

Effect of pH and Hydrogen Peroxide on Ozonic Decomposition of NCW-1001

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Abstract

This investigation was conducted in an effort to determine the effect of pH and hydrogen peroxide content in ozone / hydrogen peroxide based advanced oxidation process prior to adsorption treatment by Ion-Exchange Resin (IER) on the alteration of an alkyl ether type non-ionic surfactant (NCW-1001). The alteration of the surfactant was estimated by observing the change in adsorption to the anion-exchange resin. In advanced ozone / hydrogen peroxide oxidation, the initial hydrogen peroxide concentration and pH value were increased from 0 to 20 mg/L and 7 to 11, respectively. The ability to adsorb to anion-exchange resin decreased whereas the mineralization slightly advanced. This result suggests that oxidation of NCW-1001 by molecular ozone is a more effective method to increase the adsorption of NCW-1001 to anion-exchange resin compared with oxidation by a hydroxyl radical.

Keywords: ozonation, pH, hydrogen peroxide, non-ionic surfactant, NCW-1001

1. Introduction

Non-ionic surfactants are widely used in industry, especially in electronics applications. Non-ionic surfactants such as polyoxyalkylene alkyl ethers are abundantly used in ultra pure water to clean wafers and circuit boards. Therefore, much industrial wastewater contains non-ionic surfactants.

In an effort to reduce the loading of pollutants into the environment, recycling of treated wastewater containing non-ionic surfactants is necessary. Unfortunately, non-ionic surfactants are often persistent biodegradable substances in conventional aerobic biodegradation processes. Accordingly, the development of economically viable treatment methods to reduce organic contents in wastewater is necessary.

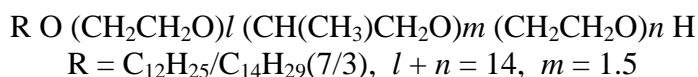
The biodegradability and adsorbability of non-ionic surfactants on Ion-Exchange Resin (IER) increase upon ozonation. However, ozonation does not decompose the surfactants into CO₂ or H₂O. Upon addition of hydrogen peroxide to the ozonation (ozone / hydrogen peroxide oxidation: represented as O₃/H₂O₂), the hydroxyl radical, which is the most reactive species, is formed by the reaction of a hydroperoxide ion with ozone, thus decreasing the Total Organic Carbon (TOC) in the wastewater.

Although it is possible to reduce the TOC by O₃/H₂O₂, it may not be feasible to reduce the TOC by O₃/H₂O₂ oxidation, because a large amount of ozone is required, and the cost of this method is high. Therefore, for a more efficient reduction of the TOC in wastewater, non-ionic surfactants are often adsorbed on IER after oxidation by O₃/H₂O₂, thus increasing the ability of the IER to adsorb pollutants. However, until recently, little information has been published on the effects of O₃/H₂O₂ oxidation on the ability of non-ionic surfactants to adsorb to IER. Thus, in order to achieve effective adsorption of non-ionic surfactants to IER, the basic behavior of O₃/H₂O₂ oxidation must be understood.

The effects of O₃/H₂O₂ oxidation on organic contents of wastewater depend on the ozone and hydrogen peroxide dosage, the pH, the temperature, the liquid and gas properties, and the geometry of reactors. Herein, the effects of ozone, hydrogen peroxide dosage, and pH on the ability to adsorb non-ionic surfactants onto IER were experimentally investigated in an effort to determine the optimal conditions for O₃/H₂O₂ oxidation. The results of this investigation are analyzed and discussed.

