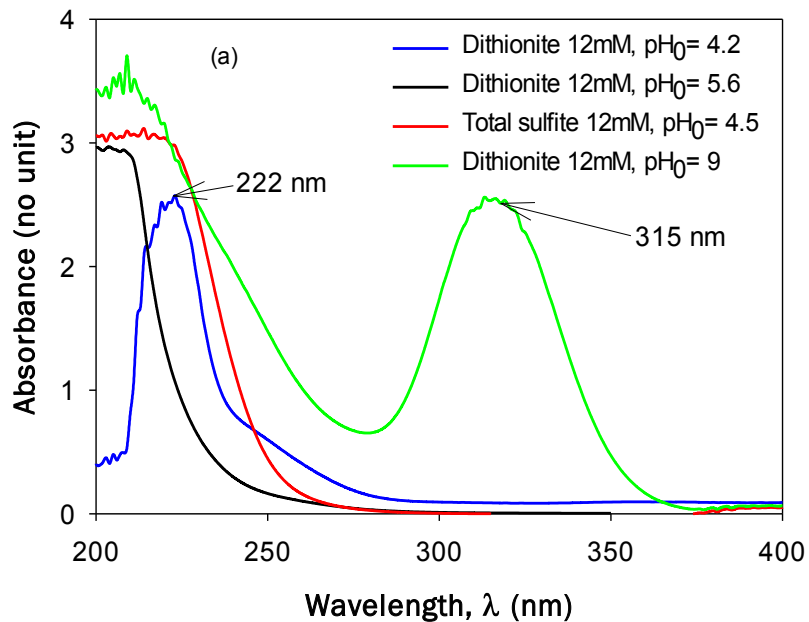
Figure 14: Absorption spectra of solutions prepared with dithionite, bisulfite, thiosulfate, and metabisulfite at different pH or concentrations. Conditions: length of light path= 1cm, respective pH was measured when the solution was prepared at given conditions. Total