氯離子和碳酸根同時存在時之 H_2O_2/UV 氧化程序模式探討

計畫編號: NSC88-2211-E-041-005
執行期限: 87 **年** 8 **月** 1 **日至** 88 **年** 7 **月** 31 **日**

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中文摘要

本篇論文嘗試探討氯離子與碳酸根離子對 H_2O_2/UV **程序效能之影響模式，亦即，針對模式化合物正氯丁烷與過氧化氫之去除效率進行模擬。在本研究中，根據所提之反應機構，建立了一組數學模式方程式。結果顯示，在不同** pH **值及不同氯離子與碳酸根離子莫耳濃度比之條件下，該模式能夠定性地描述正氯丁烷與過氧化氫之殘餘趨勢。在模式測試中發現，在酸性** pH **範圍** 3-5，**正氯丁烷之檢測與預測值，存在有顯著之差異，而在鹼性** pH **範圍** 6-9，**其相對誤差為** 2%-26%。**有關過氧化氫檢測與預測值之相對誤差，在所調查之所有** pH **範圍內，其值為** 11%-57%。**當氯離子與碳酸根離子莫耳濃度比從** 0.1 **變化至** 100，**有關正氯丁烷與過氧化氫之相對誤差範圍分別為** 18%-27%**與** 28%-140%。

關鍵字：過氧化氫、紫外光、氫氧自由基、氯離子、碳酸根離子

ABSTRACT

This paper attempts to model the effect of carbonate and chloride ions on the H_2O_2/UV process performance, in terms of removal of model compound butyl chloride (BuCl) and decomposition of H_2O_2. A set of mathematical model equations were established according to the reaction mechanism proposed in this study. As a result, the model can describe the trends of residual fractions of BuCl and H_2O_2 qualitatively at different pH values as well as different molar ratios of chloride versus carbonate ion. In model test, a significant discrepancy was found between the measured and the predicted data of BuCl with acidic pH range of 3 to 5, while 2% – 26% of relative error were obtained with alkaline pH range of 6 – 9. The relative errors regarding the H_2O_2 data range from 11% – 57% for the whole range of pH investigated. As the molar ratio of chloride versus carbonate ion was varied from 0.1 to 100, 18% – 27% and 28% – 140% of relative error were obtained for the BuCl and H_2O_2 data, respectively.

Keywords: Hydrogen peroxide; ultraviolet light; hydroxyl radical; chloride ion; carbonate ion

INTRODUCTION

Advanced oxidation processes (AOPs), which produce strong oxidant of hydroxyl radical (HO•), have gained widespread attention for the treatment of all kinds of contaminated waters and industrial wastewaters. As understood, the performance of AOPs is governed mainly by the concentration level of HO• produced in the reaction mixture. The HO• concentration level in turn is affected by the background impurities present in the solution. Of the impurities, inorganic anions such as nitrate, carbonate, and chloride ions are very common to exist in most of water and wastewater. For example, the former two occur in most of natural waters, and the last one is found in high concentration in some effluents like landfill leachate, municipal, tannery and dye manufacturing wastewaters. In some cases of wastewater treatment, carbonate species is often added into a chemical coagulation unit as a pH adjuster or stabilizer. Hence, when it comes to use AOPs as a pollution control measure, the co-effect of these inorganic anions on the process efficiency can not be overlooked. Carbonate ion consumes HO• effectively and thus provides protection of water contaminant from HO• attack (Liao and Gurol, 1995). Chloride ion inhibits the decomposition of dichlorvos (Lu et al., 1997) and 2, 4-dichlorophenol (Tang and Huang, 1996) in the Fenton process, which produces HO• under acidic pH conditions efficiently.