2. Experimental

All experiments were conducted in a bubble column with 0.16 m inside diameter and a length of 1.0 m, as shown in Figure 1. The bubble column was made of transparent acrylic resin. The working volume of the column used in the current work was 18 L. All runs were conducted at room temperature in the range of 293-298 K. NCW-1001 (polyoxyethylene alkyl ether, Wako Pure Chemical Industries, Japan) was used as a model non-ionic surfactant. The structural formula of NCW-1001 is as follows:



The nominal molecular weight of NCW-1001 is approximately 2300. The initial concentration of NCW-1001 was 7 mg (TOC / L). Ozone was continuously bubbled into the semi-batch reactor for 30 minutes in order to react with NCW-1001. The ozone gas was generated from pure oxygen as the feed gas using a corona discharge ozone generator (PO-10 ozonizer, Fuji electric systems Co., Japan) and introduced at the bottom of the bubble column through a perforated plate. The flow rate and inlet concentration of ozone gas were 2 L/min and 20 mg/L, respectively. All ozone gas streams were flowed through Teflon tubes and valves. The gas flow rate was measured using a gas flow meter. Since the gas flow rate used in this work was low, a little foam layer was formed on the free surface of the liquid. The exit gas from the top of the bubble column was fed to the catalytic ozone destruction unit and then released to the ambient atmosphere.

The ozone concentrations in the inlet gas and exit gas were monitored using an ozone meter (OZ-30, TOA DKK, Japan). The dissolved ozone concentrations in the liquid were measured by an ozone meter (OZ-20, TOA DKK, Japan). The TOC dissolved in the solutions was measured using the combustion-infrared TOC meter (TOC-V CSN, Shimadzu, Japan).

In order to examine the effects of H_2O_2 and pH on the decomposition of NCW-1001, H_2O_2 and NaOH were added into the reactor just before ozonizing. Table 1 shows the initial hydrogen peroxide concentrations and pH values. A buffer solution was not added to the solution. Therefore, the pH was not controlled during oxidation. All other chemicals used in the experiments and measurements were of reagent grade.

The effectiveness of $\text{O}_3/\text{H}_2\text{O}_2$ oxidation for the degradation of NCW-1001 was estimated by measuring the extent of decrease in the TOC. The alteration of NCW-1001 was measured by the TOC adsorbed onto a strong base Anion-Exchange Resin (AER) (Rohm & Haas Japan), because most organic compounds oxidized with ozone or hydroxyl radical form electronegative intermediates such as organic acids. After AER treatment, the residual organic compounds were represented as nonAER-C.

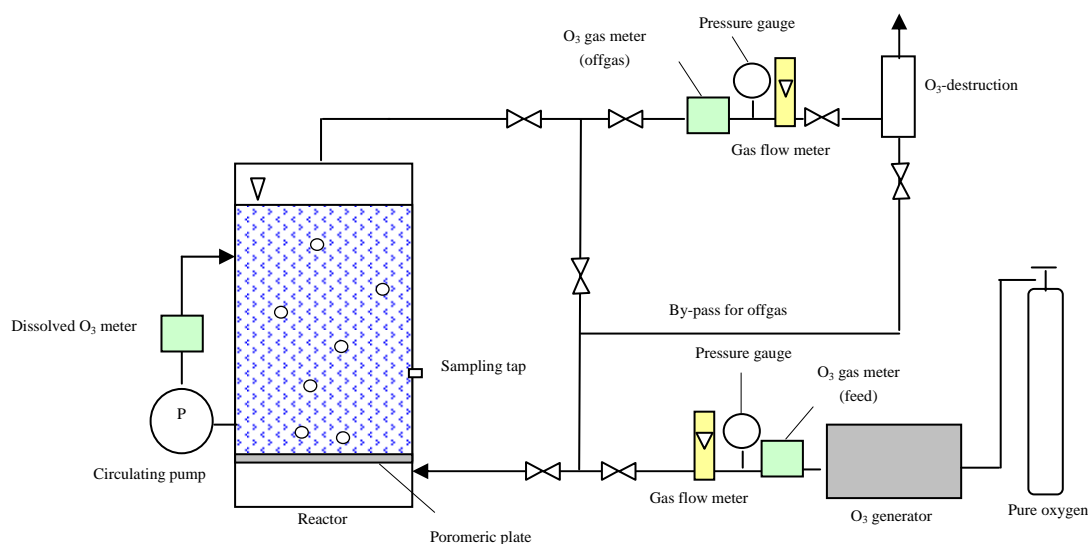


Figure 1. A schematic diagram of experimental apparatus for $\text{O}_3/\text{H}_2\text{O}_2$ oxidation of non-ionic surfactant (NCW-1001) solutions.

Table 1. Initial hydrogen peroxide concentrations and pH values.

		initial pH				
initial H_2O_2	0 mg/L	6.4	7.8	8.9	10.0	11.0
	5 mg/L	6.4	7.4	8.9	10.0	11.1
	10 mg/L	6.9	8.0	9.1	10.1	11.1
	20 mg/L	7.0	7.9	9.1	10.2	11.1

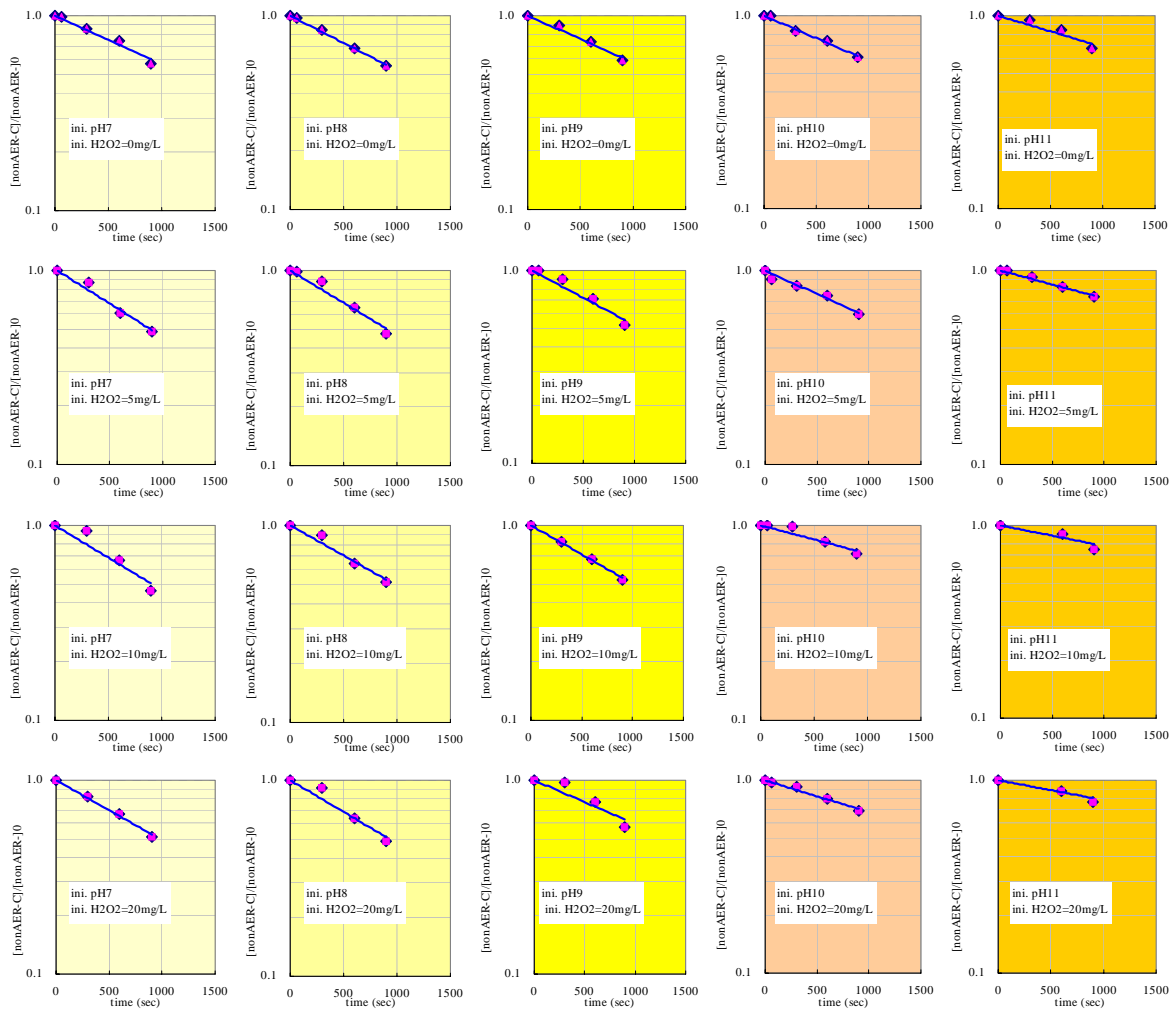


Figure 2. Changes in residual nonAER-C ratio with time in all experiments.

3. RESULTS AND DISCUSSION

1) Alteration Rate

Figure 2 shows the change in the ratio of residual nonAER-C with time during $\text{O}_3/\text{H}_2\text{O}_2$ oxidation of NCW-1001. The majority of the experimental results can be described by a pseudo-first-order law, as shown in Figure 2. The effects of initial hydrogen peroxide concentration and pH value on the alteration rate of NCW-1001 can be estimated with the decay rate constant (k_1) for nonAER-C.

Figure 3 shows effects of pH and H_2O_2 on k_1 . Further, k_1 was shown to significantly depend on pH and H_2O_2 dosage. For $\text{H}_2\text{O}_2 = 0$ mg/L, k_1 was small and was relatively stable in the