sulfite solution was prepared with the addition of sodium bisulfite in Figure 14a and 14c, and prepared with sodium metabisulfite in Figure 14d
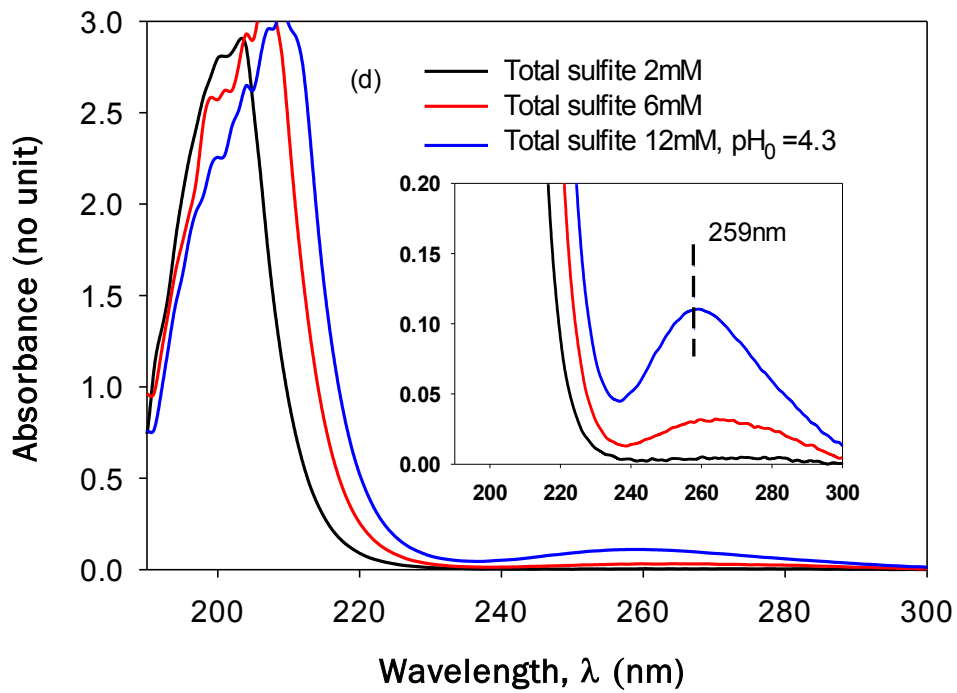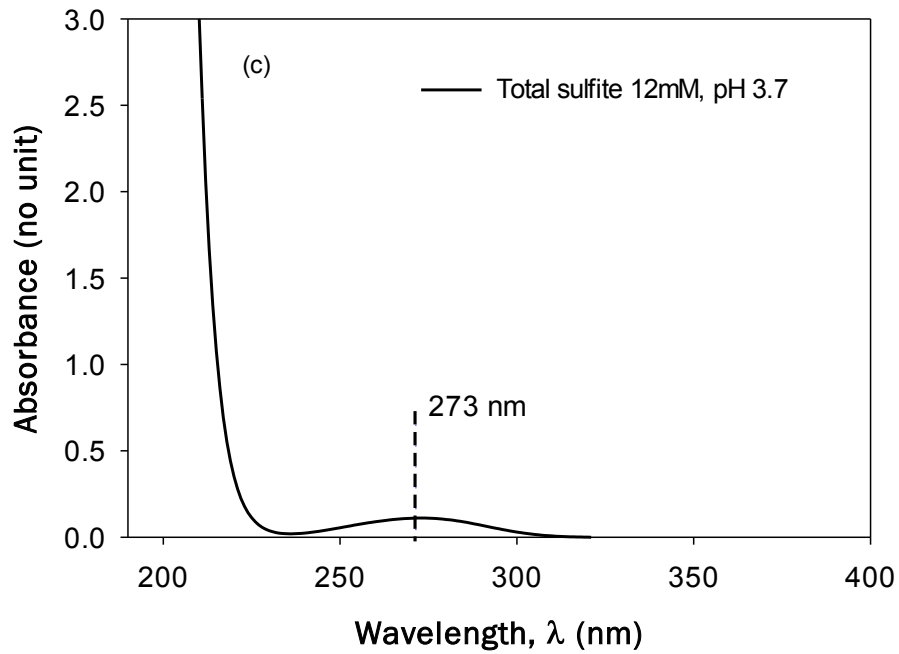
Figure 14: Continued
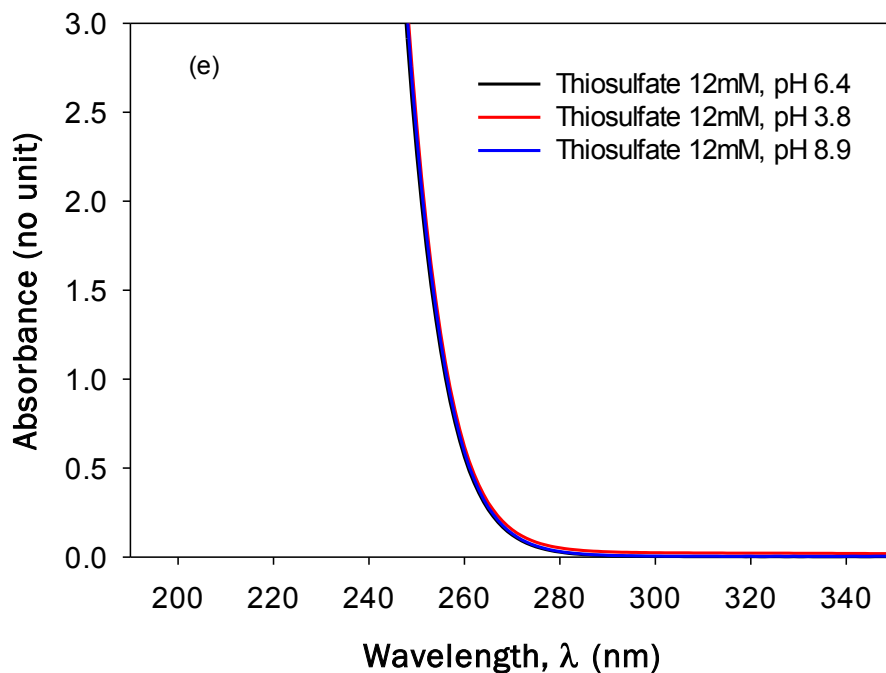
Figure 14: Continued