In our previous work, we presented and verified a model in regard to the photolytic decomposition of hydrogen peroxide in the presence of inorganic carbonate ion and dissolved natural organic matter (Liao and Gurol, 1995). As a continuous work, the focus of this study was placed on the co-effect of carbonate and chloride ions on the H_2O_2/UV process, in terms of removal of refractory model contaminant and decomposition of hydrogen peroxide. The model compound used in this study is butyl chloride (BuCl), which does not decompose under UV irradiation and does not become oxidized by hydrogen peroxide (Haag and

Hoigne, 1985). As shown below, reaction Scheme I - IV were proposed in the presence of carbonate and chloride ions.

Scheme I: In pure water $H_2O_2 + UV \rightarrow 2HO\bullet$ k_1 (1) $HO\bullet + H_2O_2 \rightarrow HO_2\bullet + H_2O$ $k_2=2.7x10^7$ (2) $HO\bullet + HO_2^- \rightarrow O_2^-\bullet + H_2O$ $k_3=7.5x10^9$ (3) $HO_2\bullet \leftrightarrow O_2^-\bullet + H^+$ $pK_{a,4} = 4.8$ ($k_{+4}=7.9x10^5$; $k_{-4}=5x10^{10}$) (4) $HO_2\bullet + H^+ \leftrightarrow H_2O_2^+$ $pK_{a,5} = 1.2$ ($k_{+5}=3.3x10^5$; $k_{-5}=2.1x10^4$) (5) $HO_2\bullet + HO_2\bullet \rightarrow H_2O_2 + O_2$ $k_6=8.3x10^5$ (6) $HO_2\bullet + O_2^-\bullet + H_2O \rightarrow H_2O_2 + O_2 + OH^-$ $k_7=9.7x10^7$ (7)	*Scheme II: In the presence of carbonate ion* $HCO_3^- + HO\bullet \rightarrow HCO_3\bullet + OH^-$ $k_8=8.5x10^6$ (8) $CO_3^{=} + HO\bullet \rightarrow CO_3^-\bullet + OH^-$ $k_9=3.9x10^8$ (9) $HCO_3\bullet \leftrightarrow CO_3^-\bullet + H^+$ $pK_{a,10} = 7.9$ (10) $HCO_3\bullet + H_2O_2 \rightarrow HO_2\bullet + HCO_3^-$ $k_{11a}=4.3x10^5$ (11a) $CO_3^-\bullet + H_2O_2 \rightarrow HO_2\bullet + CO_3^{=}$ $k_{11b}=4.3x10^5$ (11b) $HCO_3\bullet + HO_2^- \rightarrow O_2^-\bullet + H_2CO_3$ $k_{12a}=3x10^7$ (12a) $CO_3^-\bullet + HO_2^- \rightarrow O_2^-\bullet + HCO_3^-$ $k_{12b}=3x10^7$ (12b) $CO_3^-\bullet + O_2^-\bullet \rightarrow CO_3^{=} + O_2$ $k_{13}=6.5x10^8$ (13)
Scheme III: In the presence of chloride ion $HO\bullet + Cl^- \leftrightarrow HOCl^-\bullet$ $k_{+14}=4.3x10^9$; $k_{-14}=6.1x10^9$ (14) $HOCl^-\bullet + H^+ \leftrightarrow Cl\bullet + H_2O$ $k_{+15}=2.1x10^{10}$; $k_{-15}=1.3x10^3$ (15) $Cl\bullet + Cl^- \leftrightarrow Cl_2^-\bullet$ $k_{+16}=2.1x10^{10}$; $k_{-16}=1.1x10^5$ (16) $Cl_2^-\bullet + HO_2\bullet \rightarrow Cl_2 + HO_2^-$ $k_{17}=1x10^9$ (17) $Cl\bullet + H_2O_2 \rightarrow H^+ + Cl^- + HO_2\bullet$ $k_{18}=1x10^8$ (18) $Cl_2^-\bullet + H_2O_2 \rightarrow Cl_2 + HO\bullet + OH^-$ $k_{19}=1.4x10^5$ (19)	*Scheme IV: HO• –probe compound* $HO\bullet + BuCl \rightarrow BuCl_{oxi}$ $k_{BuCl}=3x10^9$ (20) $BuCl_{(aq)} \xrightarrow{stripping} BuCl_{(g)}$ $k_s=7.83x10^{-5}$ (measured in this study) (21)

