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Treatment of Organic Wastewater by Supercritical Water Oxidation

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Supercritical water oxidation (SCWO) is a robust process in removing the hazardous organic wastes. Therefore, it is necessary to improve the SCWO process to eliminate the organic hazardous wastes. In present work, SCWO process used cyclohexylamine (CHA) as the organic chemical model. The co-oxidizers consisted of propylene glycol (PG), methanol and the oxygen source was hydrogen peroxide. The experiments were conducted using at a laboratory scale. A plug-flow reactor was utilized at different operating temperatures ranging from 425 to 525 ºC, the critical pressure was 25 MPa. At working temperatures, the co-oxidizer and the oxidant ratios were also investigated . The results indicated that the temperature had an impact on the removal efficiency of cyclohexylamine. The maximum total organic carbon removal (TOC) in the presence of propylene glycol was achieved with 98% at 525 ºC and the residence time was 14 s.

Keywords: Supercritical water oxidation, Cyclohexylamine, Dihydric alcohol, Monohydric alcohol, Organic wastewater.

INTRODUCTION

Cyclohexylamine (CHA) is considered as an essential organic intermediate used in different manufacturing industries of dyes, insecticides, antiseptics and plasticizers. Cyclohexylamine has received increased attention due to its toxicity and is regarded as a weak carcinogen [1]. Several biological treatments was reported, but the findings are inadequate, as limited microorganisms are employed to remove carcinogenic cyclohexylamine from the wastewaters [2,3].

Supercritical water oxidation (SCWO) is regarded as green technology in removing hazardous organic wastes. Pure water is fully miscible with gases, organic wastes and its chemical properties are suitable for dissolving them. The supercritical water phase takes place at 374 ºC and 22.1 MPa. The effect of the hydrogen bonds becomes minimal due to decreasing their density in the homogenous supercritical phase, giving pure water unique properties [4-6]. As a result, the dielectric constant is very low and the organic waste's solubility is higher than in ambient conditions. In addition, the residence time is short as the kinetic reaction is fast. Although the supercritical water method is suitable for dissolving organic wastes, organic salts accumulate on the inner wall of the reactor. As a result, this issue influences the use of SCWO on the commercial scale [7]. Another problem is the corrosion formed, since aggressive materials attack the reactor's inner wall and the heat exchanger [8,9].

The disposal of nitrogen containing wastes is a significant problem [10]. However, the destruction of nitrogen containing wastes by SCWO removes ammonia effectively. Nitrate is another byproduct that requires complete oxidation to be converted to nitrogen [11-13]. Several researchers applied the SCWO process in nitrogen containing compounds, leading to significant 99.99% removal of the nitrogenous wastes [14-16]. Various methods are also cited in the literature to enhance the SCWO process using monohydric alcohol [17]. In addition, various co-fuels have been applied to improve the efficiency of removing nitrogenous wastes, such as methanol, ethanol and isopropyl alcohol [18-23]. Various catalysts have also been employed to enhance the destruction of organic wastes. For example, Ni/Al_2O_3 was used to improve the efficiency of removing the landfill leachate [24], whereas MnO_2/CeO_2 [25] was used to increase the ammonia conversion.

This study investigates the influence of monohydric and dihydric alcohols on the efficiency of removing organic substances and their byproducts. The effect of temperature and oxidants ratio on the removal of organic compounds in the presence and absence of alcohol were also investigated.

EXPERIMENTAL

Cyclohexylamine (≥ 99.9%) was used as a nitrogen containing hazardous substance model whereas propylene glycol (≥ 99.5%) and methanol (≥ 99.9%) were used as co-fuels. The source of oxygen was hydrogen peroxide (≥ 30%). All chemical substances were purchased from Sigma-Aldrich,U.K.

Experimental procedure: Both co-fuels and organic solvent were pumped *via* two HPLC pumps (Jasco/PU-2086) to 25 MPa. Reactants were preheated *via* coiled-pipe heaters to a required temperature and then two streams were mixed at an entrance of the reactor. The length of reactor was 9 m (SS-316/316L) and an inner diameter was 1.397 mm. The effluent of reactor was cooled in a cooler then the pressure of produced stream was depressurized through a manual back pressure regulator (BP66, GO). The effluent was separated into liquid and gas streams. The liquid samples were preserved for the total organic carbon analysis. Additionally, methanol or propylene glycol was premixed with cyclohexylamine before being pumped into the SCWO system at the required concentration. The reactor's input and output temperatures were measured by thermocouples.

