

APPLICATION OF ADVANCED OXIDATION PROCESSES (AOPs) WITH OZONE TO WASTEWATER TREATMENT

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1. OBJECTIVES

AOPs are designed to promote the formation of hydroxyl free radicals (OH^*) and thereby accelerate oxidation of organics to rates practicable for wastewater treatment [1]. Moreover, AOPs involve two oxidation mechanisms that are molecular ozone and hydroxyl radical's reaction pathways [2]. In this study, the oxidation of glucose in aqueous solutions was investigated and two ozonation processes have been considered, a) ozone and b) ozone combined with hydrogen peroxide (H_2O_2). The main objective is to propose models that allow determining quantitatively the contribution for glucose decomposition between free radicals and direct ozonation.

2. EXPERIMENTS

Aqueous solutions of glucose (20 mg/l) were prepared in pure water. Ozone was fed continuously into a 500 ml cylindrical reactor through a porous plate gas sparger located at the reactor base. Two series of experiments were carried out i) for the study of molecular ozone reactions at various pH and with use of radical scavenger (NaHCO_3), and ii) for the study of peroxone ($\text{H}_2\text{O}_2/\text{O}_3$ system) reaction with different H_2O_2 initial concentrations (Table 1). Ozone was fed continuously to the reactor. The oxidation reaction by ozone was stopped by the addition of small amounts of sodium thiosulfate $\text{Na}_2\text{S}_2\text{O}_3$ before analyzing glucose by TOC measurement.

Table 1: Experimental conditions

Run	pH	Radical Scavenger (mg/l)	Glucose Conc. (mg/l)	Run	pH	H_2O_2 Conc. (mg/l)	Glucose Conc. (mg/l)
1	3	0	20	6	7	12.5	20
2	7	0	20	7	7	25	20
3	11	0	20	8	7	50	20
4	11	1000	20	9	7	100	20
5	7	0	20	10	7	25	0

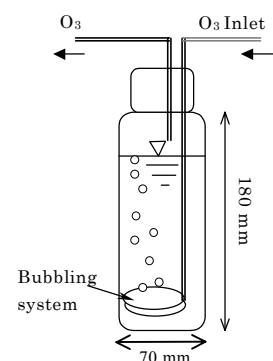


Fig. 1: Ozonation system

3. RESULTS AND DISCUSSION

-The ozonation of glucose was found dominant by pseudo-first-order reaction, and the rate constant increased with implement of pH (data not shown in this paper). Oxidation by free radicals at high pH was also qualitatively verified by the use of free radical scavengers whereby the involvement of free radicals in the oxidation of organic solutes at high pH was analyzed (Fig.2).

- The peroxone system which showed similar pseudo-first order reaction, enhanced considerably the oxidation efficiency till a total degradation of glucose by accelerating free radicals generation, but the increase in reaction rate constant k was limited beyond an optimal concentration of $\text{H}_2\text{O}_2^{t=0}=25\text{mg/l}$ obtained for the present experimental conditions, this was an important result for the modeling of radical reaction pathway (Fig. 3).

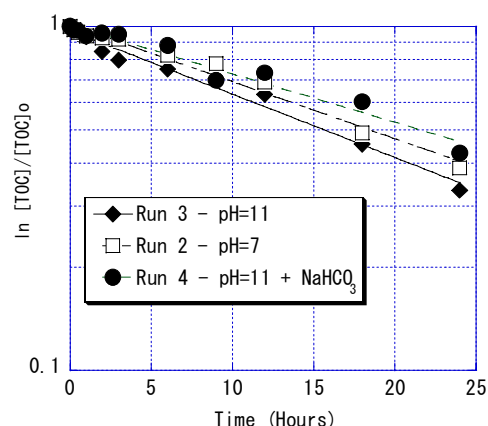


Fig.2: Influence of pH and radical scavenger on TOC removal of glucose

Keywords—Glucose, Ozone, Peroxone, Hydroxyl free radicals, Advanced oxidation, Oxidation reaction pathways, kinetic models

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4. KINETIC MODELING

The chemical and physical reaction rate equations for the peroxone system are described by the equation system {(1), (2), (3) and (4)} where we assume that i) the oxidation of glucose by molecular ozone is being neglected and ii) attention is focused on oxidant-oxidant interaction.