range of $\text{pH} < 10$. For $\text{H}_2\text{O}_2 = 5$ mg/L, k_1 was large and decreased remarkably with pH in the range of $\text{pH} > 8$. For $\text{H}_2\text{O}_2 = 10$ mg/L, k_1 was large and decreased very little in the range of $\text{pH} < 9$, however; decreased significantly with pH in the range of $\text{pH} > 9$. For $\text{H}_2\text{O}_2 = 20$ mg/L, k_1 increased very

little with pH in the range of $\text{pH} < 8$, however; decreased remarkably with pH in the range of $\text{pH} > 8$.

These findings suggest that an increase of initial pH value decreased k_1 , while an increase of H_2O_2 dosage increased k_1 . However, from pH 7 to 9, k_1 was little affected by the hydrogen peroxide dosage. These trends suggest that the dissociation of hydrogen peroxide significantly influences nonAER-C reduction.

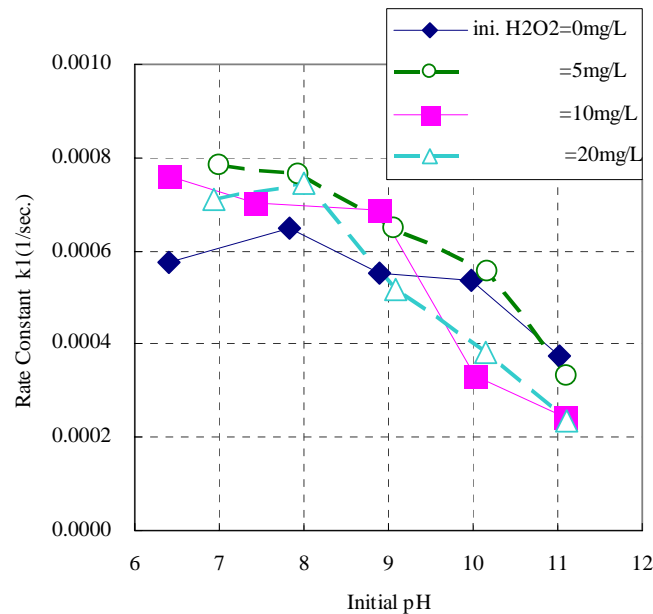


Figure 3. Relationship between decay rate constant k_1 and initial pH.

2) Relation between Ozone Consumption and NonAER-C Reduction.

