

# EFFICIENT TREATMENT OF ACTUAL PHARMACEUTICAL WASTEWATER BY WET OXIDATION PROCESS IN SUBCRITICAL WATER APPARATUS

Umme Marium Ahmad,<sup>1,2</sup> Yuan Pu,<sup>1,2\*</sup> Weikang Qi,<sup>2</sup> Neil R. Foster,<sup>1,3</sup> Jian-Feng Chen<sup>1,2</sup> and Dan Wang<sup>1,2\*</sup>

1. State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China

2. College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, China

3. Department of Chemical Engineering, Curtin University, Perth, Western Australia 6102, Australia

Pharmaceutical wastewater is a typical persistent refractory organic industrial wastewater. In this work, a simple, one-step method for the treatment of pharmaceutical wastewater was developed using wet oxidation (WO) in a subcritical water apparatus, with detailed studies on the effects of operating parameters, including the temperature of the system, the ratio of reactants, and pH of the wastewater. Under optimized experimental conditions, efficient treatment of actual pharmaceutical wastewater was achieved, with removal of 100 % chemical oxygen demand (COD), 98 % nitrate ion, 98 % nitrite ion, and 68 % ammonium ion. Our results suggest that the WO process, using a subcritical water apparatus, is a promising method of treatment for pharmaceutical wastewater.

**Keywords:** subcritical water apparatus, wet oxidation, pharmaceutical industry, wastewater treatment

## INTRODUCTION

Pharmaceuticals in surface water, wastewaters, and drinking water have recently been recognized as emerging environmental contaminants. They are leached into the world's water supply mainly through pharmaceutical industry effluents, hospital waste, and residential waste.<sup>[1]</sup> Currently, more than 80 different pharmaceuticals up to the ppm levels have been reported in aquatic environments around the world. Some of the more frequently observed chemicals found are anti-inflammatories like ibuprofen and diclofenac, antibiotics like azithromycin and clarithromycin, antipyretic analgesic paracetamol, and psychomotor stimulants like caffeine. These are now characterized as wastewater-marking pharmaceuticals; they serve as wastewater tracers. The growing concern over the dangers of these particular types of pollutants in the water supply are due to the fact that these chemical drugs found in pharmaceutical wastewater are designed specifically to exert biological effects at low concentrations.<sup>[2]</sup> The swell in demand for prescription drugs today will likely cause an increase in the proportion of pharmaceutical residuals present in the world's water supply and their effect on the urban aquatic environment, wildlife, agriculture, and human health could be devastating.<sup>[3]</sup>

Research has confirmed that conventional technologies do not eliminate pharmaceuticals from wastewater completely and they require advanced treatment technologies to be destroyed, in order to prevent pharmaceuticals ending up in the world's water supply. More and more methods have been developed in recent years such as sulphate anion radical oxidation,<sup>[4]</sup> dissolved air precipitation,<sup>[5]</sup> electrocoagulation,<sup>[6]</sup> anaerobic sludge blanket,<sup>[7]</sup> two phase anaerobic digestion,<sup>[8]</sup> and continuous heterogeneous catalytic wet peroxide oxidation,<sup>[9]</sup> to name a few.<sup>[10–13]</sup> However, these advanced technologies require wastewater to undergo multiple phases of treatment. Wet oxidation (WO) is a one-step process in which oxidation takes place under high temperatures

and pressures, subcritical conditions, with the help of an oxidant. By maintaining subcritical conditions, the fluid inside the system remains in liquid form. However, having surpassed its boiling point, the fluid's chemical properties are altered allowing for a higher degree of solvation.<sup>[14]</sup> Commonly used oxidants are oxygen gas, ozone, peroxides, halogens, etc. The key to a successful oxidation is the creation and multiplication of radicals. The free radical reactions are typical in oxidation which occurs in three stages: initiation, propagation, and termination.<sup>[15]</sup> The initiation phase sees the creation of the radicals usually through the decomposition of the oxidant. The propagation phase is where the radicals multiply and regenerate, and finally the termination phase occurs as the oxidant is depleted or there are no more chemicals to oxidize.

This type of study usually sees the use of Teflon-lined autoclaves in an oven setup. Laboratory studies of wet oxidation usually use wastewater matrixes of relatively low COD.<sup>[16–18]</sup> However, this particular study treats actual pharmaceutical wastewater with an initial COD of 21 412 mg/L. At this level a larger amount of oxidant is required to treat it. Teflon-lined autoclaves cannot withstand the amount of pressure given off by the decomposition of hydrogen peroxide leading to warping of the Teflon and loss of product. Furthermore, their inability to withstand the pressure build-up also hinders the system's ability to treat the water as efficiently. Thus, for this work a micro bench-top pressure reactor was used to conduct tests.

\* Author to whom correspondence may be addressed.

E-mail address: puyuan@mail.buct.edu.cn (Y. Pu);

wangdan@mail.buct.edu.cn (D. Wang)

Can. J. Chem. Eng. 95:2056–2062, 2017

© 2017 Canadian Society for Chemical Engineering

DOI 10.1002/cjce.22885

Published online 18 August 2017 in Wiley Online Library (wileyonlinelibrary.com).

The objective of this study is to analyze the effects of various factors on the WO of pharmaceutical wastewater using hydrogen peroxide as an oxidant under subcritical conditions for effective organic load reduction, to determine the advantages and limitations of the WO process and finally develop a simple and environmentally friendly method of pharmaceutical wastewater treatment based on the optimum operational conditions of the system. Several critical parameters affect the WO process and their influence on the pharmaceutical wastewater was recorded, including reaction time, temperature, oxidant dosage, pH, and adsorbent dosage. All untreated and treated samples underwent tests for COD, ammonium ion, nitrate ion, and nitrite ion detection to investigate the optimized experimental conditions.

## MATERIALS AND METHODS

### Reagents

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), granular activated carbon, and all relevant analytical test chemicals were provided by Beijing Chemical Works (Beijing, China). All chemicals were used without further purification. Pharmaceutical wastewater used for this study was obtained from Hebei Molansi Environmental Science and Technology Corporation (Hebei, China). In every experiment conducted, the wastewater was used without any filtration or pre-treatment. Initial appearance of the wastewater was brown and cloudy. Untreated wastewater was tested for COD, nitrate and nitrite ions, and ammonium ions.

### Procedure

The setup of subcritical water apparatus is similar to our previous reports with some modifications.<sup>[19,20]</sup> A micro bench-top reactor (Parr Instrument Company 4590), fitted with a 100 mL reactor, was used for the wastewater treatment studies. The reactor was loaded with 20 mL pharmaceutical wastewater and the appropriate quantity of oxidant H<sub>2</sub>O<sub>2</sub> was added (according to the experiment design) and sealed. Approximately 50 mL of head space was left in the cell. All static (non-flowing) reaction cells must contain sufficient headspace so that the pressure inside the cell is controlled by the steam/liquid equilibrium. A full cell must never be used since the system could reach very high pressures. Once sealed, the reactor was heated to the desired temperature. Upon reaching this temperature, the reaction would be timed for the required residence time. The addition of the appropriate quantities of

H<sub>2</sub>O<sub>2</sub> was carried out just before the experiment in order to avoid H<sub>2</sub>O<sub>2</sub> photo-decomposition.

### Analysis

The concentrations of aqueous organic components in the pharmaceutical wastewater and final products from the reactor were characterized by measuring COD, nitrate ion concentration, nitrite ion concentration, and ammonium ion concentration.

#### Chemical oxygen demand

Treated samples were mixed with aqueous mercury sulphate, potassium chromate, and acidic silver sulphate solutions and open refluxed at 164 °C. Samples were cooled to room temperature and placed in a centrifuge for 5 min. A UV-spectrometer was set to 440 nm to collect data.

#### Nitrate ion test

Aqueous solutions of hydrochloric acid, sulphamic acid, and potassium nitrate were added to treated samples and absorbance was measured at 220 nm and 275 nm.

#### Nitrite ion test

Solutions of hydrochloric acid, p-aminobenzenesulphonamide, N-(1-naphthyl) ethylenediamine, and sodium nitrite were mixed with treated samples and measured at 543 nm.

#### Ammonium ion test

Mixtures of sodium hydroxide, salicylic acid, and seignette salt, along with solutions of sodium hypochlorite, sodiumnitroferri-cyanide (III) dehydrate, and ammonium chloride were used to test treated samples at 697 nm.

All analyses were performed using a Cary 50 UV-Vis Spectrophotometer (Varian Inc., Australia). In order to provide accurate data, the samples were analyzed in triplicate, and averages were reported in the results section. Due to high levels of nitrate, nitrite, and ammonium ions present in the initial phase of the study, they were not reported.

## RESULTS AND DISCUSSION

The WO treatment of actual pharmaceutical wastewater was conducted using a micro bench-top pressure reactor (Figure 1). Studies were conducted on the effect of certain variables on the system. Table 1 provides a general summary of the data gathered.

**Table 1.** Summary of WO treatment data

Variable	Parameter	Conditions	Final COD (mg/L)
Oxidant concentration (H <sub>2</sub> O <sub>2</sub> )	30 %	150 °C, Reactant ratio	2039
	50 %	1:1, Initial COD 21412 mg/L	532
Temperature (°C)	70	Reactant ratio 1:1,	723
	150	Initial COD 21412 mg/L	558
	180		625
Reactant ratio	1:1	150 °C, Reactant ratio 1:1,	558
	2:1	Initial COD 21412 mg/L	712
	4:5		80
pH	4	150 °C, Reactant ratio 1:1,	60
	7	Initial COD 21412 mg/L	602
	10		1634

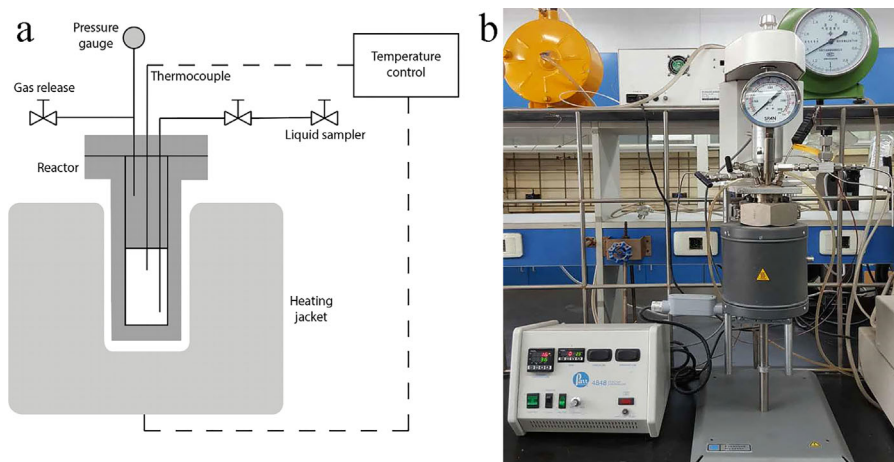


Figure 1. (a) Schematic diagram of WO apparatus, (b) actual WO apparatus, a micro bench-top pressure reactor.

#### Effect of Oxidation Time

Equal amounts of pharmaceutical wastewater and  $H_2O_2$  were loaded into the reactor cell. The system requires an average of 10 min to heat up to the experimental temperature. This period of time has been represented in Figure 3 as  $-10$  to  $0$ . Every 10 min, samples were taken and tested. The effect of time on the system was found to be surprising. It was expected that over a longer period of time, COD of the wastewater would continue to decrease until it reached zero. However, it seems that after 1 h the COD plateaus at around 560 mg/L. This demonstrates that temperature, along with  $H_2O_2$ , partially contributes to the treatment of wastewater, but there are certain contaminants that cannot be destroyed with longer heating periods. Nonetheless, from this data it was evident that the reaction time can be limited to 60 min as this is where the reactions plateau.

#### Effect of Oxidant Concentration

Commercially available 30 % and 50 %  $H_2O_2$  concentrations were compared. The reactor cell was loaded with 20 mL of pharmaceutical wastewater and 20 mL of hydrogen peroxide. All tests were conducted at a temperature of 150 °C and reaction time of 60 min. Figure 4 shows the data gathered after analysis of the treated water. At 30 % concentration,  $H_2O_2$  is only able to lower

the COD to 2039 mg/L, whereas at 50 % concentration the COD comes down to 532 mg/L. This establishes that at a low concentration,  $H_2O_2$  is not as effective. At higher concentrations,  $H_2O_2$  is able to efficiently treat the water to approximately 500 mg/L. As a point of caution, upon decomposition,  $H_2O_2$  emits large quantities of energy. In a sealed reactor cell, it is imperative to control the amount of pressure build-up or it could be potentially explosive. It is recommended to not exceed higher than 50 %  $H_2O_2$ . Unexpectedly, it can be seen from Figure 4 that both the initiation phase and the propagation phase are relatively longer at 30 %  $H_2O_2$ , with 20 min of initiation and almost 40 min of propagation, than at 50 %  $H_2O_2$ , with only 12 min of initiation and 20 min of propagation. Though this is ideal for the reaction, still it does not bear as impressive a COD. Instead this indicates that with a higher concentration, the reaction occurs faster, thus saving time and energy.

#### Effect of Temperature

Temperature has a large impact on the treatment of the wastewater. Various temperatures were tested to see their influence. Figure 5 shows the results for 70, 150, and 180 °C. It can be seen that at 70 °C the initiation phase is drawn out and 10 min into the reaction the COD still has not dropped below

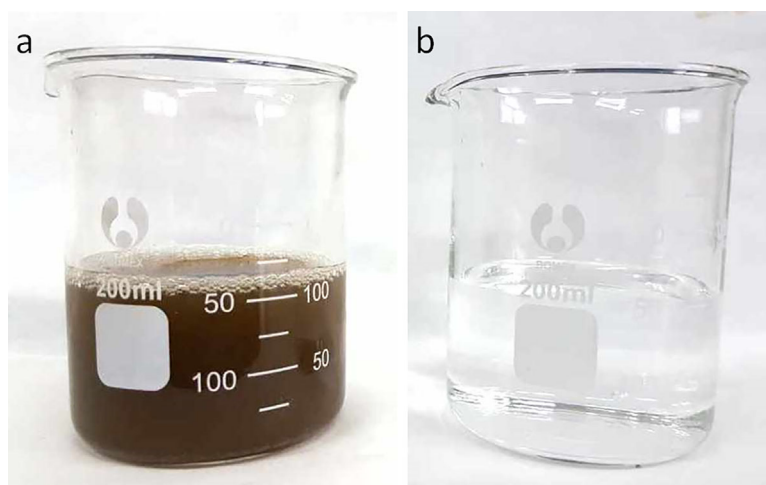
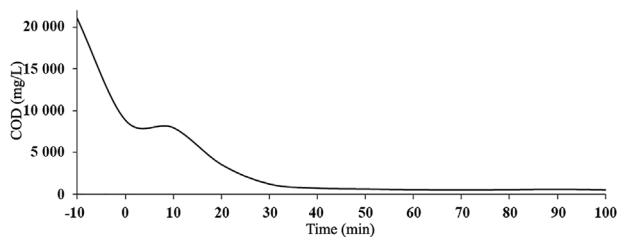
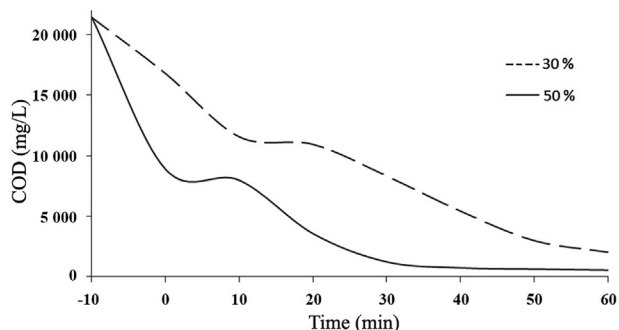


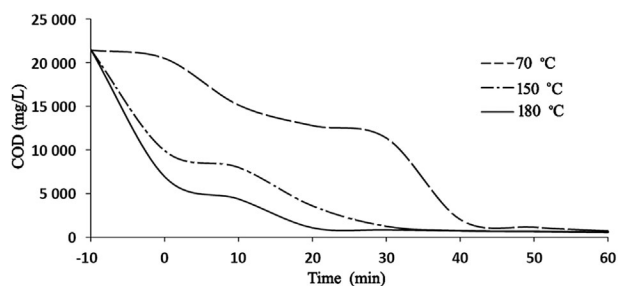
Figure 2. Visual contrast of (a) before and (b) after WO treatment of pharmaceutical wastewater.



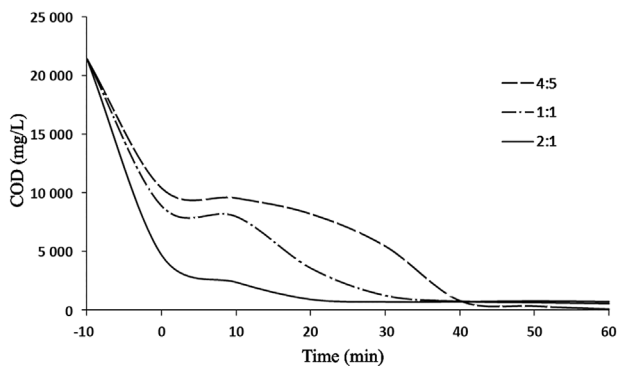
**Figure 3.** Effect of reaction time on COD at 150 °C, 50 % H<sub>2</sub>O<sub>2</sub>, reactant ratio 1:1.



**Figure 4.** Effect of oxidant concentration on COD at 150 °C, reactant ratio 1:1.



**Figure 5.** Effect of temperature of COD at 70 °C, 150 °C and 180 °C, 50 % H<sub>2</sub>O<sub>2</sub>, reactant ratio 1:1.



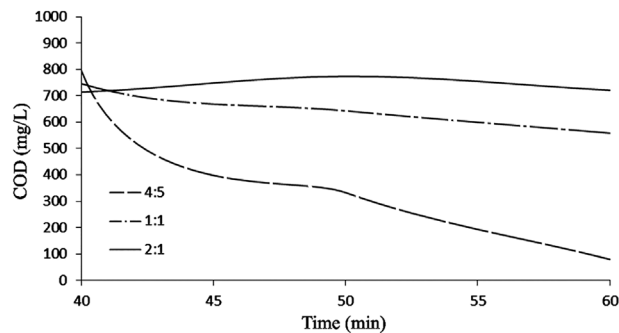
**Figure 6.** Effect of reactant ratio of COD at 150 °C for 60 min, 50 % H<sub>2</sub>O<sub>2</sub>, reactant ratio 1:1.

15 000 mg/L. Compared to this, at 150 and 180 °C the COD levels have fallen to 10 000 mg/L or below by the time the system has reached reaction temperature and have both completed their initiation phases before 5 min of reaction time. Propagation periods at 70 °C and 180 °C seem to be about 20 min. However, propagation period at 150 °C exceeds 30 min. The data demonstrates that low temperatures do not provide the correct conditions for complete decomposition of H<sub>2</sub>O<sub>2</sub> and also do not promote the multiplication radicals. On the other hand, too high a temperature may hinder the formation of radicals and promote the production of end products. The data implies that at 150 °C, the reaction has reached an optimal level where the temperature conditions are ideal for radical multiplication and maximum propagation is experienced.

#### Effect of Reactant Ratio

The next phase of the study investigates how reactant ratio can influence the outcome of the final product. Various reactant ratios were tested. Ratios of 1:1, 2:1, and 4:5 (sample:oxidant) are shown in Figure 6. The reactor cell was sealed with the appropriate amount of reactants and heated to 150 °C for 60 min. Evident from the data, reactant ratios of 1:1, 2:1, and 4:5 all have similar initiation periods of about 12 min. However, at a 2:1 ratio, the initiation has a large effect on the COD bringing it down to well below 3000 mg/L. It is possible that as the total concentration of the H<sub>2</sub>O<sub>2</sub> in the cell was much lower than that of the wastewater sample, the diffusion of oxidant throughout the mixture was faster and more balanced. At equal or higher concentrations, H<sub>2</sub>O<sub>2</sub> does not mix as well due to poor diffusion, especially as there is no stirring to allow homogenous mixing of the reactants. However, at 2:1 ratio, after a propagation period of only 1 min it rapidly goes to termination, implying that there simply were not enough radicals present to react with the wastewater and to multiply. For ratios 1:1 and 4:5 though the initiation phase only draws COD down to just below 10 000 mg/L, ratio 1:1 exhibits a propagation phase of 20 min, and ratio 4:5 exhibits a propagation period of 37 min. Lower sample:oxidant values allow the system to share the task of treating the wastewater and multiplying radicals at the same time.

Figure 7 takes a closer look at the data between 40–60 min of the reactions. The data shows that upon the completion of the reaction, COD of ratios 1:1 and 2:1 as expected are within the hundreds range, 558 mg/L and 712 mg/L, respectively. Astoundingly, at 4:5 ratio the COD comes down all the way to 80 mg/L. This implies that perhaps an even larger amount of H<sub>2</sub>O<sub>2</sub> may produce better results, closer to 0 mg/L. As there is an element of safety to be taken in to consideration with adding too much H<sub>2</sub>O<sub>2</sub>, this phase of testing was concluded here.



**Figure 7.** Effect of reactant ratio on COD at 150 °C at 40–60 min, 50 % H<sub>2</sub>O<sub>2</sub>, reactant ratio 1:1.



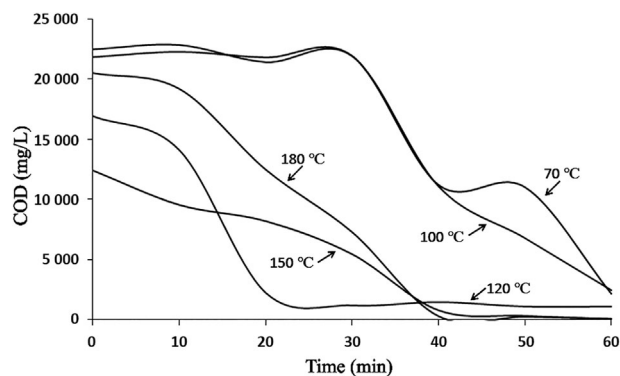


Figure 8. Effect of temperature on COD at 50 % H<sub>2</sub>O<sub>2</sub>, reactant ratio 4:5.

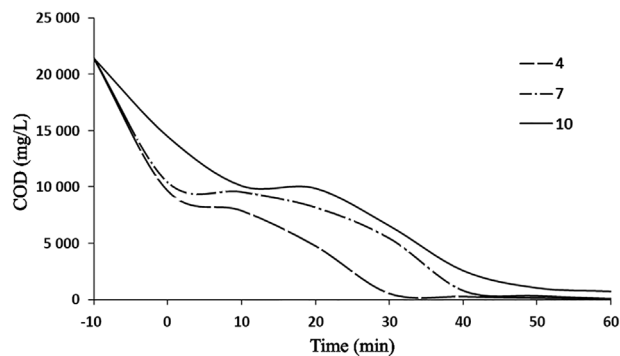


Figure 9. Effect of pH on COD at 50 % H<sub>2</sub>O<sub>2</sub>, reactant ratio 1:1.

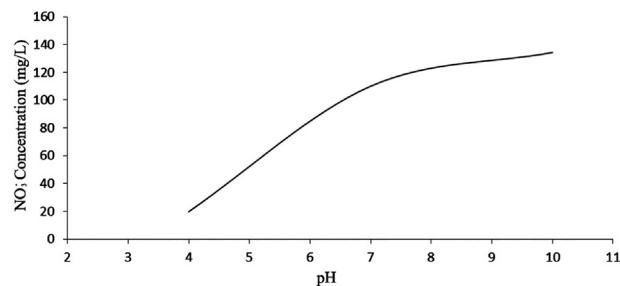


Figure 10. Effect of pH on NO<sub>3</sub><sup>-</sup> concentration at 150 °C, 50 % H<sub>2</sub>O<sub>2</sub>, reactant ratio 1:1.

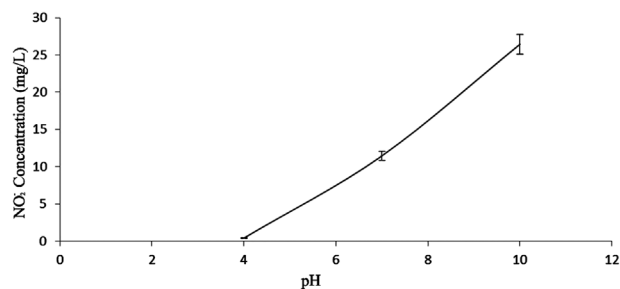


Figure 11. Effect of pH on NO<sub>2</sub><sup>-</sup> concentration at 150 °C, 50 % H<sub>2</sub>O<sub>2</sub>, reactant ratio 1:1.

The next approach was to test how the 4:5 ratio held up to different temperatures. Figure 8 shows the graphical data of the effect of temperature on COD at 4:5 sample: oxidant ratio. It is evident from the data presented in Figure 2 that WO favours higher temperatures to lower ones. At 70 °C and 100 °C the final COD was 2168 mg/L and 2455 mg/L, respectively. Even with a higher amount of H<sub>2</sub>O<sub>2</sub> the COD was not able to reach the hundreds range. This must be due to the lack of energy provided to the oxidant. It took more than 30 min to start the initiation phase which only lasted for 10 min, and then a short 10 min dip into the propagation phase concluded the reactions. The propagation period is rather steep however, suggesting that with more time it may have decreased further. Yet that would require more time and thus was considered unnecessary. Alternatively, at 120 °C a final COD of 1112 mg/L was attained suggesting that even though the final COD was still high, the increase in temperature did allow for a better treatment of the pharmaceutical wastewater. It should be noted the bulk of the treatment occurs during the propagation phase, between 10–20 min, bringing the COD down to 1193 mg/L. After this the COD sharply plateaus. Nonetheless, as expected, at temperatures of 150 °C and 180 °C the 4:5 reactant ratio works most efficiently taking the COD down to 80 mg/L and 83 mg/L respectively. This however may be a concern during scale-up. As H<sub>2</sub>O<sub>2</sub> is explosive at temperatures above 150 °C, it would be a safety risk to load any reactor with excessive amounts.

#### Effect of pH

Further studies of the system lead to investigations of the effects of pH. Figure 9 graphically presents the data gathered. The facilitating effect of pH on the decay of organic waste was also considered and thus examined in this study. The original sample had a pH value of 6 making it already slightly acidic. The sample's pH was changed to 1, 4, 7, and 10 and experiments were conducted over 60 min, with a 20 mL sample and 20 mL H<sub>2</sub>O<sub>2</sub> (50 %). It was observed that an increase in pH causes a slow-down of the rate of reaction, resulting in the final product having a relatively high COD. At pH 10 the COD of the wastewater was at 1634 mg/L. This is similar to the effects of low temperature. The conditions are not conducive for radical multiplication. The COD of the sample at pH 7 was 602 mg/L. At pH 4, however, the COD dropped sharply to 60 mg/L. A very low pH value of 1 caused some cell corrosion and sample contamination and thus was not included. In light of this, it is deemed that too low a pH is unnecessary for the system. However, in light of the fact that simply changing the nature of the wastewater to more acidic can lower the COD to well beyond that of the previous reactant ratio

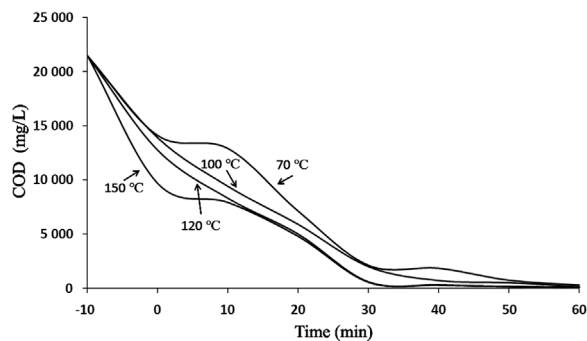
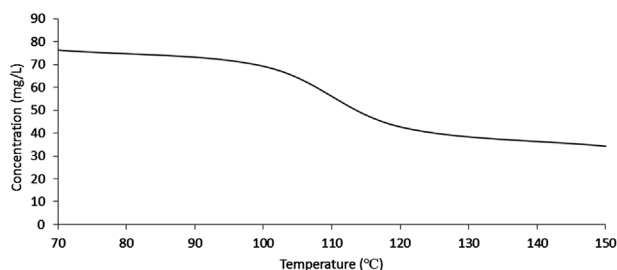


Figure 12. Effect of temperature on COD at pH = 4, 50 % H<sub>2</sub>O<sub>2</sub>, reactant ratio 1:1.



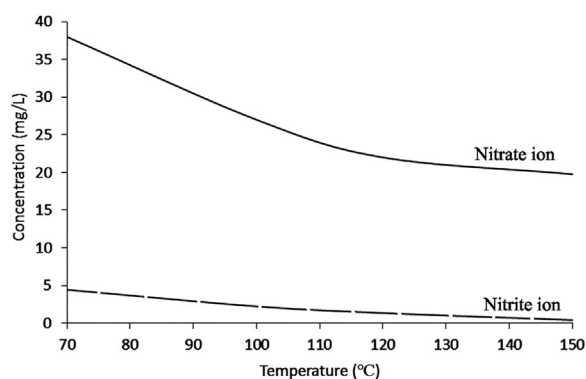
**Figure 13.** Effect of temperature at pH 4 on  $\text{NH}_4^-$ , 50 %  $\text{H}_2\text{O}_2$ , reactant ratio 1:1.

studies, suggests that it is possible to fine tune treatment greatly without using more oxidant and thus enabling researchers to maintain the safety and integrity of the studies.

In these conditions, particularly at the lower pH, the wastewater samples experience significant drops in nitrate and nitrite ion concentrations. Starting from 134 mg/L at pH 10, the nitrate concentration dropped to 24 mg/L at pH 4. As for nitrite acid, nitrite ions had significantly dropped to 26.4 mg/L at pH 10. However, it had a staggering drop to 0.41 mg/L at pH 4. These results are reflected in Figures 10 and 11.

Figure 12 graphs the influence of varying temperatures at pH 4 using 50 %  $\text{H}_2\text{O}_2$  at 1:1 reactant ratio. The data shows a generally steep initiation period at all temperatures followed by more than 30 min of propagation periods and then a swift termination. Even at 70 °C the final COD of the wastewater is 275 mg/L placing it strictly within WHO standards for disposable and reusable water. This demonstrates the pH dependency of free radical reactions. The COD of the sample at 150 °C, as expected, came down to 63 mg/L. At temperatures of 100 °C and 120 °C the initiation and propagation phases occur seamlessly, with COD decreasing to 124 mg/L and 76 mg/L, after termination, respectively. This suggests that at these temperatures the system experiences optimal conditions for not only an extended propagation, but also an early propagation.

At low pH conditions, even the ammonium ion concentration began to drop (Figure 13). Untreated pharmaceutical wastewater's ammonium concentrations did not fall within the analytical range of the ammonium ion tests. However, after treatment at pH 4, the first viable reading measured was at 70 °C coming down to 76.3 mg/L. At 100 °C, the ammonium ion concentration was 69.23 mg/L. At the highest temperature of 150 °C, the concentration was a mere 34.2 mg/L. Similarly, both



**Figure 14.** Effect of temperature at pH 4 on  $\text{NO}_2^-$  and  $\text{NO}_3^-$  concentration, 1:1.

nitrate and nitrite ion concentrations, at pH 4, drop as well, demonstrating high oxidizing efficiency in these conditions (Figure 14).

## CONCLUSIONS

WO of pharmaceutical wastewater with hydrogen peroxide was conducted using a subcritical water apparatus. This process was shown to be an efficient method for the treatment of pharmaceutical wastewater, which can be fine-tuned to different degrees of COD removal over a range of temperatures, reaction times, oxidant dosages, pH, and adsorbent dosages. The optimum conditions for maximum efficiency were demonstrated at pH 4, 1:1 reactant to oxidant ratio, and 150 °C reaction temperature over 60 min reaction time. This results in a 99.7 % removal of COD, 98 % removal of nitrate ions, 98 % removal of nitrite ions, and 68 % removal of ammonium ions. These results suggest useful applications of this method to approaching the treatment of pharmaceutical industry wastewaters.

## ACKNOWLEDGEMENTS

We are grateful for financial support from the National Key Research and Development Program of China (2016YFA0201701/2016YFA0201700), National Natural Science Foundation of China (51641201), the Fundamental Research Funds for the Central Universities (BUCTRC201601, JD1606), and the “111” project of China (B14004).

## REFERENCES

- [1] C. Gadipelly, A. Pérez-González, G. D. Yadav, I. Ortiz, R. Ibáñez, V. K. Rathod, K. V. Marathe, *Ind. Eng. Chem. Res.* **2014**, *53*, 11571.
- [2] H. Zhou, T. Ying, X. Wang, J. Liu, *Sci. Rep.* **2016**, *6*, 34928.
- [3] D. J. Larsson, C. de Pedro, N. Paxeus, *J. Hazard. Mater.* **2007**, *148*, 751.
- [4] M. M. Ahmed, S. Barbati, P. Doumenq, S. Chiron, *Chem. Eng. J.* **2012**, *197*, 440.
- [5] F. Bayati, J. Shayegan, H. Shokrollahi, J. B. Parsa, *Chem. Eng. Trans.* **2009**, *17*, 257.
- [6] M. Boroski, A. C. Rodrigues, J. C. Garcia, L. C. Sampaio, J. Nozaki, N. Hioka, *J. Hazard. Mater.* **2009**, *162*, 448.
- [7] Z. Chen, H. Wang, N. Ren, M. Cui, S. Nie, D. Hu, *J. Hazard. Mater.* **2011**, *197*, 49.
- [8] Z. Chen, N. Ren, A. