Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2016.1172030

57 (2016) 27138–27143
December

Taylor & Francis
Taylor & Francis Group

Probable problems in the analysis of chemical oxygen demand of wastewaters treated by advanced oxidation process: residual H_2O_2 and acidity of the treated waters

Xiao Ye, Takeyoshi Okajima, Takeo Ohsaka*

Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259-G1-5 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan, emails: ye.x.aa@echem.titech.ac.jp (X. Ye), okajima@echem.titech.ac.jp (T. Okajima), Tel. +81 45 924 5404; Fax: +81 45 924 5489; email: ohsaka@echem.titech.ac.jp (T. Ohsaka)

Received 6 January 2016; Accepted 23 March 2016

ABSTRACT

The remainder of H_2O_2, which is usually used in advanced oxidation processes (AOPs) treatment of wastewaters, reacts with the oxidant (e.g. $KMnO_4$) utilized in chemical oxygen demand (COD) analysis, resulting in the overestimation in COD analysis. The residual H_2O_2 was decomposed successfully using Na_2CO_3 as catalyst under a heated condition (95°C for 2 h) and consequently the H_2O_2-derived COD, typically after the AOPs treatment of oxalic acid solution using peroxone (H_2O_2−O_3 mixture), could be brought to below the detection limit. However, the overdose of acid (H_2SO_4) added for neutralizing the Na_2CO_3-containing sample solution after the decomposition of residual H_2O_2 was found to cause new interference in COD analysis. It is considered that in strong acid solutions the decomposition of $KMnO_4$ may be accelerated during COD analysis, leading to its overestimation. The results suggest that a suitable decomposition of residual H_2O_2 (e.g. after AOPs treatment) as well as a suitable control of acidity (to neutrality) of the sample solution subjected to COD analysis is essentially necessary for the correct COD estimation.

Keywords: Na_2CO_3; Oxalic acid; COD; H_2O_2 interference; Water treatment

1. Introduction

In so-called advanced oxidation processes (AOPs) treatment of wastewaters, hydrogen peroxide (H_2O_2) is commonly utilized as an oxidizing agent as well as hydroxyl radical (·OH) source [1–7]. Thus, the treated water usually contains residual H_2O_2 and it may interfere with the chemical oxygen demand (COD) analysis [8–12], which is one of the most commonly used parameters or the characterization of wastewaters because residual H_2O_2 reacts with the oxidant utilized in COD analysis (typically $K_2Cr_2O_7$ and $KMnO_4$). That is, any residual H_2O_2 in the treated water represents the corresponding COD value. Therefore, the preferable COD analysis of residual H_2O_2 in the treated water has to be carried out [8–10] or residual H_2O_2 needs to be removed suitably from the treated water prior to COD analysis [11,12]. Recently, Wu and Englehardt [11] have proposed a new method for removal of H_2O_2 interference in the analysis of COD, i.e. they have successfully removed residual H_2O_2 in wastewater prior to COD analysis by adding sodium carbonate (Na_2CO_3) as an efficient catalyst for the

---

*Corresponding author.

disproportionation of H_2O_2 to O_2 and H_2O and heating the solution.

In a preliminary experiment regarding the AOPs treatment of the phenol-containing wastewater using the mixture of H_2O_2 and O_3 (peroxone), the COD analysis was carried out by utilizing $KMnO_4/H_2SO_4$ as the oxidant. In this case, Na_2CO_3 was utilized as catalyst to decompose the residual H_2O_2 [13] and then H_2SO_4 was added for neutralizing the Na_2CO_3-containing AOP-treated wastewater. We have found that the pH of the sample solution after the decomposition of residual H_2O_2 significantly effects the COD analysis. In this communication, we will demonstrate this point, along with a complete decomposition of residual H_2O_2, using H_2O_2-containing oxalic acid (OA) solution as a model solution of the wastewater treated by AOPs utilizing H_2O_2. Note that OA is one of the typical intermediates produced during the AOP treatment of phenol-containing wastewater [14,15].

2. Materials and methods

2.1. Chemicals

Sodium carbonate (Na_2CO_3) and sulfuric acid (H_2SO_4) solutions were obtained from Kanto Chemical Co., Inc. 30 wt.% hydrogen peroxide solution and OA dihydrate were provided by Wako Pure Chemical Industries Ltd. All the chemicals were of analytical grade. The deionized water (Milli-Q, Millipore, Japan) was utilized for preparing all of the solutions used in this study.

2.2. Experimental procedure

The experimental procedure of the COD analysis utilizing $KMnO_4/H_2SO_4$ (which will be hereinafter denoted as COD_{Mn} analysis) with removal of H_2O_2 interference is shown in Fig. 1. Firstly, the sample solution containing OA (0.75 mM) and H_2O_2 which was quantified to typically 90–120 mg/L was prepared. It should be noted here that such a high concentration of H_2O_2 was used typically as "residual H_2O_2" because the COD analysis is not only one of the most widely used procedures for wastewater characterization, but also a very useful technique for fundamentally studying the mechanism (and kinetics) of the AOPs of organic compounds. And in the latter case the COD analysis is usually conducted as a function of the reaction time of AOPs (typically over the period of several minutes to several hours) and the residual H_2O_2 concentration at its initial stage is significantly high (typically several 10s to 100s of ppm). Then, 5.0 ml of the sample solution was transferred to a container and then 20.0 ml Na_2CO_3 solution (0.45 M) was added for H_2O_2 removal [11]. The mixed solution of H_2O_2 and Na_2CO_3 was kept at 95℃ for 2 h in a water bath. After this heat treatment, the residual Na_2CO_3 was neutralized with a certain amount of H_2SO_4 solution (2.5 M) and the total volume of the treated solution was adjusted to 50 ml with deionized water, meaning that the sample solution was 10 times diluted (dilution factor = 10). Immediately after that, the values of COD_{Mn}, pH and H_2O_2 concentration of the thus-diluted treated solutions were measured at 25 ± 1℃. The COD of the sample solution (COD^S_{Mn}) was calculated finally as $10 \times COD_{Mn}$.

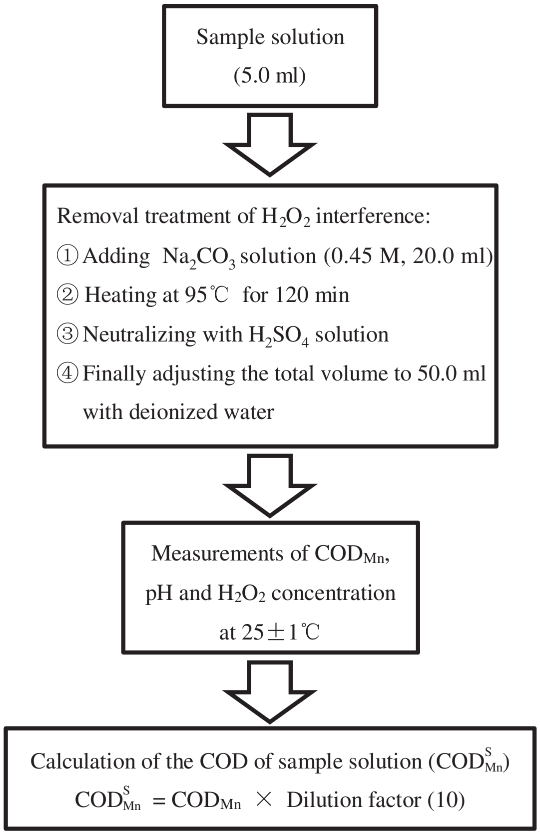

Fig. 1. Experimental procedure of COD_{Mn} analysis with removal of H_2O_2 interference.

2.3. Analytical methods

The H_2O_2 concentration of each sample solution was monitored using a photometric hydrogen peroxide measuring method (Merck KGaA, Germany), which has a detection range of 0.25–20.0 mg/L H_2O_2. COD was determined by a spectrophotometric $KMnO_4$ oxidation method [16] with a detection range of 0.5–13.0 mg/L using a spectrophotometer (PhotoLab®

6600 UV–vis, WTW, Germany). The pH of sample solution was measured with a pH meter (IM-55G, TOA Electronics Ltd, Japan).

3. Results and discussion

The preliminary experiments of minimizing H_2O_2 interference in COD_{Mn}^{S} analysis using Na_2CO_3 and heating (95℃ for 2 h) were conducted using OA-containing sample solutions and the obtained COD values are shown in Fig. 2. The initial COD_{Mn}^{S} value of the OA solution (0.75 mM) is 13.3 mg/L, while that of the mixed solution containing OA (0.75 mM) and H_2O_2 (105 mg/L) is 91.0 mg/L. Apparently, the COD_{Mn}^{S} was significantly overestimated due to the coexistence of H_2O_2, because the residual H_2O_2 could react with $KMnO_4$ utilized as the oxidant in the COD_{Mn}^{S} analysis and consume $KMnO_4$, as expressed by the following reaction [17]:

$$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5O_2 \qquad (1)$$

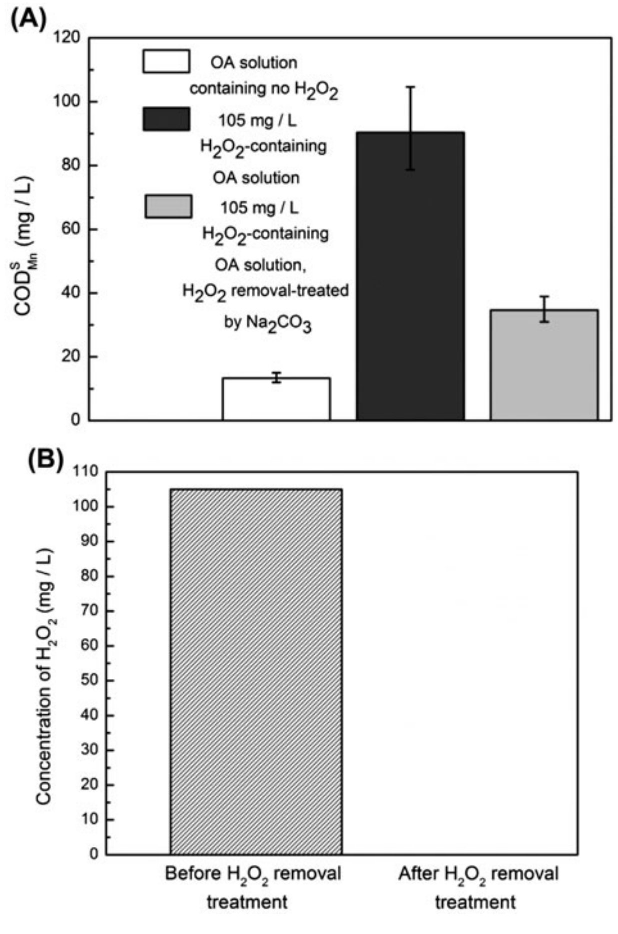

Fig. 2. (A) Comparison of COD_{Mn}^{S} values of 0.75 mM OA solutions containing no H_2O_2 and 105 mg/L H_2O_2 and further with H_2O_2 removal treatment by Na_2CO_3. The H_2O_2 removal treatment by Na_2CO_3 was conducted in the following way: 9.0 mmol Na_2CO_3 was added to the OA solution and then the solution was heat-treated at 95℃ for 2 h and after that 17.5 mmol H_2SO_4 was added into the treated solution (the final pH is 0.85) before the COD_{Mn} analysis and (B) Concentrations of residual H_2O_2 before and after H_2O_2 removal.

By the 2-h heat treatment of the Na_2CO_3-containing OA solution, the concentration of H_2O_2 was reduced below the detection limit (0.25 mg/L) of H_2O_2 in this study (Fig. 2(B)). However, as can be readily seen from the comparison of the COD_{Mn}^{S} values of the untreated OA solution and the Na_2CO_3-containing OA solution into which H_2SO_4 was added before the COD_{Mn} assay, the latter solution gave the larger COD_{Mn}^{S} value than the former one (i.e. twice), suggesting the consumption of $KMnO_4$ by any reason(s) in the case of the treated solution.

$KMnO_4$ is known to decompose in strong acidic media [18], while the COD analysis was carried out under an acidic condition: in the preliminary experiments, in order to remove (neutralize) the residual Na_2CO_3, 17.5 mmol H_2SO_4 was added to the Na_2CO_3-treated solution and its final pH was about 0.85. The results probably suggest that the acidic sample itself could lead to the overestimation in the COD analysis. Thus, the effect of extra acid addition on the COD analysis was examined, as described below.

3.1. Effect of extra acid addition on COD measurement

The sample solutions containing OA and various concentrations of H_2O_2 were prepared and their COD_{Mn}^{S} values were measured. As mentioned above, at a glance, we can see from Fig. 3(A) that the COD_{Mn}^{S} becomes larger with increasing the concentration of H_2O_2. In addition, the COD_{Mn}^{S} of each sample with 0.5 M H_2SO_4 addition (30 ml) was also measured (Fig. 3(A)). Also, it is obvious that the addition of H_2SO_4 leads to the overestimation in COD analysis. Fig. 2(B) shows the correlation between the COD_{Mn}^{S} and the concentration of H_2SO_4 for 0.75 mM OA solutions containing 113 mg/L H_2O_2 and different concentrations of H_2SO_4. The COD_{Mn}^{S} increases almost linearly with increasing the H_2SO_4 concentration, namely, the degree of the H_2SO_4 interference in COD_{Mn}^{S} measurement is proportional to its concentration. In addition, Fig. 3(C) demonstrates that H_2SO_4 itself "gives" the COD value depending on its concentration. The observation of such "abnormal" phenomena could be explained by the existence of