The k_1 value was experimentally determined, and the reaction rate constants $k_{2\text{-}19}$ can be obtained through the references cited in Liao and Gurol (1995), Jayson and Parsons (1973), Chen and Hoffman (1975), Larson and Zepp (1975), and Hasegawa and Neta (1978). Based on the proposed reaction schemes, a set of reaction rate equations can be established; the detail was presented elsewhere (Liao et al., 2000). The simultaneous solutions were solved according to the Runge-Kutta-Fehlberg method (Gerald and Wheatley, 1989).

EXPERIMENTAL

A batch photoreactor was set-up for this study. An annular quartz reactor (9.5 cm i.d. and 35 cm height) with a liquid volume of around 2 liter was placed in a photochamber, where a set of up to sixteen low pressure mercury UV lamps (8 watts each) were arranged in a circle surrounding the reactor. The UV lamp emits mostly 254 nm of wavelength.

To ensure a homogeneous solution, the water sample to be treated was mixed vigorously. A preliminary study of stripping of hydroxyl radical probe compound BuCl due to mixing was performed to understand its stripping kinetics. As a result, a first-order stripping of BuCl with a rate constant (k_s) of $7.83x10^{-5}$ $sec^{-1}$was closely followed. During the oxidation reaction, 25 ml of water sample was taken at time of 0, 1, 3, 5, 10, 20, 30, and 40 min for subsequent analyses. The residual concentration of BuCl was measured by using a head-space gas chromatography analysis with pentyl chloride (PeCl) as an internal standard (Ioffe and Vitenberg, 1984). The residual H_2O_2 was determined with a spectrophotometric method using Co^{++} and bicarbonate (Masschelein et al., 1977). The experimental reagents used in this study include sodium bicarbonate ($NaHCO_3$) and sodium chloride (NaCl), the initial concentrations of which were determined by weight in the solution. The pH was adjusted by sulfuric acid (H_2SO_4) or sodium hydroxide (NaOH).

RESULTS AND DISCUSSION

Effect of pH

Both the residual BuCl and H_2O_2 were measured over the reaction period of 40 min, given different pH conditions. To test the model, we calculate from the residual profiles the initial pseudo-first order rate constants of BuCl and the first order rate constants of H_2O_2 at different pH values. The former one was obtained by using the residual data within the initial reaction time of 10 min, and the latter one within 40 min. As a result, Figure 1 shows the comparison of predicted and measured data of first order rate constants. In visual comparison, the change of rate constant along with pH value appears to be in the same trend for both the predicted and the measured. In other words, the proposed model can describe qualitatively the removal of model compound and the decomposition of H_2O_2 under different pH conditions.

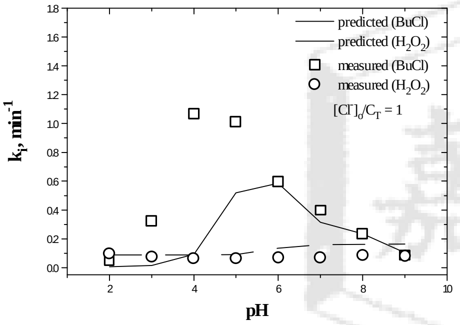

Figure 1. The (Initial) Pseudo-first Order Rate Constants (k_i) of BuCl and H_2O_2 with Different pH Values. $[Cl^-]_o/C_T = 1$ ($C_T = 2.5x10^{-2}$ M); $k_1 = 1.48x10^{-3}$ sec^{-1}; $[H_2O_2]_o = 2.06x10^{-4}$ M; $[BuCl]_o = 1.6$ $x10^{-5}$ M.

Quantitatively speaking, the predicted data of H_2O_2 is quite close to the measured; the relative errors range from 11% – 57%. The discrepancy for BuCl removal between the predicted and the measured occurs when the pH falls within the acidic range; the measured data is much larger than the predicted, especially at pH = 4. Within the range of alkaline pH, the predicted agree with the measured remarkably well; the relative errors are 2% – 26%. As we further look at the measured data of BuCl, the maximum of initial rate constant corresponds to a value of pH = 4. There are two pH units shift from pH = 6 to pH = 4 regarding the maximum of rate constant, when the predicted and the measured data are compared to each other. The reason for the significant discrepancy between the predicted and the measured within acidic pH conditions remains unknown up to this point. Further study needs to be performed to settle this variation.

Effect of $[Cl^-]_o$

In model test, Figure 2 illustrates the comparison of the predicted and the measured data with the molar ratio of $[Cl^-]_o$ versus C_T ranging from 0.1 to 100. By visualization, the trends for the predicted and the measured first order rate constants of BuCl are similar to each other; it remains unchanged in the range of molar ratio 0.1 – 10 and then drops significantly in the range of 10 – 100. As for the rate constants of H_2O_2, the predicted data show a slight drop in the high end of molar ratio, whereas, the measured data is maintained a constant within the whole range of molar ratio.

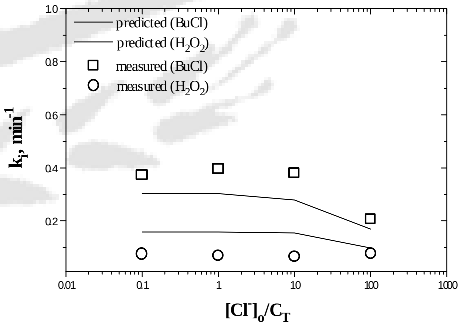

Figure 2. The Initial Pseudo-first Order Rate Constants (k_i) of BuCl and H_2O_2 with Different $[Cl^-]_o$. pH = 7; $k_1 = 1.48x10^{-3}$ sec^{-1}; $[H_2O_2]_o = 1.98x10^{-4}$ M; $[BuCl]_o = 1.6x10^{-5}$ M

In general, the proposed model is seemingly able to describe in a qualitative way the removal of BuCl and the decomposition of H_2O_2 under different concentration combinations of chloride and carbonate ions. However, there still exists a discrepancy between the predicted and the measured data from the viewpoint of accuracy of model prediction. The initial rate constant of BuCl was predicted lower than the measured data, whereas, the predicted H_2O_2 data was a little higher than the measured data. The relative errors at different molar ratio range from 18 to 27 % for BuCl data and 28% – 140% for H_2O_2 data.

CONCLUSION

Based on the proposed reaction mechanism, a set of mathematical equations were established for model predictions of BuCl removal and H_2O_2 decomposition rates. When the pH values varied from 2 – 9, the initial rate constants of BuCl were poorly predicted in the pH range of 3 – 5, whereas, the predicted data agree with the measured data remarkably well at pH = 6 – 9, the relative errors being 2% – 26%. By varying the molar ratio of chloride ions versus total carbonate content from 0.1 to 100, the relative errors of the initial rate constant of BuCl range from 18% – 27% and those of H_2O_2 were found in a broader range of 28% – 140%.

According to the measured data, a maximum concentration of HO• occurs at pH = 4 in the presence of chloride and carbonate ions. The chloride ion concentrations with the molar ratio range of 0.1 – 10 lead to a HO• concentration comparable to each other, but the HO• concentration becomes relatively lower when the molar ratio increases to as high as 100. In addition, the decomposition of H_2O_2 appears to be independent of pH and chloride ion concentration, and a first order reaction is closely followed over the reaction period of 40 min. To improve the accuracy of the proposed model, additional important reactions need to be identified.

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