Experimental conditions: Table-1 shows the experimental conditions at different temperatures, where the initial cyclohexylamine (CHA) concentration was 4 mM and the molar ratio [co-oxidizer]/$[CHA]_o$ was 1.

TABLE-1
EXPERIMENTAL CONDITIONS

Variable	Experimental values
Temperature (°C)	425, 450, 475, 500, 525
Oxidant ratio (nSR)	0.75, 1, 1.5, 2
Initial CHA concentration (mM)	2, 4, 6, 8
$[PG]/[CHA]_o$ ratio	0.5, 1, 1.5, 2, 2.5, 3
$[Methanol]/[CHA]_o$ ratio	0.5, 1, 1.5, 2, 2.5

All the experiments were conducted at 25 MPa. In this work, the main conditions were initial concentration of CHA = 4 mM; temperature: 425 ºC; the mixing ratio co-oxidizer and CHA is 1:1 and the stoichiometric ratio of the oxidant dosage (nSR) is 1.0. The amount of oxygen required for the decomposition of cyclohexylamine (CHA) was calculated using eqns. 1-3:

$$C_6H_{13}N + 9.25O_2 \longrightarrow 6CO_2 + 6.5H_2O + 0.5N_2 \quad (1)$$

$$C_3H_8O_2 + 4O_2 \longrightarrow 3CO_2 + 4H_2O \quad (2)$$

$$CH_3OH + 1.5O_2 \longrightarrow CO_2 + 2H_2O \quad (3)$$

The stoichiometric ratio (SR) is the molar flow rate of oxygen delivered to achieve the cyclohexylamine decomposition. In Table-1, n refers to the multiples of SR used in the reaction. Hence, $n > 1$ is oxygen excess, $n < 1$ is oxygen deficiency and $n = 1$ refers to the stoichiometric amount of oxygen.

Water was formed ≥ 99%, since the thermodynamic properties of water under supercritical conditions were applied to the relevant calculations. As the furnace was isothermal, it was assumed that the thermodynamic properties of water remained the same inside the reactor. Each residence time was calculated based on the total flow rate (oxidant and organic) and the reactor's volume in different supercritical conditions.

RESULTS AND DISCUSSION

Impact of operating temperature: Experimental results were obtained for temperatures ranging from 425 to 525 ºC at an initial concentration of 4 mM (CHA). The efficiency of total organic carbon (TOC) removal improved as the temperature increased and also raised the reaction rate. These results agreed with the several comparative studies [26-29]. In this study, the TOC removal of cyclohexylamine reached 93.6% without fuel at 525 ºC and the residence time was 14 s. According to Al-Duri *et al.* [30], the oxidation of alcohol under supercritical conditions generates free radicals, which in turn accelerate the reaction rate.

Removal efficiency of TOC: The efficiency removal of of TOC improved with the use of propylene glycol. At 10 s, TOC conversion increased from 83.8% at 425 ºC to 96.8% at 525 ºC (Fig. 1). Unfortunately, influence of methanol on the TOC conversion was limited. These results confirmed that two hydroxyl groups had a better effect than a single methanol hydroxyl group. Although methanol was considered a significant co-fuel to improve the reaction rate in several studies [19, 23], however, others researchers also found that the methanol's influence was not of interest [31].

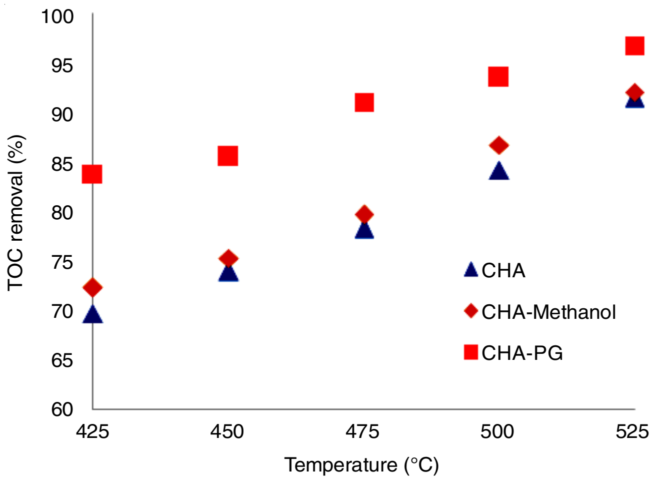

Fig. 1. Effect of temperature on removal efficiency of TOC, at time 10 s, 4 mM cyclohexylamine, 4 mM methanol, 4 mM PG and SR of 1

Yield of nitrogen species: Fig. 2 represents the influence of the operating temperatures on the yield nitrogen species. The primary byproducts of nitrogen containing organic compounds are the undesirable substances. Ammonium is a main byproduct of cyclohexylamine; therefore, this result is predictable, since ammonia is considered a resistant compound and requires a high temperature for its removal under supercritical conditions [32-34]. In absence of fuel, the ammonium yield is increased with high temperature. Therefore, degradation of cyclohexylamine at high temperatures led to an increased ammonium yield. The maximum ammonium yield was 29.5%

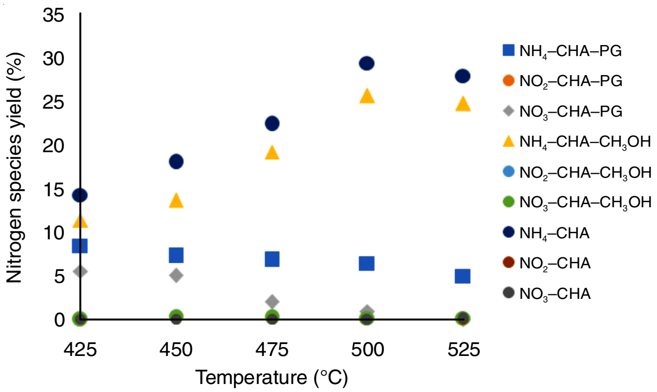

Fig. 2. Effect of temperature on the yield of nitrogen species, at time 10 s, 4 mM cyclohexylamine, 4 mM methanol, 4 mM PG and SR of 1

obtained at 500 °C and the residence time was 10 s. In addition, traces of nitrate and nitrite were apparent.

In the presence of fuel, the results were different; methanol had a limited effect on the ammonium reduction, while propylene glycol had a significant influence on removal of ammonium removal. The maximum reduction in the ammonium yield using dihydric alcohol was 4.95% at 525 °C, while the yield of ammonium using monohydric alcohol was 24.8% in the same conditions. The occurrence of nitrate in the presence of propylene glycol confirmed the oxidation of ammonia. In addition, the two hydroxyl groups contributed to the generation of more reaction pathways than a single hydroxyl group.

Removal of nitrogen (%): Isopropyl alcohol is considered a significant fuel to enhance the removal of nitrogen [22]. The enhancement of nitrogen removal using temperature was positive but limited without propylene glycol. The nitrogen removal increased from 68.6% at 425 °C to 76.8% at 525 °C in absence of co-oxidizer (Fig. 3). The removal efficiency (%) improved from 84% at 425 °C to 90% at 525 °C by using dihydric alcohol. Thus, the influence of propylene glycol is significant as compared to methanol. This enhancement confirmed that with single hydroxyl group, the effect of methanol on removal of nitrogen removal is inferior and methanol oxidation releases low heat [22].

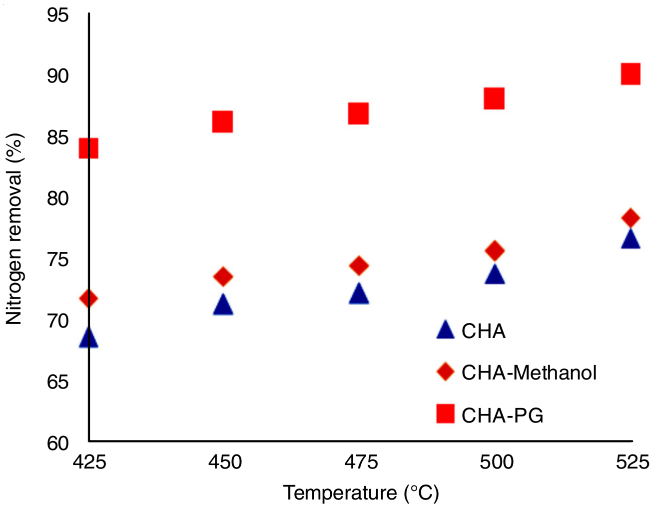

Fig. 3. Effect of temperature on nitrogen removal percentage at 10 s, 4 mM cyclohexylamine, 4 methanol, 4 mM PG and SR of 1

Impact of co-oxidizer ratio

Removal efficiency of TOC: Various oxidants were used to improve the performance of the SCWO process. Most of the studies applied monohydric alcohol as a co-oxidizer, such as methanol, ethanol and isopropyl alcohol. According to several studies [30,35], the SCWO process is improved when a fuel ratio is included. In present study, the efficiency of TOC removal was increased by increasing the co-oxidizer ratio. The TOC removal reached 80.7% at a co-oxidizer ratio of 0.5 at 425 °C. A low concentration of propylene glycol led to this result and confirmed the role of dihydric alcohol. The effect of methanol was negligible in the same conditions. This result demonstrated that the single hydroxyl group in methanol has a limited influence on the generation of free radicals. However, a high concentration of methanol would enhance the performance of the SCWO process. At the co-oxidizer ratio of 2.5, TOC conversion increased from 78% with methanol to 91% with propylene glycol (Fig. 4). A simple comparison between the effects of dihydric alcohol and monohydric alcohol showed that a low concentration of propylene glycol at the ratio of 0.5 influenced TOC conversion better than a high concentration of methanol at the ratio of 2.5.

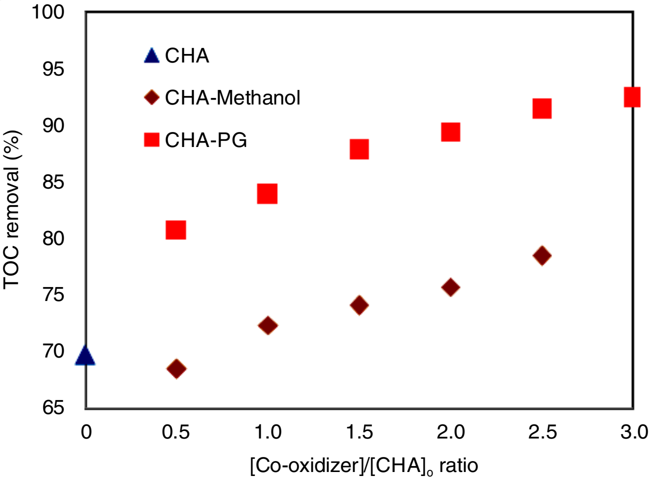

Fig. 4. Effect of co-oxidizer ratio on the TOC removal percentage at 425 °C, 4 mM cyclohexylamine, 10 s and SR of 1

Yield of nitrogen species: Fig. 5 demonstrates the positive influence of the co-oxidizer ratio on the nitrogen byproducts. The effect of propylene glycol and methanol was positive, while the ammonium yield decreased with an increased co-oxidizer ratio. The influence of methanol on the ammonium yield occurred at the co-oxidizer ratio of 1, while the significant effect of propylene glycol on the ammonium yield appeared at the ratio of 0.5. Using methanol, ammonium yield (%) decreased from 14% to 7% at the co-oxidizer ratio of 0.5 and 2.5, respectively. In same context, the ammonium yield decreased to 4.95% at the ratio of 2.5 using propylene glycol. The existence of nitrate in presence of dihydric alcohol further confirmed the oxidation of ammonia into N_2 and nitrate [36].

Removal of nitrogen (%): The effect of co-oxidizer ratio on TOC conversion and nitrogen species was significant in the presence of dihydric alcohol. The removal (%) of nitrogen using

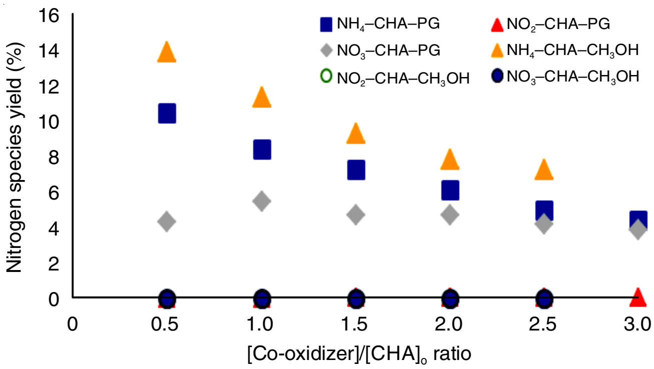

Fig. 5. Effect of co-oxidizer on the yield of nitrogen species at 425 °C, 4 mM cyclohexylamine, 10 s and SR of 1

methanol was positive, but enhancement occurred at the co-oxidizer ratio of 1. The nitrogen removal efficiency of nitrogen increased 80% at the ratio of 0.5 using propylene glycol, while methanol did not improve nitrogen removal under the same conditions (Fig. 6). This improvement in nitrogen removal is occured since propylene glycol adds more heat to the reaction than methanol [35]. In addition, the reaction between propylene glycol and oxygen in the supercritical medium generates the free radicals, which accelerate the conversion of TOC and nitrogen removal [22,30].

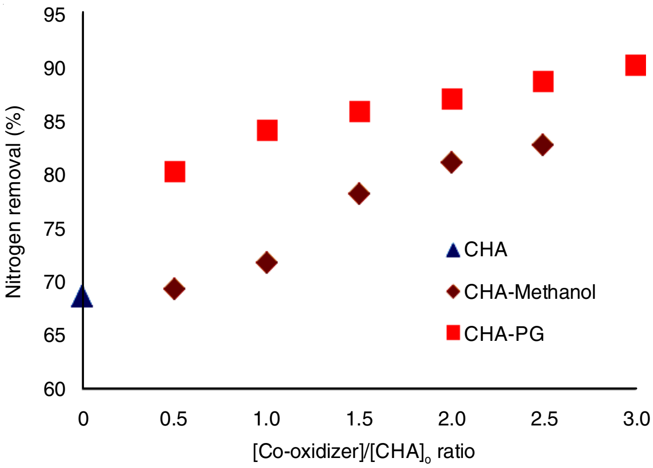

Fig. 6. Effect of co-oxidizer on the efficiency of nitrogen removal at 425 °C, 4 mM cyclohexylamine, 10 s and SR of 1

Impact of oxidant ratio (SR)

Removal efficiency of TOC: The influence of hydrogen peroxide as an oxygen source was essential in achieving a effective oxidant ratio. In this study, at laboratory conditions were 4 mM cyclohexylamine, 4 mM propylene glycol, 4 mM methanol at 425 ºC and the oxidant ratio was ranged from 0.75 SR to 2 SR. Additionally, the use of high oxygen amount to generate N_2O must be considered [35]. A significant effect of the oxidant ratio on TOC conversion is shown in Fig. 7. The removal(%) of TOC was enhanced by increasing the amount of oxygen in the absence and presence of co-oxidizer. The primary reaction mechanism in supercritical water conditions is free radicals [37]. In addition, an abundance of free radicals enhances the removal(%) of TOC in the absence of co-oxidizer.

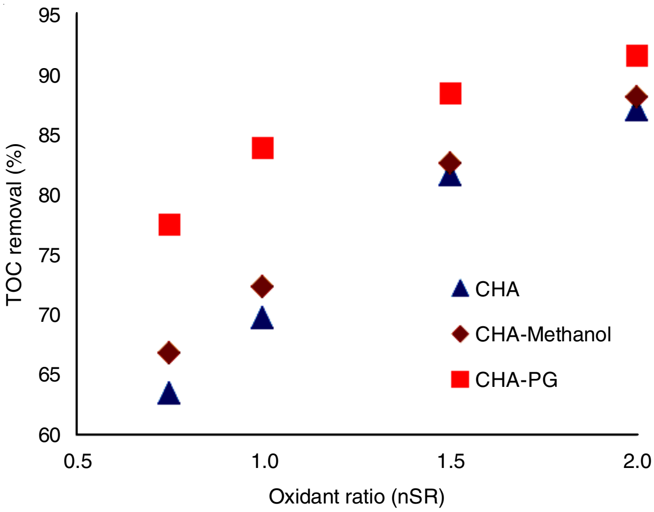

Fig. 7. Effect of the oxidant ratio on TOC removal efficiency at 425 °C, 4 mM cyclohexylamine, 4 mM PG, 4 mM methanol and 10 s

In this study, TOC conversion improved with the utilized oxidant ratio and 10 s, from 63.0% at 0.75 SR to 86.97% at 2 SR. However, by using co-oxidizer, free radicals increased due to the oxidation of alcohol. Therefore, this parameter can be included to increase the pathways for producing free radicals [30]. The results confirmed that propylene glycol plays a remarkable role at a low oxidant ratio, while methanol has a limited positive influence. In a simple comparison between the increments of TOC conversion in the presence of co-oxidizer, it was found that an increase with propylene glycol reached more than four times increase with methanol at the low oxidant ratio.

Yield of nitrogen species: The influence of oxidant ratio on the nitrogen byproducts was significant. The ammonium yield was reduced by increasing the oxygen amount. Thus, the ammonium yield decreased from 16.6% at 0.75 SR in the absence of co-oxidizer to 10.8% in the same conditions with propylene glycol (Fig. 8). At 2 SR, the ammonium yield decreased to 9.0% in the fuel-free system and 5% using propylene glycol. The findings confirmed that alcohol with multi-hydroxyl groups has a positive effect on ammonium yield [30]. The nitrite yield was still a trace amount. Moreover, the concentration of nitrate was also low in the fuel-free and methanol systems.

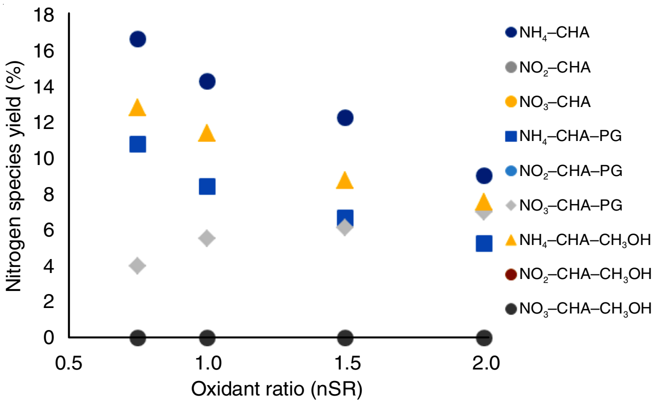

Fig. 8. Effect of the oxidant ratio on the nitrogen species yield at 425 °C, 4 mM cyclohexylamine, 4 mM PG, 4 mM methanol and 10 s

Removal of nitrogen (%): Fig. 9 presents the oxidant ratio's effect on the nitrogen removal%. The results confirmed that propylene glycol was a significant co-oxidizer as compared to methanol. The removal efficiency rose from 64.8% at 0.75 SR to 81% at 2 SR without co-oxidizer. In propylene glycol system, with SR of 1, nitrogen removal% increased from 68.6% in the fuel-free system to 84% with propylene glycol.

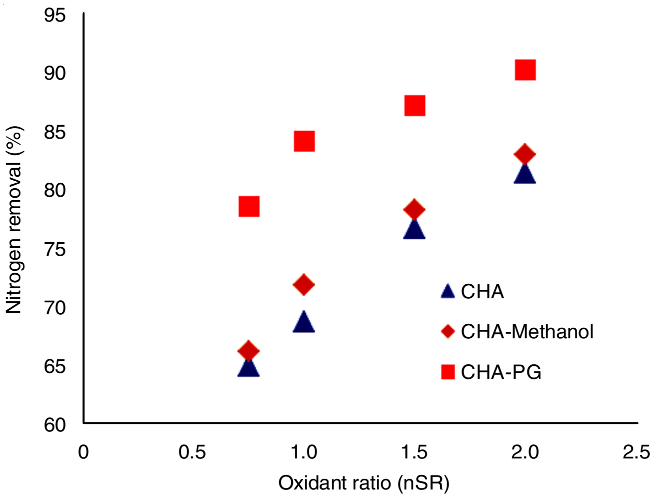

Fig. 9. Effect of oxidant ratio on the efficiency(%) of nitrogen removal at 425 ºC, 4 mM cyclohexylamine, 4 mM PG, 4 mM methanol and 10 s

Conclusion

In summary, an enhanced supercritical water oxidation (SCWO) method was proposed for the decomposition of cyclohexylamine in the presence of two co-oxidizers (methanol and propylene glycol). The results demonstrated the significant effect of dihydric alcohol on the efficiency of TOC removal, nitrogen byproduct reduction and nitrogen removal using SCWO method. Propylene glycol with two hydroxyl groups is more active than methanol in generating more free radicals. Several operating conditions also influenced the SCWO process, where temperature is one of the essential parameter and contributes to enhance TOC conversion and nitrogen removal. The maximum total organic carbon removal (TOC) in the presence of propylene glycol was achieved with 98% at 525 ºC and the residence time was 14 s.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. S. Takayama, A.G. Renwick, S.L. Johansson, U.P. Thorgeirsson, M. Tsutsumi, D.W. Dalgard and S.M. Sieber, *Toxicol. Sci.*, **53**, 33 (2000); https://doi.org/10.1093/toxsci/53.1.33
2. Y. Shen, D. Yan, X. Chi, Y. Yang, D.J. Leak and N. Zhou, *World J. Microbiol. Biotechnol.*, **24**, 1623 (2008); https://doi.org/10.1007/s11274-007-9651-9
3. H. Zhou, Z. Han, T. Fang, Y. Chen, S. Ning, Y. Gan and D. Yan, *Front. Microbiol.*, **9**, 2848 (2018); https://doi.org/10.3389/fmicb.2018.02848
4. J. Guolin and L. Mingming, *Recent Patents Chem. Eng.*, **4**, 29 (2011); https://doi.org/10.2174/2211334711104010029
5. B. Veriansyah and J.-D. Kim, *J. Environ. Sci. (China)*, **19**, 513 (2007); https://doi.org/10.1016/s1001-0742(07)60086-2
6. E. Adar, M. Ince and M.S. Bilgili, *Desalin. Water Treat.*, **161**, 243 (2019); https://doi.org/10.5004/dwt.2019.24297
7. V. Vadillo, J. Sánchez-Oneto, J.R. Portela and E.J.M. de la Ossa, *Ind. Eng. Chem. Res.*, **52**, 7617 (2013); https://doi.org/10.1021/ie400156c
8. A. Leybros, A. Roubaud, P. Guichardon and O. Boutin, *Process Saf. Environ. Prot.*, **88**, 213 (2010); https://doi.org/10.1016/j.psep.2009.11.001
9. V. Vadillo, M.B. García-Jarana, J. Sánchez-Oneto, J.R. Portela and E.J.M. de la Ossa, *J. Supercrit. Fluids*, **72**, 263 (2012); https://doi.org/10.1016/j.supflu.2012.09.011
10. Y. Zhao, Q. Zhou, K. Hidetoshi and L. Luo, *Ecotoxicol. Environ. Saf.*, **208**, 111596 (2021); https://doi.org/10.1016/j.ecoenv.2020.111596
11. P. Cabeza, M.D. Bermejo, C. Jiménez and M.J. Cocero, *Water Res.*, **45**, 2485 (2011); https://doi.org/10.1016/j.watres.2011.01.029
12. M.J. Cocero, E. Alonso, R. Torío, D. Vallelado and F. Fdz-Polanco, *Ind. Eng. Chem. Res.*, **39**, 3709 (2000); https://doi.org/10.1021/ie990852b
13. W.R. Killilea, K. Swallow and G.T. Hong, *J. Supercrit. Fluids*, **5**, 72 (1992); https://doi.org/10.1016/0896-8446(92)90044-K
14. C. Aymonier, P. Beslin, C. Jolivalt and F. Cansell, *J. Supercrit. Fluids*, **17**, 45 (2000); https://doi.org/10.1016/S0896-8446(99)00040-6
15. K.M. Benjamin and P.E. Savage, *Ind. Eng. Chem. Res.*, **44**, 5318 (2005); https://doi.org/10.1021/ie0491793
16. H. Schmieder and J. Abeln, *Chem. Eng. Technol.*, **22**, 903 (1999);
17. J. Li, S. Wang, L. Qian, J. Zhang, T. Xu, Y. Li and D. Xu, *Chemosphere*, **307**, 135858 (2022); https://doi.org/10.1016/j.chemosphere.2022.135858
18. P. Cabeza, B. Al-Duri, M. Bermejo and M. Cocero, *Chem. Eng. Res. Des.*, **92**, 2568 (2014); https://doi.org/10.1016/j.cherd.2014.01.017
19. T. Oe, H. Suzugaki, I. Naruse, A.T. Quitain, H. Daimon and K. Fujie, *Ind. Eng. Chem. Res.*, **46**, 3566 (2007); https://doi.org/10.1021/ie070168u
20. J.M. Ploeger, M.A. Mock and J.W. Tester, *AIChE J.*, **53**, 941 (2007); https://doi.org/10.1002/aic.11127
21. P.E. Savage, J. Rovira, N. Stylski and C.J. Martino, *J. Supercrit. Fluids*, **17**, 155 (2000); https://doi.org/10.1016/S0896-8446(99)00052-2
22. B. Yang, Z. Cheng, T. Yuan and Z. Shen, *J. Supercrit. Fluids*, **138**, 56 (2018); https://doi.org/10.1016/j.supflu.2018.03.021
23. J. Zhang, S. Wang, Y. Guo, D. Xu, X. Li and X. Tang, *Ind. Eng. Chem. Res.*, **52**, 10609 (2013); https://doi.org/10.1021/ie400704f
24. F. Civan, D.H. Özaltun, E. Kipçak and M. Akgün, *J. Supercrit. Fluids*, **100**, 7 (2015); https://doi.org/10.1016/j.supflu.2015.02.018
25. Z. Ding, L.X. Li, D. Wade and E. Gloyna, *Ind. Eng. Chem. Res.*, **37**, 1707 (1998); https://doi.org/10.1021/ie9709345
26. B. Yang, Z. Cheng, M. Fan, J. Jia, T. Yuan and Z. Shen, *Chemosphere*, **205**, 426 (2018); https://doi.org/10.1016/j.chemosphere.2018.04.029
27. G. Zhang and I. Hua, *Ind. Eng. Chem. Res.*, **42**, 285 (2003); https://doi.org/10.1021/ie010479j

28. B. Al-Duri, L. Pinto, N.H. Ashraf-Ball and R.C.D. Santos, *J. Mater. Sci.*, **43**, 1421 (2008); https://doi.org/10.1007/s10853-007-2285-3
29. G. Lin, D. Xu, Z. Ma, S. Wang and Y. Guo, *Energy Procedia*, **107**, 357 (2017); https://doi.org/10.1016/j.egypro.2016.12.176
30. B. Al-Duri, F. Alsoqyani and I. Kings, *Philos. Trans.- Royal Soc., Math. Phys. Eng. Sci.*, **373**, 20150013 (2015); https://doi.org/10.1098/rsta.2015.0013
31. P.A. Webley, J.W. Tester and H.R. Holgate, *Ind. Eng. Chem. Res.*, **30**, 1745 (1991); https://doi.org/10.1021/ie00056a010
32. E. Shimoda, T. Fujii, R. Hayashi and Y. Oshima, *J. Supercrit. Fluids*, **116**, 232 (2016); https://doi.org/10.1016/j.supflu.2016.05.052
33. M. Bermejo, M. Cocero and F. Fernández-Polanco, *Fuel*, **83**, 195 (2004); https://doi.org/10.1016/S0016-2361(03)00256-4
34. M. Cocero, E. Alonso, M. Sanz and F. Fdz-Polanco, *J. Supercrit. Fluids*, **24**, 37 (2002); https://doi.org/10.1016/S0896-8446(02)00011-6
35. B. Al-Duri, F. Alsoqyiani and I. Kings, *J. Supercrit. Fluids*, **116**, 155 (2016); https://doi.org/10.1016/j.supflu.2016.05.002
36. N. Segond, Y. Matsumura and K. Yamamoto, *Ind. Eng. Chem. Res.*, **41**, 6020 (2002); https://doi.org/10.1021/ie0106682
37. L.D.S. Pinto, L.M.F. dos Santos, B. Al-Duri and R.C.D. Santos, *J. Chem. Technol. Biotechnol.*, **81**, 912 (2006); https://doi.org/10.1002/jctb.1420