The relationship between the consumption of ozone per L of solution and the residual ratios of nonAER-C are presented in Figure 4. When no hydrogen peroxide was added, the ozone consumption increased as the initial pH increased. However, the nonAER-C reductions changed very little in the range of pH 7 to 9. When the initial pH was 10 to 11, the ozone consumption increased remarkably, whereas the nonAER-C reductions decreased to values lower than those in the range of initial pH 7 to 9. This is thought to be because the ozone reacted more rapidly with strong base compared with nonAER-C in NCW-1001.

In the case in which hydrogen peroxide was added, the nonAER-C reductions and the ozone consumptions were the same as those in the case in which no hydrogen peroxide was added in the range of initial pH from 7 to 9. However, in the range of initial pH from 10 to 11, as the hydrogen peroxide dosage increased, the ozone consumption increased much more drastically compared with case in which no hydrogen peroxide was added, although nonAER-C reductions did not increase. As the hydrogen peroxide dosage increased at $\text{pH} = 11$, nonAER-C in NCW-1001 was mineralized, although the residual TOC ratios in the solution were slightly reduced.

Figure 5 shows the ratio of the decrease in moles of nonAER-C per mol of ozone consumed in each $\text{O}_3/\text{H}_2\text{O}_2$ experiment. As seen in Figure 5, as the hydrogen peroxide

dosage increased above initial pH = 10, more ozone was consumed for the reaction with basic radicals such as OH⁻ or HO₂⁻ than for the reduction of nonAER-C.

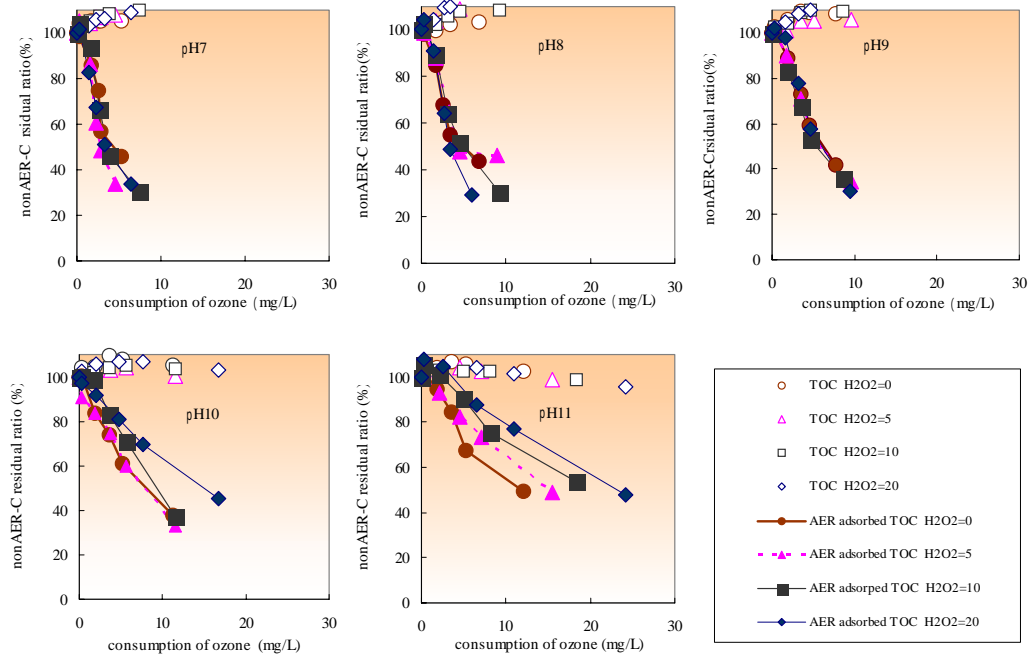


Figure 4. Relationship between O₃ consumption and reduction of nonAER-C.