$$\frac{dH_2O_2}{dt} = -k_1 \times H_2O_2 \times O_3 - k_2 \times OH^* \times H_2O_2 \quad (1)$$

$$\frac{dO_3}{dt} = k_3(O_3 - O_3^*) - k_1 \times H_2O_2 \times O_3 \quad (2)$$

$$\frac{dOH^*}{dt} = k_1 \times H_2O_2 \times O_3 - k_2 \times OH^* \times H_2O_2 - k_4 \times OH^* \times G \quad (3)$$

$$\frac{dG}{dt} = -k_4 \times G \times OH^* \quad (4)$$

In order to solve this system, an experiment was carried out excluding glucose from the peroxone process (Run 10) where hydrogen peroxide consumption over time exhibited a linear variation in a semi-log plot. This has made possible the simplification of the mathematical description of the overall reaction rate of OH^* , O_3 and Glucose concentrations, respectively (Eq. (2, 3 and 4)). These were solved and compared to the experimental data as shown in fig. 4-a and 4-b. A consistency was obtained between the calculated and observed data whereby rate constants could be determined. Equation (5) expresses the free radicals variation over time and equation (6) describes mathematically the decomposition of the organic solute over time as follows:

$$R(t) = \frac{K_2 \times K^2}{K_1} \times \exp\left(\frac{K_1}{K} \times \exp(-K \times t)\right) \times \left(\exp\left(-\frac{K_1}{K} \times \exp(-K \times t)\right) - \exp\left(-\frac{K_1}{K}\right)\right) \quad (5)$$

Where: K , K_1 , K_2 : Reaction rate constants.

$$dG = -k_4 \times G \times \frac{K_2 \times K^2}{K_1} \times \exp\left(\frac{K_1}{K} \times \exp(-K \times t)\right) \times \left(\exp\left(-\frac{K_1}{K} \times \exp(-K \times t)\right) - \exp\left(-\frac{K_1}{K}\right)\right) \times dt \quad (6)$$

5. CONCLUSION

The results obtained in this study showed that ozone combined with hydrogen peroxide system has increased the oxidation rate compared to the ozone system where a complete TOC removal of glucose from the water was successfully reached. Also, the optimal condition for the oxidation process efficiency was determined and a scavenging effect on OH^* radicals by hydrogen peroxide was detected. The proposed models exhibited a stability and consistency with the experimental data allowing the determination of rate constants and the prediction of the concentration profiles of both organic matter and oxidants.

Reference:

- [1] Hoigne J, Bader H (1976): Role of hydroxyl radical reactions in ozonation Processes in Aqueous solutions, *Water Research* 10: 377-386
 [2] C. Gottschalk, J. A. Libra, A. Saupe, 2000 *Ozonation of Water and Waste Water*, WILEY-VCH.

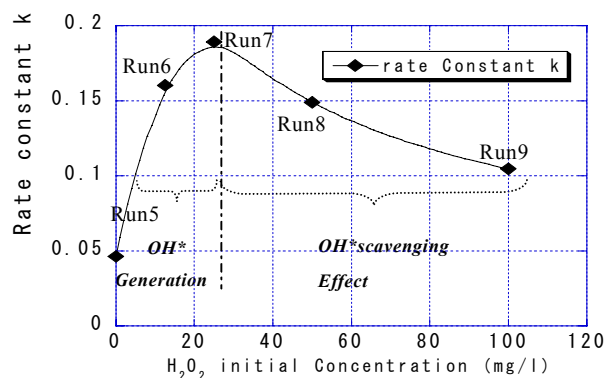


Fig. 3: Reaction rate constants as a function of initial hydrogen peroxide concentrations

$k_1 \sim k_4$: reaction rate constants
 k_3 : the mass transfer coefficient
 O_3 : Dissolved ozone concentration
 O_3^* : Dissolved ozone conc. at saturation
 H_2O_2 : Hydrogen peroxide concentration
 OH^* : Hydroxyl free radicals concentration
 G : Glucose concentration

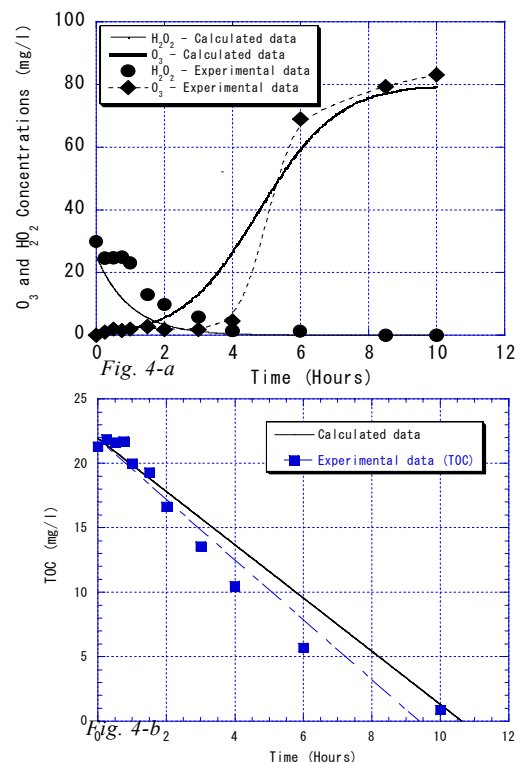


Fig4: Comparison of calculated data and experimental data of glucose (4-a) and O_3 and H_2O_2 concentration for peroxone system (4-b).