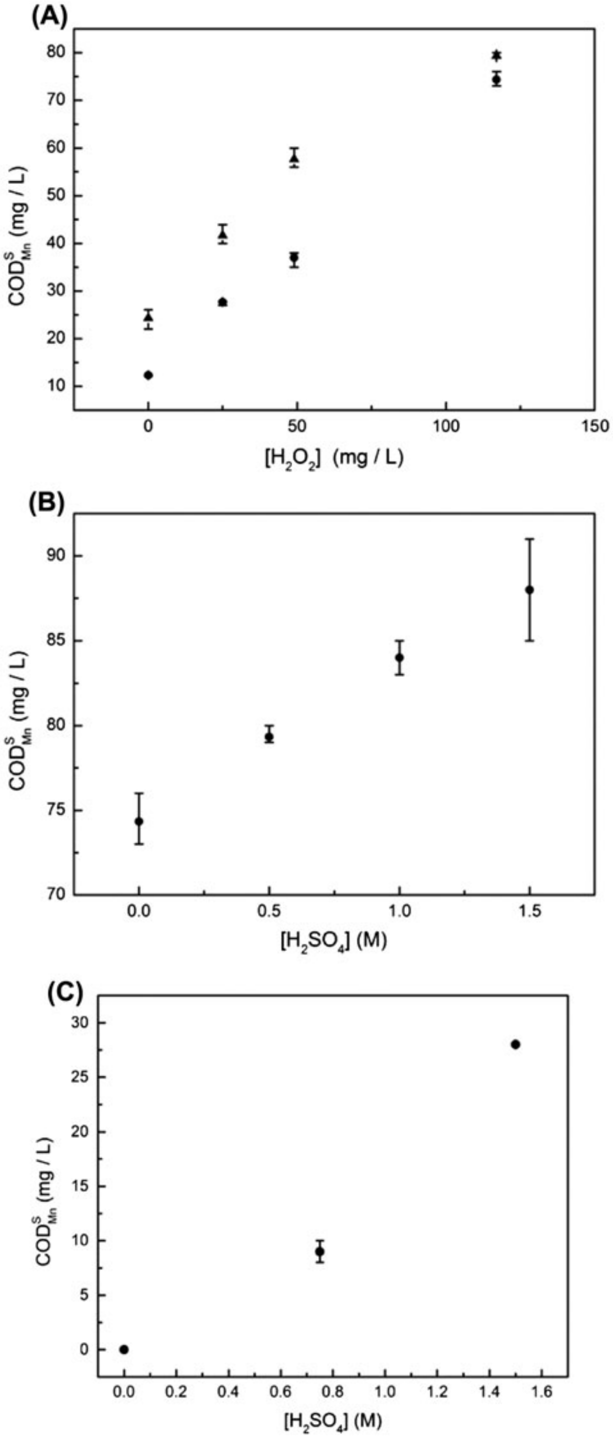

Fig. 3. Effect of acidity on $\mathrm{COD}_{\mathrm{Mn}}^{\mathrm{S}}$ analysis of different solutions: (A) Solutions containing 0.75 mM OA and various concentrations of H_2O_2 in the absence (●) and the presence (▲) of 0.5 M H_2SO_4, (B) Solutions containing 0.75 mM OA, 113 mg/L H_2O_2 and different concentrations of H_2SO_4, and (C) H_2SO_4 solutions of different concentrations.

impurities which could be oxidized by $KMnO_4$ used as the oxidant in $\mathrm{COD}_{\mathrm{Mn}}^{\mathrm{S}}$ analysis and/or the decomposition of $KMnO_4$ in strong acidic media. All the containers which were cleaned carefully by deionized water several times were used, and the H_2SO_4 solution used was of analytical grade, and all the sample solutions were utilized immediately after their preparation. Thus, we may assume that the above-mentioned "abnormal" phenomena originating from the addition of H_2SO_4 could be due to the decomposition of $KMnO_4$ in strong acidic media.

3.2. Optimization of H_2O_2 removal by Na_2CO_3

7.5, 12.5, and 17.5 mmol H_2SO_4 was added into the 0.45 M Na_2CO_3 containing solutions (20.0 ml) to neutralize them and their COD and pH were measured, and the results are shown in Fig. 4(A). This figure indicates that the 7.5 mmol H_2SO_4-added Na_2CO_3 neutral solution (X, pH 7.31) gave the $\mathrm{COD}_{\mathrm{Mn}}^{\mathrm{S}}$ value of 0, while the $\mathrm{COD}_{\mathrm{Mn}}^{\mathrm{S}}$ values could be evaluated significantly in the 12.5–17.5 mmol H_2SO_4-added Na_2CO_3 solutions (Y (pH 1.34) and Z (pH 0.79)) and in this case the latter gave the larger $\mathrm{COD}_{\mathrm{Mn}}^{\mathrm{S}}$ value than the former. If there are any impurities which could be oxidized by $KMnO_4$ in the H_2SO_4 solution, then some value of $\mathrm{COD}_{\mathrm{Mn}}^{\mathrm{S}}$ (more than 0) should be obtained also for the neutral solution (X). Thus, again, Fig. 4(A) demonstrates that the acidity of the solution subjected to the $\mathrm{COD}_{\mathrm{Mn}}^{\mathrm{S}}$ analysis might cause the interference in its analysis.

Next, the effects of heating and neutralization of sample solution on its COD analysis were investigated with OA-containing solutions (Fig. 4(B)). The solution A contained only 0.75 mM OA, and the others (B–G) contained 0.75 mM OA and 9.0 mmol Na_2CO_3 and in addition 7.5, 12.5, or 17.5 mmol H_2SO_4 was added. After H_2SO_4 addition, solutions C, E, and G were heated at 95℃ for 2 h. In strong acidic solutions (D and F) the $\mathrm{COD}_{\mathrm{Mn}}^{\mathrm{S}}$ values are found to be overestimated by comparing with that of solution A. After the heat treatment the overestimation of $\mathrm{COD}_{\mathrm{Mn}}^{\mathrm{S}}$ was also observed in acidic solutions (see E and G), but not in the neutral solution (C). The results demonstrate that the correct $\mathrm{COD}_{\mathrm{Mn}}$ analysis cannot be achieved for strong acid solutions. In other words, the sample solutions subjected to $\mathrm{COD}_{\mathrm{Mn}}$ analysis are required to be neutral solutions or weak acids.

3.3. Removal of H_2O_2 interference in $\mathrm{COD}_{\mathrm{Mn}}^{\mathrm{S}}$ analysis

The solutions containing 0.75, 1.57, or 3.09 mM OA and 118 mg/L H_2O_2 were prepared for examining the

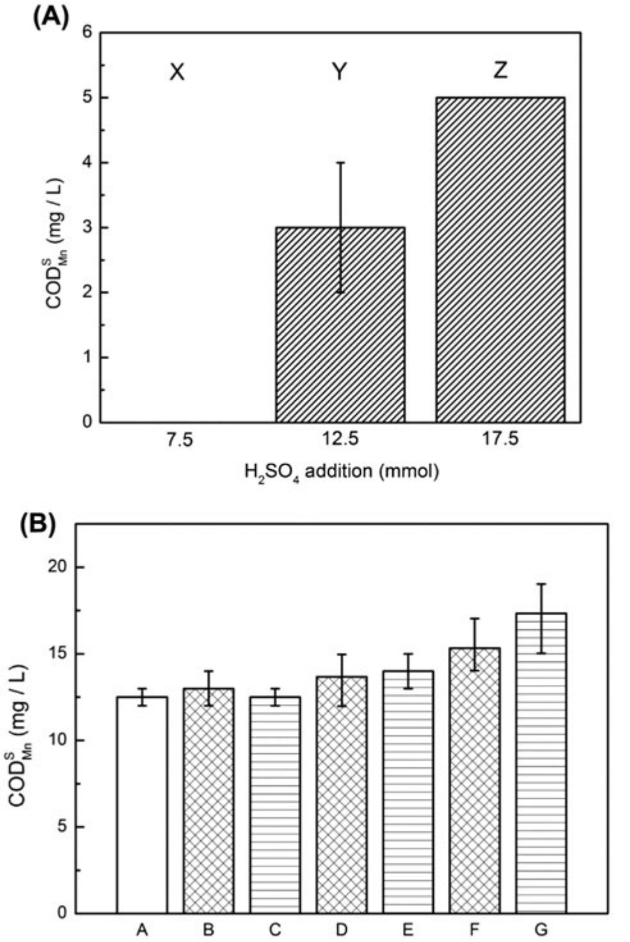

Fig. 4. (A) Comparison of COD^S_{Mn} values of 0.45 mM Na_2CO_3 solutions (20 ml) into which H_2SO_4 was added: 7.5 (X), 12.5 (Y), and 17.5 (Z) mmol. The final pH value: (X) 7.31, (Y) 1.34, and (Z) 0.79 and (B) Comparison of COD^S_{Mn} values of 0.75 mM OA solutions (5 ml) into which Na_2CO_3 was added: (A) 0 and (B–G) 9.0 mmol and also H_2SO_4 was added: (A) 0, (B, C) 7.5, (D, E) 12.5, and (F, G) 17.5 mmol. pH of OA solutions: (A) 3.08, (B) 6.94, (C) 7.19, (D) 1.30, (E) 1.27, (F) 0.81, and (G) 0.80. Solutions (A, B, D, F) were not heat-treated, while solutions (C, E, F) were heat-treated at 95˚C for 2 h.

