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Continuous determination of hydrogen peroxide formed in advanced oxidation and electrochemical processes

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ABSTRACT

A hydrogen peroxide (H_2O_2) auto-analyzer was developed to continuously detect H_2O_2 present in water, using a flow injection analysis (FIA) technique, during several advanced oxidation processes (AOPs) involving H_2O_2, such as ozone/H_2O_2, UV/H_2O_2, and ozone/UV, and an electrochemical process. The analytical method was based on a fluorometric method, using the reaction of *p*-hydroxyphenyl acetic acid and H_2O_2 in the presence of peroxidase enzyme. H_2O_2 was analyzed within the high (100–2,000 μg/L) and low (0–500 μg/L) concentration ranges, using both long and short reaction coils, respectively. The standard deviation and detection limit were 0.5 and 1.6 μg/L, respectively, and the coefficient of variation at 1 μg/L was 7.8%. This study also investigated the effects of $Na_2S_2O_3$ and NH_4Cl, which were used to quench the ozone and hypochlorous acid (HOCl) present in the samples, on the measurement of H_2O_2 during the ozone-based AOPs and electrochemical process.

Keywords: Hydrogen peroxide auto-analyzer; Flow injection analysis; Advanced oxidation process

1. Introduction

Hydrogen peroxide (H_2O_2) is widely used as an initiator in advanced oxidation processes (AOPs), where it can increase the rate of hydroxyl radical (**.**OH) formation due to the reaction between ozone and its conjugate base, HO_2^- [1]. Therefore, the utility of AOPs involving H_2O_2 has recently increased for the effective oxidation of hazardous pollutants in water [2]. Especially, in the ozone/H_2O_2, UV/H_2O_2, and ozone/UV AOPs, since their ability to oxidize greatly depends on the H_2O_2 experimental conditions, in terms of injection dosage and residual concentrations, the precise and simple measurement of H_2O_2 is significantly important for engineers to deal with these processes under the optimum operation conditions [1]. In this study, the UV/H_2O_2, and ozone/UV processes were selected as target processes for observing the residual H_2O_2. The direct degradation of H_2O_2 in the UV/H_2O_2 process and the formation pattern in ozone/UV process were able to be observed. Meanwhile, the utility of the electrochemical process in the field of water treatment, for the purposes of oxidation and disinfection, has only recently been realized. The electrochemical process, in general, produces mixed oxidants, such as hypochlorous acid (HOCl), ozone, H_2O_2, and several radicals (e.g. ·OH, ·O, $\cdot O_2^-$) [3]. However, there has been no success in the separation

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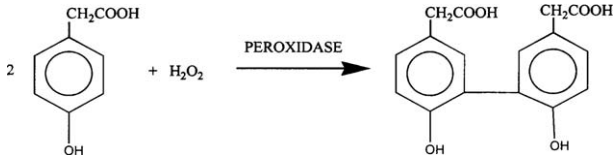
and determination of these mixed oxidants and, thus, this study made great efforts to measure the H_2O_2 formed during the electrolysis of water.

Various techniques for the analysis of H_2O_2 have been reported over the years; early studies on H_2O_2 in precipitation were performed using iodometric techniques, and then the luminol chemiluminescence method provided the first approach for determining H_2O_2 at the 10 nM level [4]. Thereafter, the luminol technique has been modified with the use of hemin as a catalyst [5]. In 1985, for the determination of H_2O_2 in the liquid phase, an automated analytical technique was developed using a fluorometric method with peroxidase, an enzyme characterized by its selectivity toward hydroperoxides [6]. In the presence of *p*-hydroxyphenyl acetic acid, the enzyme peroxidase catalyzes the reduction of H_2O_2, via the following reaction [7]:



The dimeric product fluoresces with peak excitation and emission wavelengths of 320 and 400 nm, respectively [7]. The stoichiometry of reaction (1) indicates that one dimer is formed for every hydroperoxide (–O–O–H) bond broken. The fluorescence of this dimer is, therefore, directly proportional to the peroxide concentration. In this study, since the peroxidase fluorometric method, compared to other methods, is hardly affected by interferences commonly found in environmental aqueous samples, an instrument (an H_2O_2 auto-analyzer) was developed using an automated analytical technique based on this fluorometric method, which made the continuous measurement of the H_2O_2 present in water samples possible using flow injection analysis (FIA). For its practical application, the H_2O_2 auto-analyzer was tested in order to measure the residual H_2O_2 concentrations during several processes, such as the UV/H_2O_2, ozone/UV, and electrochemical processes.

2. Experimental

2.1. Development of H_2O_2 auto-analyzer

Fig. 1 shows the schematic diagram of the FIA H_2O_2 auto-analyzer developed in this study. Three DC drive pumps (Cole-Parmer Peristaltic pump, USA)

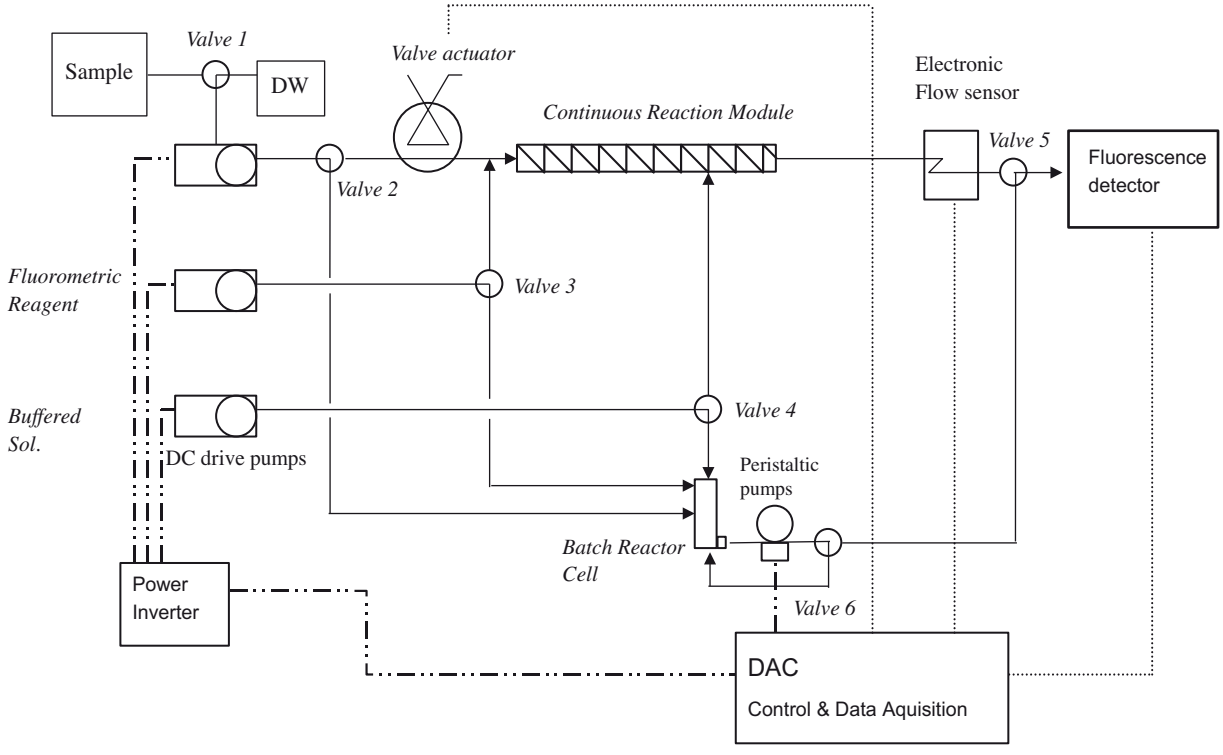


Fig. 1. Schematic diagram of the H_2O_2 auto-analyzer.

continuously injected the following reagents; fluorometric reagent (0.35 M potassium hydrogen phthalate (KHP), 8.0×10^{-3} M *p*-hydroxyphenyl acetic acid (POPHA), 2 purpurogallin units of peroxidase/ml reagent, buffered solution (0.5 M NaOH), and the sample into the H_2O_2 auto-analyzer, with tubing connected to the inlet and outlet of the instrument. The mixing procedure of each reagent was as follows, first, the sample was loaded into a sampling line, and if necessary, a quenching solution was added to the sample stream, using a peristaltic pump (Gilson) and three-way valve, for a few seconds. Thereafter, the fluorometric reagent enters the sample stream. When either the baseline became unsteady or significant degradation of the linearity of signal response was observed, the fluorometric reagent was discarded. Finally, buffer solution was added to the sample stream to maintain the sample above pH 10.0, as the fluorescence quantum yield of the POPHA dimer decreases below pH 9.0, but remains at a maximum above pH 10.0.

After the addition of each reagent, the reaction stream passed through either a short or a long reaction coil, according to the H_2O_2 concentration in the sample. Solenoid valves were used for the control of mixture order of each reagent and the sample. The POPHA dimer was analyzed using a fluorescence detector (SOMA, Japan) with excitation and emission of wavelengths 320 and 400 nm, respectively. Data signals were converted into actual H_2O_2 concentration units (μg/l) and recorded by a computer system via an interface card (Labview, USA). In this manner, the H_2O_2 auto-analyzer could be controlled electronically.

H_2O_2 standards were prepared by serial dilution of a stock H_2O_2 standard, with the concentration determined by both titration with $KMnO_4$ and a H_2O_2 assay kit (Merck). A 1% H_2O_2 standard was prepared by dilution of commercially available 30% H_2O_2. The H_2O_2 standards were freshly prepared for each experiment.

2.2. Tested processes

For the experiments involving UV/H_2O_2 and ozone/UV, a 20 L reactor, equipped with four UV lamps (total UV intensity = 8 W/L and effective light path = 21 cm) and an ozone diffuser, was set up. For the experiment involving the electrochemical process, a 0.3 L reactor, equipped with a plate-type Pt/Ti electrode and a power supply (30 V), was used. In both reactors, the sample water for the H_2O_2 measurement was able to be directly injected via a PTFE tube connected to the H_2O_2 auto-analyzer.

3. Results and discussion

3.1. Analysis of H_2O_2 standard solutions

Figs. 2 and 3 show the calibration curves for the H_2O_2 standard solutions, which yielded good correlation between the H_2O_2 concentrations and signal responses. The H_2O_2 auto-analyzer was operated selectively using short and long reaction coils for low and high concentration ranges, respectively. From the result, the standard deviation and detection limit of 0.5 and 1.6 μg/L, respectively, were obtained from seven replicate tests (at 1 μg/L), with a coefficient of variation of 7.8%.

3.2. Analysis of H_2O_2 during UV/H_2O_2 AOP

When UV is irradiated into the water, H_2O_2 is degraded by the reaction with photons, yielding two

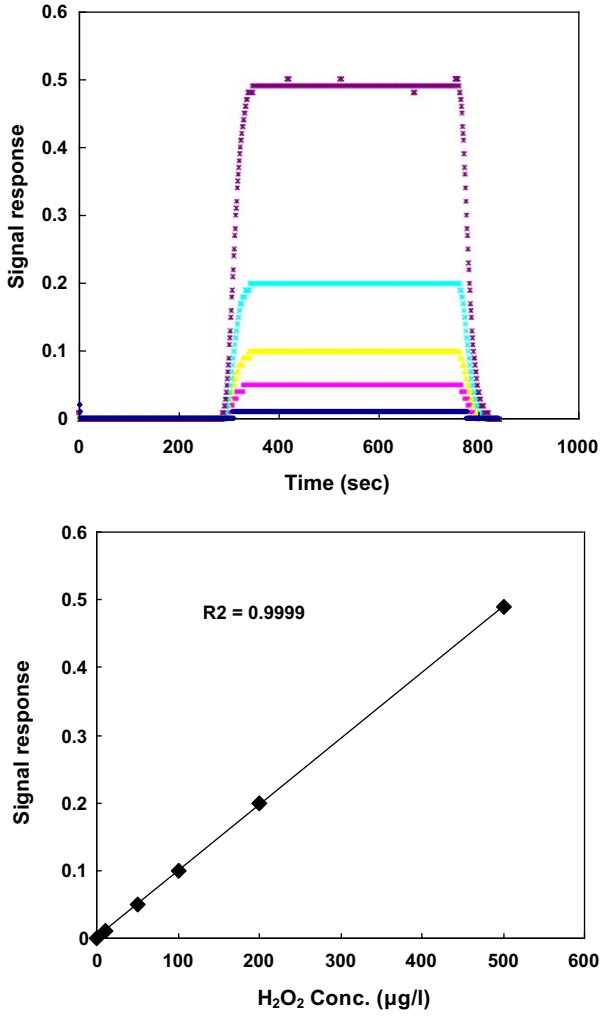


Fig. 2. Calibration curve for H_2O_2 standard solutions at concentrations of 10, 50, 100, 200, and 500 μg/L with a short reaction coil.

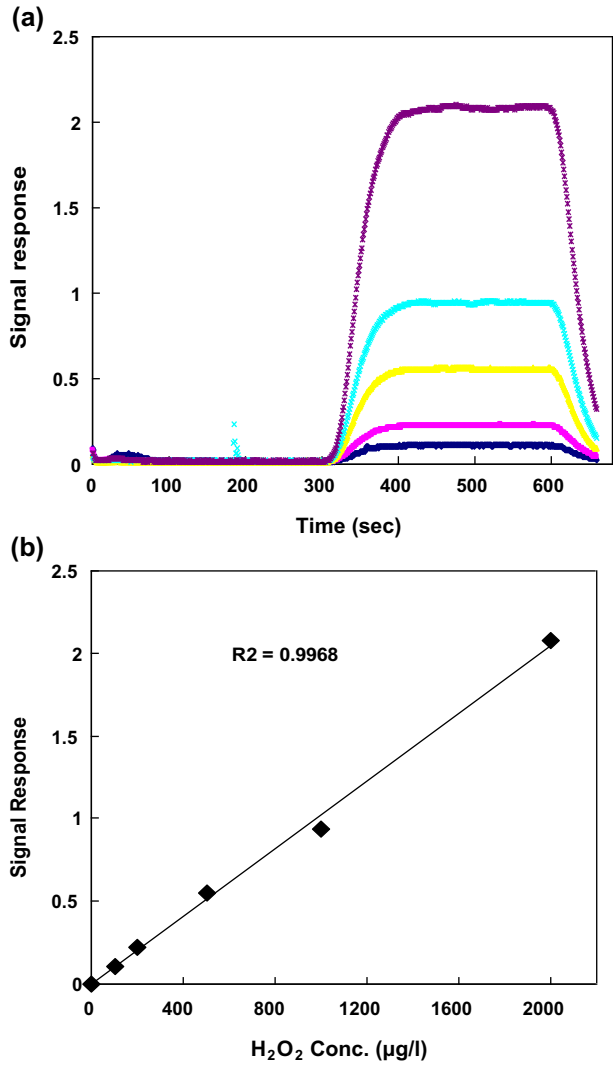


Fig. 3. Calibration curve for H_2O_2 standard solutions at concentrations of 100, 200, 500, 1,000, and 2,000 µg/L with a long reaction coil.

moles of OH° per mole of radiation absorbed, as given by Eq. (2) [8].

$$H_2O_2 + h\nu \rightarrow 2OH^\circ \quad (1)$$

The rate change of H_2O_2 is given by the following Eq. (3):

$$-d[H_2O_2]/dt = \Phi_{per,t} I_o f_{per}\{1 - \exp(-2.3\varepsilon_{per} b[H_2O_2])\} \quad (2)$$

where $\Phi_{per,t}$ (= about 1.0) is the overall quantum yield of the H_2O_2 decomposition at 254 nm, as measured by Baxendale and Wilson [8], I_o is the UV intensity, f_{per} (= about 1.0) is the photolysis fraction of H_2O_2, and ε_{per} (= 17.9 $M^{-1}cm^{-1}$) the molar extinction coefficient of hydrogen peroxide at 254 nm. In Eq. (3), if the concentration of H_2O_2 is enough low, the term of exp ($-2.3_{per} b$ $[H_2O_2]$) can be replaced with $\varepsilon_{per} b$ $[H_2O_2]$, according to the Taylor series equation [9]. Therefore, Eq. (3) can be simplified and integrated as follows:

$$-d\ln[H_2O_2]/dt = \Phi_{per,t} I_o f_{per} \varepsilon_{per} b[H_2O_2] \quad (3)$$

Fig. 4 shows the removal patterns of H_2O_2 during UV irradiation for various UV intensities (I_o), where the H_2O_2 decay rate increases with increasing UV intensity, as shown in the inset. This result was reasonable according to Eq. (4). From this result, the pattern of H_2O_2 decay could be clearly observed using the H_2O_2 auto-analyzer.

3.3. Analysis of H_2O_2 during ozone/UV AOP

When measuring H_2O_2 in the samples, the residual ozone has to be quenched as soon as the sample is injected to prevent decomposition of the H_2O_2 from its reaction with ozone within the sampling loops. Therefore, the H_2O_2 auto-analyzer was devised so that the residual ozone in sample could be continuously quenched, via the injection of sodium thiosulfate ($Na_2S_2O_3$) using a peristaltic pump with a three-way valve connecting the $Na_2S_2O_3$ solution and sample lines. The quenching of the residual ozone in the sample took a few seconds, and the sample reached the fluorescence detector in 1 min. Fig. 5 shows the signal responses of H_2O_2 at concentrations of 10, 50 100, 200, and 500 µg/L, both with and without $Na_2S_2O_3$ solution. The $Na_2S_2O_3$ solution concentrations of 14 and 24 mM were employed, which were two times higher than theoretical concentrations able to quench 3 and 5 mg/l residual ozone, respectively. As a result, the

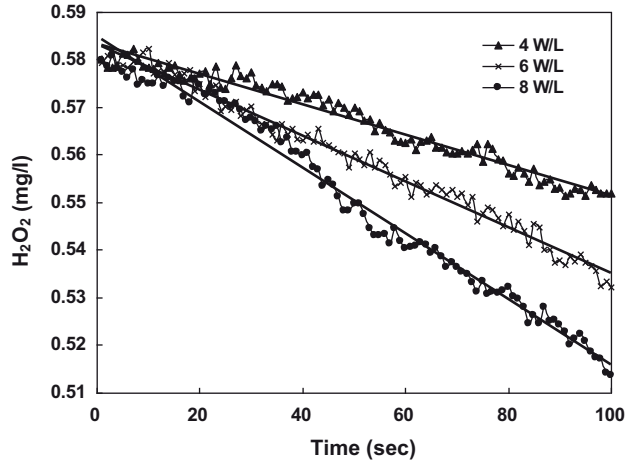


Fig. 4. Analysis of H_2O_2 in the UV/H_2O_2 process, $[H_2O_2]_o$ = 0.58 mg/L.

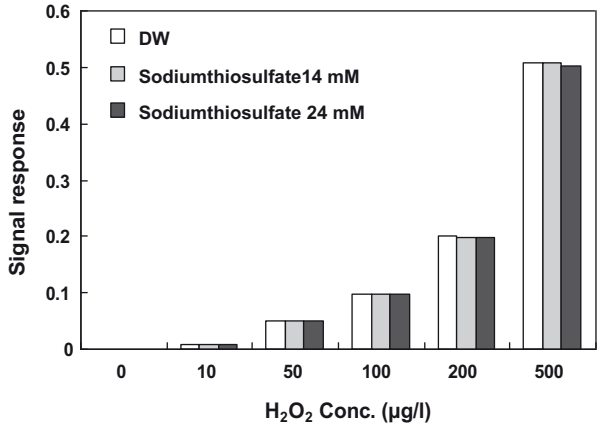


Fig. 5. Effect of sodium thiosulfate ($Na_2S_2O_3$) on signal response of H_2O_2.

presence of $Na_2S_2O_3$ was confirmed to not affect the residual H_2O_2 measurement at all.

To test the H_2O_2 auto-analyzer, the residual H_2O_2 was measured during the ozone/UV process, where ozone photolysis, due to UV irradiation at a wavelength of 254 nm, forms H_2O_2 as an intermediate is the first step to obtain OH°. Taube reported that ozone photolysis in aqueous acetic acid solution led to the production of a "stoichiometric amount" of hydrogen peroxide, as shown in Eq. (5) [10]:

$$O_3 + H_2O + h\nu \rightarrow O_2 + H_2O_2 \quad (4)$$

where the H_2O_2 formed decays by several routes. The first is the photolysis of H_2O_2, which is known to yield two moles of OH° per mole of radiation absorbed,[10] and the second is the reaction between the conjugate base of H_2O_2 (pKa = 11.8), HO_2^- and ozone as, given by Eqs. (2) and (6) [11].

$$HO_2^- + O_3 \rightarrow O_2^{-\circ} + HO_2^\circ \quad (5)$$

In Fig. 6a, the H_2O_2 formed during the ozone/UV process was measured at various ozone dose rates. Under all ozone dose conditions, the H_2O_2 concentration was increased with a 3 min reaction time, after which it began to decrease and then reached a steady-state level. The H_2O_2 concentration in the ozone/UV process means that the rates of H_2O_2 formation by ozone photolysis (Eq. (5)) and that of the decay (Eqs. (2) and (6)) were the same. It was also found that the steady-state concentration of H_2O_2 was in proportion to the ozone dose rate, as shown in Fig. 6b. This result indicates that the H_2O_2 auto-analyzer can be a particularly useful tool for understanding the mechanism of the ozone/UV process, and for its operation under optimum conditions.

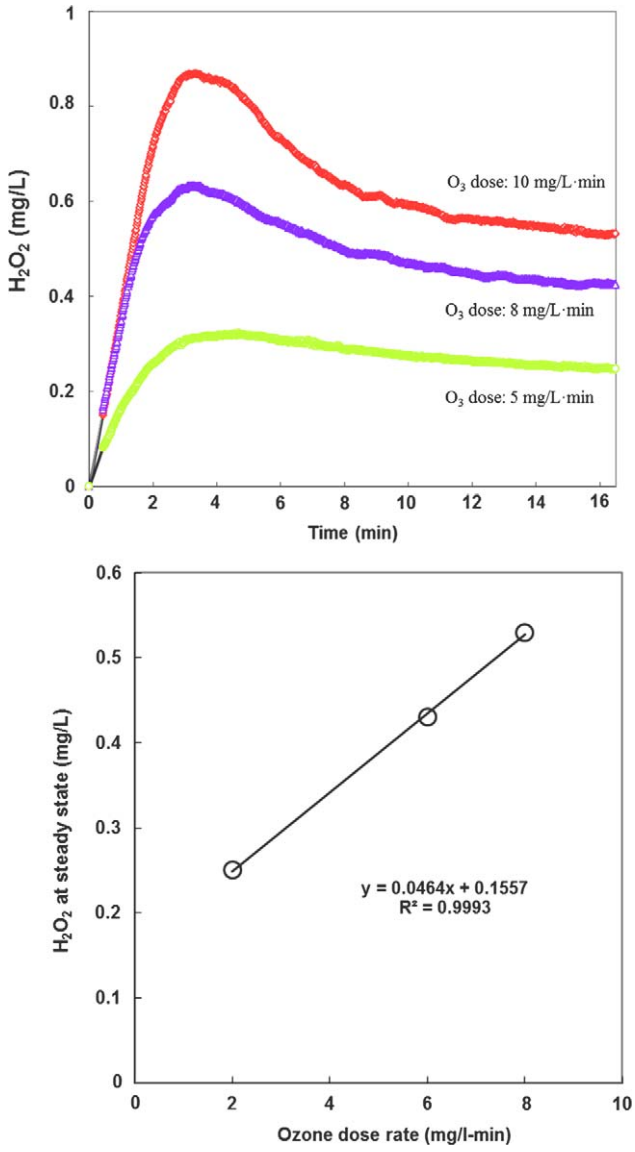


Fig. 6. Analysis of H_2O_2 in the O_3/UV process, UV intensity = 8 W/L.

3.4. Analysis of H_2O_2 during electrochemical process

The H_2O_2 formation in the electrochemical process is due to the oxidation of water that takes place at the electrode, as in the following series of equations [3]:

$$2H_2O \Leftrightarrow O_2 + 4H^+ + 4e^- \quad (6)$$

$$O_2 + 2H^+ + 2e^- \Leftrightarrow H_2O_2 \quad (7)$$

The H_2O_2 formed can convert back to water:

$$H_2O_2 + 2H^+ + 2e^- \Leftrightarrow 2H_2O \quad (8)$$

This experiment was performed to detect the H_2O_2 formed in pure water during the electrochemical process using a plate-type Ti/Pt electrode. The pH was controlled at 4 and 7 using H_2SO_4 and NaOH solutions. Fig. 7 shows the result. Under both pH conditions, the formation of H_2O_2 increased during the run time, but finally stabilized at a constant concentration. The H_2O_2 formation rate was higher at pH 7 than 4. This result might be attributable to the competitive reaction between H_2O_2 formation (Eq. (8)) and H_2O_2 degradation (Eq. (9)). Therefore, it can be concluded that increasing the H^+ concentration led to unfavorable conditions for H_2O_2 formation (Eq. (8)) compared to its degradation (Eq. (9)).

When chloride ions are present in water during the electrochemical process, hypochlorous acid (HOCl) can be formed in the water, as given by Eqs. (10) and (11) [12]:

$$2Cl^- + 2e^- \rightarrow Cl_2 \quad (9)$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+Cl^- \quad (10)$$

Therefore, the effect of HOCl on the measurement of H_2O_2 by the H_2O_2 auto-analyzer was investigated. As shown in Fig. 8, HOCl had no effect on the signal response of the H_2O_2 auto-analyzer. However, when 200 μg/L H_2O_2 was measured using the H_2O_2 auto-analyzer, the H_2O_2 concentration was immediately below half its initial level as soon as HOCl was added to the sample after approximately 4 min, and then rapidly decreased. Even though the addition of the NH_4Cl solution into the same stream, for quenching the HOCl, was performed in the same manner as that of the $Na_2S_2O_3$ solution for the quenching of ozone, the H_2O_2 concentration was only increased slightly

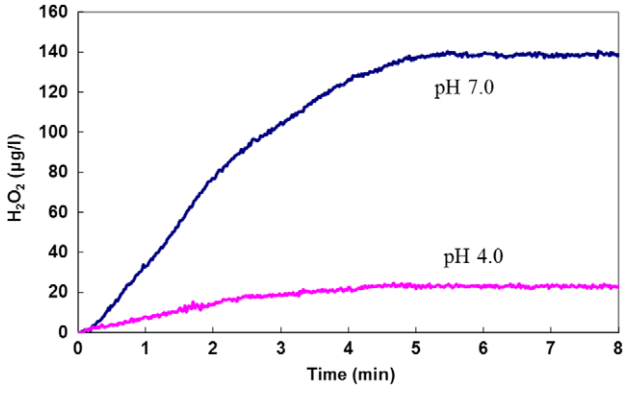


Fig. 7. Formation of H_2O_2 during the electrochemical process at pH 7.0 and 4.0.

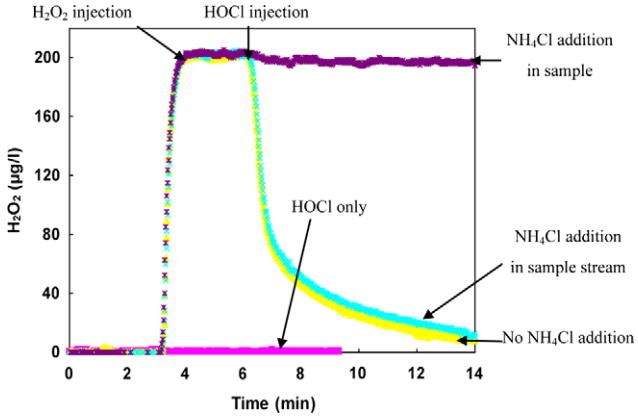


Fig. 8. H_2O_2 reduction by HOCl, $[H_2O_2]_o = 50$ μg/L, $[HOCl]_o = 1$ mg/L, $[NH_4Cl]_o = 100$ mg/L.

compared with that of no addition. This result indicates that the H_2O_2 auto-analyzer can measure the pattern of H_2O_2 decayed due to HOCl, but it is impossible for this instrument to measure the H_2O_2 formation pattern during the electrochemical process in the presence of Cl^- leading to the formation of HOCl. In an effort to separate and detect the H_2O_2, the NH_4Cl solution was added to the sample itself. When the NH_4Cl solution was present in the sample, the H_2O_2 concentration rarely decreased.

As shown in Fig. 9, to investigate the effect of NH_4Cl solution on the measurement of H_2O_2, a few samples, under various conditions, were analyzed with the H_2O_2 auto-analyzer. Sample 2 (H_2O_2 in NH_4Cl solution) showed almost the same signal response as Sample 1 (H_2O_2 in DW), indicating that the NH_4Cl solution did not affect the H_2O_2 measurement at all. Sample 4 (H_2O_2 + HOCl (1 mg/L) in

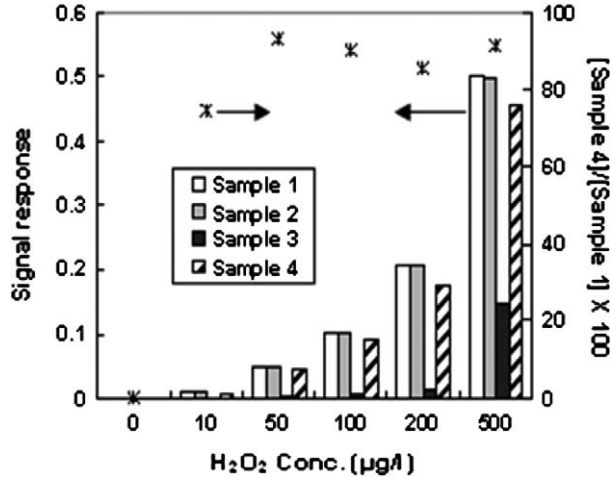


Fig. 9. Measurement of H_2O_2 in the presence of HOCl and/or NH_4Cl during the electrochemical process, $[HOCl]_o = 5$ mg/L, $[NH_4Cl]_o = 100$ mg/L.

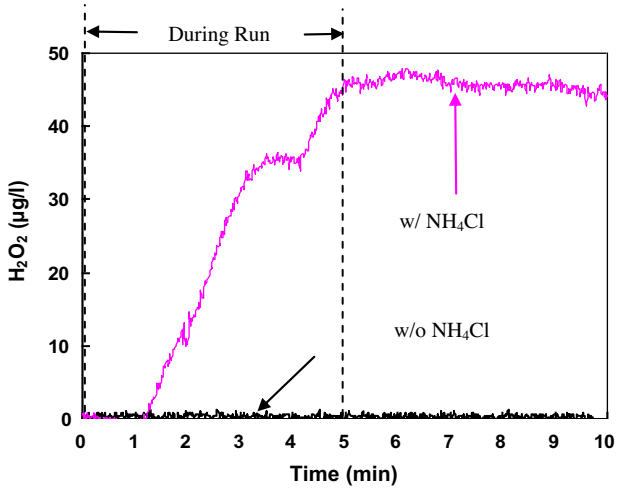


Fig. 10. Analysis of H_2O_2 during the electrochemical process of tap water, pH = 7.5, $[NH_4Cl]_o$ = 100 mg/L, $[Cl^-]$= 8.5 mg/L.

NH_4Cl solution) showed a level adjacent to that of Sample 1, overcoming the H_2O_2 degradation seen in Sample 3 (H_2O_2 + HOCl (1 mg/L) in DW). The symbol (*) represents the value calculated by (Sample 4)/(Sample 1) × 100, with a reproducibility for Sample 4 of 85–93% within the concentration range 50–500 H_2O_2 µg/L (75% in 10 µg/L H_2O_2).

Fig. 10 shows the H_2O_2 concentrations present in tap water collected from Wonju city, Korea, both with and without NH_4Cl addition during the electrochemical process. For a run time of 5 min, no H_2O_2 was detected in the tap water without the addition of NH_4Cl, but the formation of H_2O_2 was observed with the addition of NH_4Cl. This confirmed that the H_2O_2 auto-analyzer could be effectively used for measuring the H_2O_2 formed in the electrochemical process.

4. Conclusions

This study focused on the development and testing of an H_2O_2 auto-analyzer for measuring H_2O_2 using a fluorometric FIA method with peroxidase. The standard deviation and detection limit obtained were 0.5 and 1.6 µg/L, respectively. No effects of the additions of $Na_2S_2O_3$ and NH_4Cl to the sample stream, for the quenching of residual ozone and HOCl, respectively, were observed on the measurement of H_2O_2. To test the H_2O_2 auto-analyzer, the H_2O_2 removal and formation patterns in the UV/H_2O_2 and ozone/UV processes, respectively, were investigated, with the results confirming that the H_2O_2 auto-analyzer could effectively measure the residual H_2O_2 in each process. The analysis of H_2O_2 in the electrochemical process was successfully performed, but in the presence of chloride ions, leading to the formation of HOCl, no H_2O_2 formation was observed, due to the very fast reaction rate between the H_2O_2 and HOCl. The addition of NH_4Cl solution into the sample made the measurement of H_2O_2 possible, by inhibiting the reaction with HOCl. The reproducibility of the sample measurements, including H_2O_2 and HOCl (1 mg/L) in NH_4Cl solution, was 85–93% within the H_2O_2 concentration range 50–500 µg/L.

Acknowledgements

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