When bisulfite concentration is approximately 10 mM (Figure 15), the absorbance peak of metabisulfite ion was not clearly displayed. Connick et al., (1982) demonstrated that it is necessary to increase the bisulfite concentration to large values to produce considerable conversion to the metabisulfite ion, because the equilibrium constant is small. Since the equilibrium concentration of metabisulfite is proportional to the square of the bisulfite concentration and the bisulfite concentration is nearly equal to the total sulfite concentration at low pH, the concentration of metabisulfite should be approximately proportional to the square of the total sulfite concentration. This means that the increase in absorbance due to metabisulfite will increase more than proportionally to an increase in total sulfite concentration and this was observed (Figure 14d, Figure 15). Although it is

difficult to estimate how much metabisulfite ion is produced because of variability in reported equilibrium constants, it is present in total sulfite solutions with sufficiently high concentration and it does absorb some light in the wavelengths produced by the UV-B lights used in these experiments (280 - 320 nm). Neither the bisulfite ion nor the thiosulfate ion is expected to absorb appreciable amounts of light in this wavelength range. Therefore, it is proposed that metabisulfite ion is responsible for the degradation of chlorate during UV-B irradiation.

Though metabisulfite is not directly responsible for the degradation of chlorate during UV- irradiation, as most of the chlorate is removed by total sulfite even without the help of UV- irradiation, the main purpose of metabisulfite species is to convert the intermediate reduced product of chlorate degradation to chloride. This is based on the observation that although maximum amounts of chlorate was reduced even before UV- irradiation, very small amounts of chloride was formed in all the experiments. Hence, metabisulfite acts upon the reduced intermediate chlorine containing byproduct to form chloride.

Figure 15: Absorption spectra of aqueous solutions prepared from (a) sodium bisulfite and (b) sodium metabisulfite at different concentrations. Conditions: Total sulfite solution was prepared with sodium bisulfite and sodium metabisulfite respectively

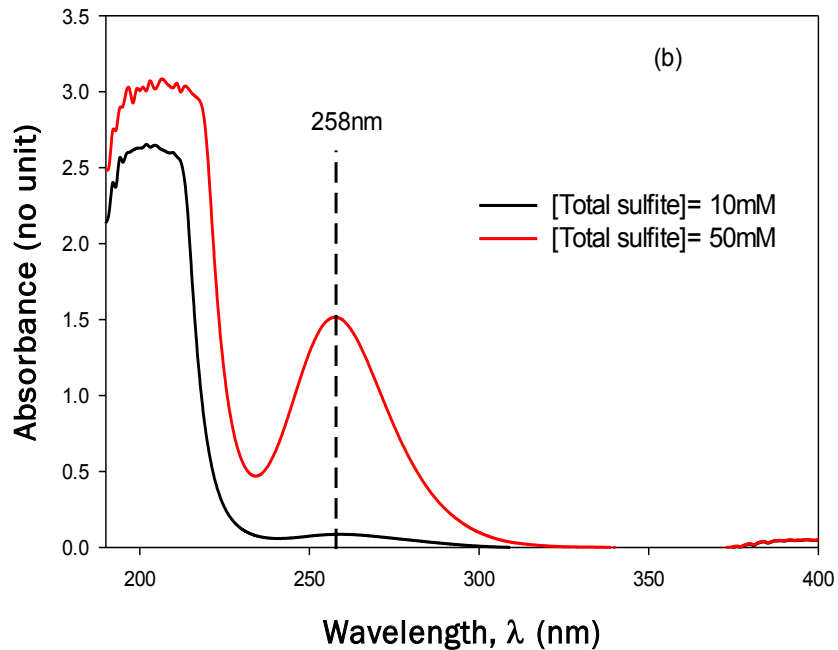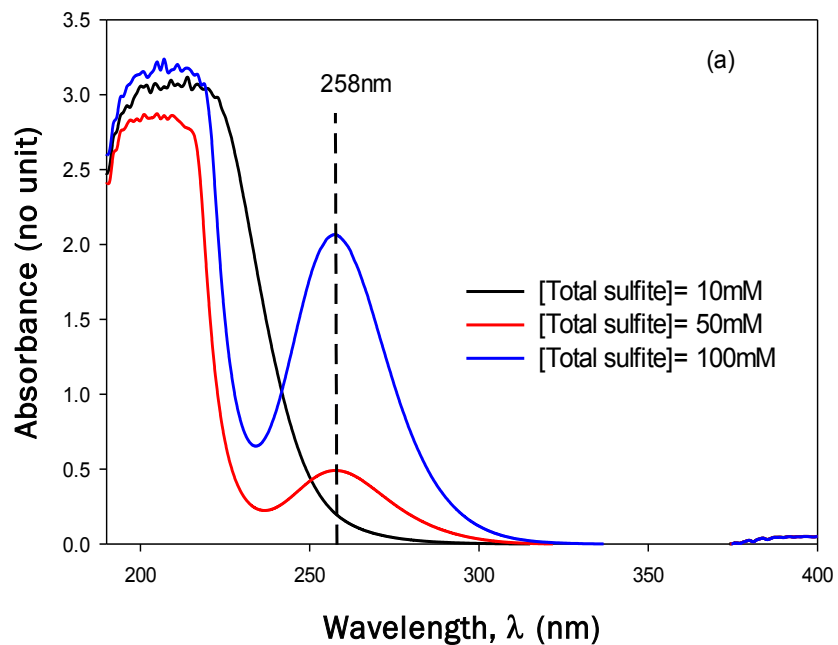Further our previous study investigated perchlorate removal by the sulfite/UV ARP and reported that perchlorate (ClO_4^-) was reduced to chloride (Cl^-) (Vellanki and Batchelor, 2013). Chlorate was detected as an intermediate, but not chlorite, which as believed to be formed as an intermediate, but rapidly converted to chloride. In this study, chloride was a major product of chlorate reduction. Although enough dithionite was added to completely reduce all of the chlorate in the experiments presented here, formation of chloride ion was limited to approximately 80% of the chlorine initially in chlorate. Incomplete chloride ion recovery can be explained by loss of a volatile intermediate such as hypochlorous acid or by the formation of a product that is not measureable by IC. This could be a compound formed by reaction between a chlorate radical and dithionite degradation product such as sulfite shown in the following reaction:

$$SO_3^{2-} + ClO_3^{2-\bullet} \rightarrow SO_3ClO_3^{4-\bullet} \tag{4.11}$$

An example of such a reaction is given by Horvath and Nagypal, (2006) who have studied the reaction between sulfite and chlorine dioxide (ClO_2). They proposed that the reaction between sulfite ion and $^\bullet ClO_2$ forms an anion radical $^\bullet SO_3ClO_2^{2-}$ as shown below:

$$SO_3^{2-} + ClO_2^\bullet \rightarrow SO_3ClO_2^{2-\bullet} \tag{4.12}$$

Chlorate radical anion can be formed from the reaction with hydrated electrons although it's formation is slow (Ershov et al., 2000).

$$e_{aq}^- + ClO_3^- \rightarrow ClO_3^{2-\bullet} \tag{4.13}$$

Table 5 presents the literature data for chlorate removal by various treatments.

Table 5: Literature data for chlorate removal

Technique	Optimum pH	Optimum temperature	Time for maximum chlorate removal	Removal (%)	Catalysts	Catalyst concentration (ppm)	References
Chlorate reducing microorganisms in a gas- lift reactor supplied with H_2	Varied between 7-8.5	35 ºC	2-3 weeks	100	No	-	(Kroom and Ginkel, 2004)
Chemoheterotrophic microorganisms in a suspended biofilm carrier	Optimum performance: pH 9	43 ºC	2- 3 months	100	No	-	(Malmqvist and Welander, 1994)
Catalytic reduction by a noble metal catalyst in presence of H_2	4	70 ºC	2 h	99	Rh on activated charcoal	16000	(Santen et al., 2001)