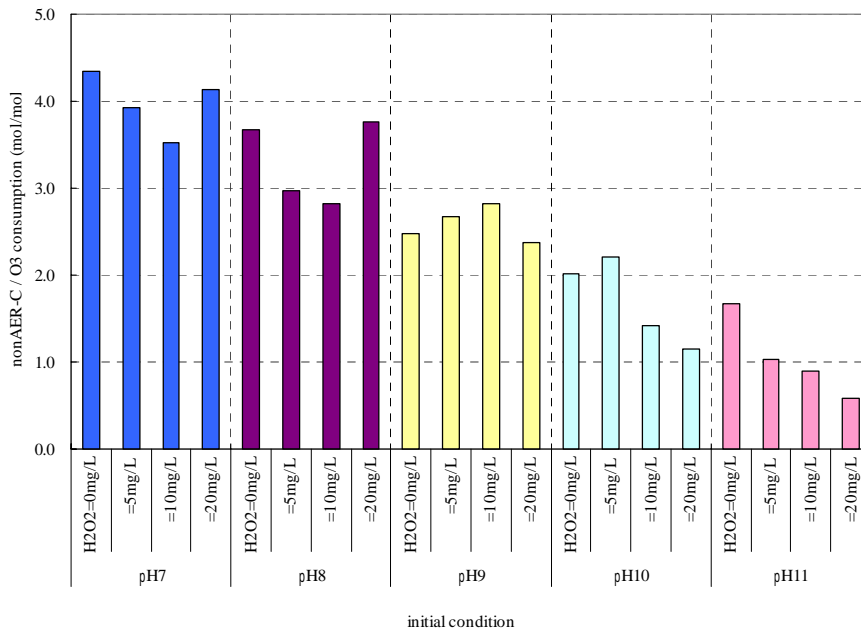
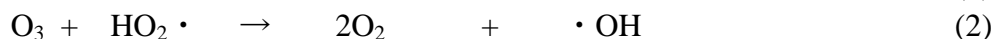
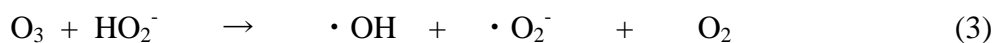


Figure 5. Influence of initial hydrogen peroxide and pH values on efficiency of reaction with ozone and nonAER-C.

Ozone is decomposed at alkaline pH according to Eqns. (1) and (2), thus forming the hydroxyl radical, which is the most reactive species.



Hydroperoxide ion also reacts with ozone and forms a hydroxyl radical according to Eqns. (3) and (4). The formed hydroxyl radical enhances decomposition of ozone due to initiating radical chain reactions (T. Morioka et al., 1994).



Therefore, at alkaline pH, as the hydrogen peroxide dosage increases, ozone rapidly reacts with HO_2^- and OH^- . Therefore, the nonAER-C reductions decrease while the ozone consumption increases with an accelerating rate of formation of the hydroxyl radical. This indicates that the ozone molecule is more effective than the hydroxyl radical for enhancing adsorbability of non-ionic surfactants such as NCW-1001 on AER.

4. Conclusions

The objective of this study was to investigate the effects of pH and hydrogen peroxide on the ability of a non-ionic surfactant (NCW-1001) on an AER to absorb pollutants in $\text{O}_3/\text{H}_2\text{O}_2$ oxidation. This was investigated in an effort to develop a more effective method of $\text{O}_3/\text{H}_2\text{O}_2$ oxidation with subsequent IER adsorption. The results are summarized as follows:

(1) Hydroxyl radicals generated in $\text{O}_3/\text{H}_2\text{O}_2$ oxidation processes were much less effective for enhancing adsorbability than ozone molecules, although hydroxyl radicals were more effective for mineralization of organics in solutions.

(2) Hydrogen peroxides in $\text{O}_3/\text{H}_2\text{O}_2$ markedly increased the dissociation of hydrogen peroxides in the range of pH greater than 10.

(3) The mechanism of alteration of NCW-1001 by $\text{O}_3/\text{H}_2\text{O}_2$ remains unclear.

References

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