Disinfectant demand of sulfur based hydrogen peroxide quenching intermediates after ultraviolet advanced oxidation of drinking water

Abstract and Specific Aims

The proposed research will isolate and examine the kinetics of specific chemicals used in ultraviolet radiation and hydrogen peroxide oxidation (UV/ H_2O_2) which is an advanced oxidation process used in drinking water treatment. After UV/ H_2O_2 disinfection process, residual H_2O_2 must be removed from the water through the addition of quenching agents. Common non-chlorine agents include sulfite (SO_3^{2-}) or thiosulfate ($S_2O_3^{2-}$). Chlorine must then be added to ensure water disinfection throughout the water distribution system. During the quenching of hydrogen peroxide, intermediates form that may remain in the solution, then react with and consume this added chlorine.

This primary goal of this research is to examine the hypothesis that intermediates produced in the reactions of hydrogen peroxide with sulfite or thiosulfate remain in the system and significantly contribute to the consumption of chlorine. Results of this work will be presented at UAA's undergraduate research symposium as well as prepared for submission to the ASCE Journal of Environmental Engineering as a technical note. This note will provide engineering guidance in how a drinking water treatment plant can minimize chemical usage when quenching of residual hydrogen peroxide is necessary after ultraviolet advanced oxidation treatment.

Introduction

While disinfection is the primary concern in drinking water treatment, advanced unit processes such as UV/H_2O_2 are being implemented more frequently due to their ability to destroy organic pollutants inadvertently added to drinking water supplies by human development (see Pal et al., 2010; Koplin et al., 2002). Ultraviolet irradiation mixed with H_2O_2 oxidation has been shown to be effective in neutralizing these emerging pollutants, such as pharmaceuticals (Rosario-Ortiz et al., 2010) and endocrine-disruptors (Rosenfeldt and Linden, 2004) among others. Yet the effect of adding chlorine to the treatment system (as required by the USEPA) after UV/H_2O_2 application has not been thoroughly researched. Unpredictable chlorine demand was experienced in UV/H_2O_2 research conducted by Dotson et al. (2010) after the application of UV/H_2O_2 and quenching of hydrogen peroxide, and the source of the excess chlorine demand was unidentified.

The quenching of H_2O_2 through non-chlorine agents, including sulfite (SO_3^{2-}) and thiosulfate ($S_2O_3^{2-}$), have been well-developed in literature. The mechanism of H_2O_2 with sulfite was developed by Frerichs and Thompson (1998); whereas Rabai and Hanazaki (1999) developed the kinetics of the pH dependent consumption of the intermediate bisulfite (HSO_3^-) within the H_2O_2 and sulfite reaction, as well as further examining the Frerichs and Thompson model. Due to the variant pathways through which H_2O_2 can be consumed by sulfite, and the pH dependence of the rate of consumption of the intermediate bisulfite, there is a possibility bisulfite may remain in the solution once hydrogen peroxide has been quenched from the solution.

Lu et al. (2010) has developed a detailed kinetic model of the H_2O_2 and thiosulfate reaction. The mechanism between thiosulfate and hydrogen peroxide is complex and pH dependent. Primary intermediates produced in the reaction include include bisulfite (HSO_3^-), tetrathionate ($S_4O_6^{2-}$), and sulfite (SO_3^{2-}). The rate of consumption of tetrathionate and bisulfite are pH dependent and proceed slowly in alkaline solutions. Consequently, tetrathionate and bisulfite may remain in the solution once hydrogen peroxide has been quenched from the solution.

To summarize, primary intermediates formed in the quenching of hydrogen peroxide that may remain in the solution include bisulfite (HSO_3^-), tetrathionate ($S_4O_6^{2-}$), and sulfite (SO_3^{2-}, formed in the thiosulfate reaction). According to Varga et al. (2006), tetrathionate and bisulfite may react relatively quickly with chlorine (in the form $HOCl$). The reaction of sulfite with chlorine (as $HOCl$ and OCl^-) analyzed by Roy and Rochelle (2004), may also proceed quickly. The final products of these reactions are sulfate (SO_4^{2-}) and chloride (Cl^-among others. Consequently, chlorine in its effective forms (as $HOCl$ and OCl^-) could quickly be consumed by these identified intermediates.

The experiments outlined in the next section examine the isolated reaction of chlorine with the intermediates above, as well as the kinetics of chlorine added to a quenched hydrogen peroxide solution. Examining these reactions in an ideal water environment (stable, no organic matter, etc.), is necessary to determine the extent to which chlorine is consumed by intermediates as opposed to other possible causes.

Experiment Design

All experiments will be conducted in the Environmental Quality Lab for Natural and Engineered Systems. Glassware used in laboratory experiments will be baked for 4 hours at 550°C to eliminate oxidant demand; and control experiments of representative concentrations of oxidants and quenching agents will be used to observe the rate of self-decomposition and/or volatization. In order to reduce the effect of volatization reactors will be covered. Measurement methods will be checked for accuracy by testing known concentrations of oxidants, quenching agents, and available intermediates in solution through their respective methods. No substances known to interfere with measurement methods will be used.

During experiments, reacting solutions will be mixed at a constant mixing intensity; and pH monitored electrochemically throughout the reaction. If excessive variations in pH (>±1.0) are experienced, the experiment will be redesigned to include pH buffers. Experiments will be conducted with safe laboratory practices in mind and all excess solutions and products disposed of safely.

The first set of experiments conducted will identify the presence of chlorine-consuming intermediates in quenched hydrogen peroxide solutions. 10 mg/L H_2O_2 will be reacted with stoichiometric solutions of sodium sulfite (37 mg/L) or sodium thiosulfate (12 mg/L) in a completely mixed batch reactor. Concentrations of reactants and the primary product (sulfate,SO_4^{2-}) of each reaction will be measured, using published spectrophotometric methods, at regular intervals until the reactants fall below detectable levels.

Intermediates suspected to be in the solution will then be determined through published measurement methods. Once intermediates have been measured, 2.0 mg/L free chlorine (Cl_2, in the form $NaOCl$) will be added to the quenched solution. The rate of chlorine consumption, and extent to which it is consumed, will be determined.

In the final set of experiments, chlorine will be reacted with the intermediates identified in previous experiments. 2.0 mg/L free chlorine (Cl_2) will be reacted with stoichiometric solutions of sodium sulfite (3.6 mg/L), sodium bisulfite (2.9 mg/L), and potassium tetrathionate (17 mg/L) as necessary. Concentrations of reactants and the primary product (sulfate,SO_4^{2-}) will be measured at regular intervals until the concentration of chlorine falls below a detectable level. The rates of chlorine consumption will be identified and compared with published rates, as well as the rates of chlorine consumption determined in the previous experiments.

Data will be reduced and analyzed through traditional statistical methods to determine the mean reaction rates and associated standard deviations. Each reaction will be repeated at least three times to allow for statistical analysis and provide ample quality assurance and quality control. If results fall beyond the expected standard deviation, the experiment will be repeated a fourth time. Results of experiments will be compared with computer based chemical kinetic models and literature published governing rate constants.

Anticipated Results

The first set of experiments involved the isolated quenching of hydrogen peroxide in an ideal (dissolved content free and chemically stable) water environment, removing any interferences that may also affect chlorine consumption. As an isolated system, the factors which may affect chlorine consumption within these experiments include pH variations, remaining reactants (primarily H_2O_2), and remaining intermediates. Because pH will be controlled within ±1, and chlorine will not be added until all reactants are below detectable levels, remaining intermediates are theoretically the primary factor contributing to chlorine consumption.

Once chlorine is added to the solution, through regular measurement of chlorine the rate of chlorine consumption will be determined through kinetic analysis, given the measured concentrations at known time intervals and rate laws known from literature. It is anticipated that chlorine will be consumed at a significant rate once added to the quenched solution of H_2O_2 and thiosulfate, due to the probable remaining concentrations of bisulfite (HSO_3^-), tetrathionate ($S_4O_6^{2-}$), and sulfite (SO_3^{2-}). Molar ratios required for sulfite and thiosulfate to consume hydrogen peroxide will also be confirmed with ratios determined from literature.

Tetrathionate is anticipated to be the primary remaining intermediate in the H_2O_2 and thiosulfate reaction. Through measurement of tetrathionate concentrations in the solution and data regarding the rate of the free chlorine-tetrathionate reaction obtained from the secondary set of experiments as well as literature, the effect of tetrathionate consumption of chlorine will be analyzed.

The secondary set of experiments provides isolated reactions between the intermediates known to be in the quenched H_2O_2 solutions and free chlorine. Data gathered will be used to verify rates between stoichiometric solutions of free chlorine and bisulfite, tetrathionate, and sulfite known from literature. Rates from these experiments will also be compared with the rates of chlorine consumption determined from the quenched H_2O_2 solutions. Through comparison of reaction rates between the two sets of experiments, the extent of intermediate contribution to chlorine consumption within the quenched H_2O_2 solutions will be determined. Molar ratios required for listed intermedites to consume free chlorine will also be confirmed with ratios determined from literature.

Production of long-lived intermediates in the quenching of H_2O_2 will also be compared with data from computer based chemical kinetic models based upon published mechanisms between hydrogen peroxide and sulfite or thiosulfate. These computer models were previously produced (over the Summer of 2011) through use of Acuchem chemical modeling software.

Project Budget

Category	Description	Quantity	Unit Cost	Subtotal	Supplier	Catalog No.
Reagents	Hydrogen Peroxide, 29-32% (or 8.8 M) (500 mL)	1	74.38	74.38	VWR	MK524005
	Sodium Hypochlorite, 4-7% (of 0.07 M) (500 mL)	1	63.30	63.30	VWR	JT9416-1
	Sodium Thiosulfate, Pentahydrate (500 g)	1	45.19	45.19	VWR	EM-SX0815-1
	Sodium Sulfite (500 g)	1	45.10	45.10	VWR	MK806404
	Potassium Tetrathionate (100 g)	1	138.00	138.00	Sigma Aldrich	P2926-100G
	Sodium Bisulfite (60.4%), w Sodium Metabisulfite (500 g)	1	51.76	51.76	VWR	MK744812
Measurement Reagents	Potassium Hydrogen Phthalate (250 g)	2	45.27	90.54	VWR	AA33351-30
	Potassium Iodide (500 g)	1	135.55	135.55	VWR	EMPX1507-1
	Sodium Hydroxide (500 g)	1	48.61	48.61	VWR	EM-SX0593-1
	Ammonium Molybdate Tetrahydrate (125 g)	1	101.95	101.95	VWR	EM-AX1310-3
Measurement Supplies	Cell (10 mL, 2/pkg) - for Chlorine & Sulfate	1	95.29	95.29	Hach	2495402
	DPD Free Chlorine Reagent Powder Pillows (100/pkg)	1	19.65	19.65	Hach	2105569
	SulfaVer 4 Reagent Powder Pillows (100/pkg) - for Sulfate	1	26.89	26.89	Hach	2106769
	Sulfite Reagent Set, Buret Titration - for Sulfite	1	67.00	67.00	Hach	2459800
General Lab Supplies	sensION 156 pH/DO meter electrode	1	172.00	172.00	Hach	5193500
	Buffer solution, pH 4.01 (500 mL)	1	10.59	10.59	Hach	2283449
	Buffer solution, pH 7.00 (500 mL)	1	10.59	10.59	Hach	2283549
	Buffer solution, pH 10.01 (500 mL)	1	10.59	10.59	Hach	2283649
	Pipette (20 uL to 200 uL)	1	296.30	296.30	Rainin	PR-200
	Pipette (500 uL to 5000 uL)	1	296.30	296.30	Rainin	PR-5000
	Pipette Tips (250 uL, 1000/pkg)	1	35.45	35.45	Rainin	RC-250
	Pipette Tips (5000 uL, 1000/pkg)	1	81.00	81.00	Rainin	RC-5000
Estimated S & H	Estimate of Shipping and Handling	1	83.97	83.97		

Grand Total = **2000.00**

Budget Justification

All chemicals listed under the category, "reagents" are the primary chemicals to be used in experiments. Reagents outlined in the budget include hydrogen peroxide (H_2O_2), sodium hypochlorite ($NaOCl$), sodium thiosulfate ($Na_2S_2O_3$) as pentahydrate, sodium sulfite (Na_2SO_3), potassium tetrathionate ($K_2S_4O_6$), and sodium bisulfate ($NaHSO_3$) in concentration with sodium metabisulfite. Amounts listed for the reagents are estimated to be the minimum amounts needed to complete experiments including repetitions needed to assure statistical consistency.

The budget categories "measurement reagents" and "measurement supplies" include all reagents and supplies necessary for measurement of reactant and product concentrations within reacting solutions. "Measurement reagents" includes all reagents necessary for measurement of hydrogen peroxide through the spectrophotometric method published by Klassen et al. (2004).

"Measurement supplies" includes: all supplies needed for measurement of chlorine through Hach method 8021; all supplies needed for measurement of sulfite through Hach method 8071; and all supplies needed for measurement of sulfate through Hach method 8051. Amounts listed for measurement reagents and supplies are estimated to be the minimum amounts needed to complete experiments including repetitions needed to assure statistical consistency.

The budget category "general lab supplies" includes all additional supplies needed that are currently unavailable for use in the Environmental Quality Lab for Natural and Engineered Systems. These include pH calibration supplies, as well as a replacement pH electrode; and high precision pipettes and pipette tips. Estimated shipping and handling costs for all reagents and supplies have also been included in the budget.

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