Table 5: Continued

Technique	Optimum pH	Optimum temperature	Time for maximum chlorate removal	Removal (%)	Catalysts	Catalyst concentration (ppm)	References
Catalytic reduction by a noble metal catalyst in presence of H_2	2	50 ºC	2 h	35	Rh on SiC	500	(Santen et al., 2001)
Catalytic reduction by a noble metal catalyst in presence of H_2	4	70 ºC	2 h	89	Rh on ZrO_2	2000	(Santen et al., 2001)
Catalytic reduction by a noble metal catalyst in presence of H_2	6	50 ºC	2 h	10	Rh on graphite	2000	(Santen et al., 2001)

Table 5: Continued

Technique	Optimum pH	Optimum temperature	Time for maximum chlorate removal	Removal (%)	Catalysts	Catalyst concentration (ppm)	References
Carbon supported iridium catalyst in the presence of H_2	2.4 to 6.5	70 °C	45 min – 1 h	100	Ir supported on C	1000	(Kuznetsova et al., 2012)
Electrochemical reduction using Fe^0 filings as the cathode	11	N/A	8 h	70	No	-	(Srinivasan et al., 2009)
Electrochemical reduction using glassy carbon electrode as the cathode	3.75	N/A	4 h	15	$Co(NO_3)_2$	100	(Srinivasan et al., 2009)
Electrochemical reduction using nickel electrodes as the cathode	3.75	N/A	4 h	26	$CoCl_2$	100	(Srinivasan et al., 2009)

Table 5: Continued

Technique	Optimum pH	Optimum temperature	Time for maximum chlorate removal	Removal (%)	Catalysts	Catalyst concentration (ppm)	References
Electrochemical reduction using nickel electrodes dip coated with TiO$_2$ as the cathode	3.75	N/A	8 h	30	Pd/C Re	100	(Srinivasan et al., 2009)
Direct chlorate reduction at an active titanium electrode	Low pH, not specified	30 °C	N/A	100	No	-	(Brown, 1986)
Activated sludge	6.8	30 °C	20 d	83	No	-	(Jiang et al., 2009)
Reduction with acetate under anaerobic conditions	7	20 °C	10 d	100	No	-	(Ginkel, 1995)

Table 5: Continued

Technique	Optimum pH	Optimum temperature	Time for maximum chlorate removal	Removal (%)	Catalysts	Catalyst concentration (ppm)	References
Addition of hydrochloric acid into chlorate containing salt at a reduced pressure	N/A	80 °C (Pressure: 44 kPa)	8 h	85	No	-	(Okajima et al., 1996)
Photolytic decomposition by ^{60}Co gamma rays	N/A	30 °C	2 h	Exact amount not specified	No	-	(Herley and Levy, 1975)
Reduction of chlorate using dithionite/ UV-B ARP	**Varied between 3.5- 4.5**	**Room temperature**	**3 h**	**100**	**No**	**-**	**This work**

5. CONCLUSION

This study showed that both dithionite/UV-B ARP and sulfite/UV-B ARP reduced chlorate effectively, particularly at low pH, where dithionite is believed to decay to products such as bisulfite, thiosulfate and metabisulfite. This study focused on understanding the fundamental behavior of chlorate degradation in dithionite solutions and the effects of pH, reagent dose, initial chlorate concentration, and light intensity on degradation kinetics. Chlorate concentration rapidly decreased after mixing of reagents, but before initiation of UV irradiation. Slower decreases in chlorate concentration were observed during irradiation. This behavior was more pronounced at a higher reagent dose and at higher initial chlorate concentration. The maximum chlorate reduction of almost 100% was found at a high dose of dithionite (above 12 mM) and at low pH (less than 5). The efficiency of irradiation was more apparent in the formation of chloride. In the absence of UV irradiation, little to no chloride was formed, although chlorate was removed. Chlorite was not found in any experiments under the experimental and analytical conditions employed.

This study led to the following conclusions: i) metabisulfite ion formed by reaction of bisulfite ions produced by dithionite decomposition is probably responsible for reduction of chlorate without irradiation, ii) metabisulfite ion may also photolyzed to produce active species that reduce chlorate during irradiation by UV-B light, and iii) the final product of chlorate reduction was chloride ion under optimal conditions of a high dithionite dose and low pH. Finally, although the dithionite/UV-B ARP is effective at low

pH, the low-pH sulfite/UV-B ARP is a more direct way to effectively treat chlorate, a

disinfection byproduct.

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