treatment for H_2O_2 removal. After adding Na_2CO_3 and heating at 95˚C for 2 h, the solutions were neutralized (pH 7) by adding H_2SO_4. Finally, the COD^S_{Mn} value of each solution was measured. The results are given in Fig. 5. The COD^S_{Mn} value of the OA solution containing no H_2O_2 increases with increasing its concentration as expected and the presence of H_2O_2 results in the much larger COD^S_{Mn}, compared with the case of its absence, i.e. the interference of H_2O_2 is considerable and cannot be ignored as mentioned above. By treating with Na_2CO_3 and heating for decomposing H_2O_2, the interference of H_2O_2 could be eliminated effectively and as expected, the COD^S_{Mn} values of the neutralized solutions were the same as those obtained for OA solutions containing no H_2O_2 within the experimental error.

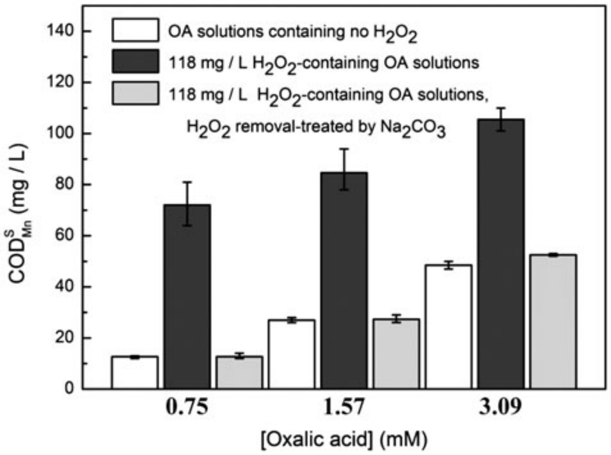

Fig. 5. Comparison of COD^S_{Mn} values of 0.75, 1.57, and 3.09 mM OA solutions (5.0 ml) containing no H_2O_2 and 118 mg/L H_2O_2 and further with H_2O_2 removal treatment by Na_2CO_3. The H_2O_2 removal treatment by Na_2CO_3 was carried out in the following way: 9.0 mmol Na_2CO_3 was added into each OA solution and then the solution was heat-treated at 95˚C for 2 h. After that, 7.5 mmol H_2SO_4 was added into the treated solution (30.0 ml, pH 6.83–7.32) before COD_{Mn} measurements.

4. Conclusions

Using Na_2CO_3 as catalyst for H_2O_2 decomposition under a heated condition, the interference of H_2O_2, which remains, e.g. after AOPs treatment, in COD analysis could be eliminated successfully. However, even without H_2O_2 interference, it was found that a strong acidic solution itself still leads to the overestimation in COD analysis, probably because in strong acid solutions, the decomposition of $KMnO_4$ may be accelerated during the COD analysis. A suitable decomposition of residual H_2O_2 in the sample solution subjected to COD assay as well as a suitable control of its pH to neutrality is required to do the COD analysis correctly.

Acknowledgments

The present work was financially supported by a Grant-in-Aid for Scientific Research to T.O. from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), Japan and from the Tokyo Institute of Technology program for Leading Graduate

Schools "Academy for Co-creative Education of Environment and Energy Science (ACEEES)". X.Y. gratefully acknowledges the Yoneyama Rotary Club for a scholarship.

References

[1] N. De la Cruz, L. Esquius, D. Grandjean, A. Magnet, A. Tungler, L.F. de Alencastro, C. Pulgarín, Degradation of emergent contaminants by UV, UV/H_2O_2 and neutral photo-Fenton at pilot scale in a domestic wastewater treatment plant, Water Res. 47 (2013) 5836–5845.

[2] R. Zhang, P. Sun, T.H. Boyer, L. Zhao, C. Huang, Degradation of pharmaceuticals and metabolite in synthetic human urine by UV, UV/H_2O_2 and UV/PDS, Environ. Sci. Technol. 49 (2015) 3056–3066.

[3] W. Qin, Y. Song, Y. Dai, G. Qiu, M. Ren, P. Zeng, Treatment of berberine hydrochloride pharmaceutical wastewater by O_3/UV/H_2O_2 advanced oxidation process, Environ. Earth Sci. 73 (2015) 4939–4946.

[4] H. Wang, S. Yuan, J. Zhan, Y. Wang, G. Yu, S. Deng, J. Huang, B. Wang, Mechanisms of enhanced total organic carbon elimination from oxalic acid solutions by electro-peroxone process, Water Res. 80 (2015) 20–29.

[5] G.A. De Vera, D. Stalter, W. Gernjak, H.S. Weinberg, J. Keller, M.J. Farré, Towards reducing DBP formation potential of drinking water by favouring direct ozone over hydroxyl radical reactions during ozonation, Water Res. 87 (2015) 49–58.

[6] A. Fischbacher, J. von Sonntag, C. von Sonntag, T.C. Schmidt, The •OH radical yield in the $H_2O_2 + O_3$ (Peroxone) reaction, Environ. Sci. Technol. 47 (2013) 9959–9964.

[7] V. Romero, S. Acevedo, P. Marco, J. Giménez, S. Esplugas, Enhancement of Fenton and photo-Fenton processes at initial circumneutral pH for the degradation of the β-blocker metoprolol, Water Res. 88 (2016) 449–457.

[8] E. Lee, H. Lee, Y.K. Kim, K. Sohn, K. Lee, Hydrogen peroxide interference in chemical oxygen demand during ozone based advanced oxidation of anaerobically digested livestock wastewater, Int. J. Environ. Sci. Technol. 8 (2011) 381–388.

[9] I. Talinli, G.K. Anderson, Interference of hydrogen peroxide on the standard cod test, Water Res. 26 (1992) 107–110.

[10] Y.W. Kang, M.J. Cho, K.Y. Hwang, Correction of hydrogen peroxide interference on standard chemical oxygen demand test, Water Res. 33 (1999) 1247–1251.

[11] T. Wu, J.D. Englehardt, A new method for removal of hydrogen peroxide interference in the analysis of chemical oxygen demand, Environ. Sci. Technol. 46 (2012) 2291–2298.

[12] Y. Wang, W. Li, A. Irini, A novel and quick method to avoid H_2O_2 interference on COD measurement in Fenton system by Na_2SO_3 reduction and O_2 oxidation, Water Sci. Technol. 68 (2013) 1529–1535.

[13] H.U. Suess, M. Janik, On the Decomposition of Hydrogen Peroxide Via the Peroxocarbonic Acid Anion, Technical Association of the Pulp and Paper Industry of Southern Africa/TAPPSA, Kloof, Durban, 2009.

[14] M.K. Ramseier, U. von Gunten, Mechanisms of phenol ozonation—Kinetics of formation of primary and secondary reaction products, Ozone Sci. Eng. 31 (2009) 201–215.

[15] A. Leitzke, E. Reisz, R. Flyunt, C. von Sonntag, The reactions of ozone with cinnamic acids: Formation and decay of 2-hydroperoxy-2-hydroxyacetic acid, J. Chem. Soc. Perkin Trans. 2 2 (2001) 793–797.

[16] S. Ishii, K. Urano, Remarkable improvement of JIS COD_{Mn} by an effective colorimetric method, J. Jpn. Soc. Water Environ. 22 (1999) 301–307.

[17] N.V. Klassen, D. Marchington, H.C.E. McGowan, H_2O_2 determination by the I_3^- method and by $KMnO_4$ titration, Anal. Chem. 66 (1994) 2921–2925.

[18] Y. Nimura, K. Itagaki, K. Nanba, Colorimetric determination of COD(Mn) using hydrogen peroxide, Nippon Suisan Gakkaishi 58 (1992) 1129–1137.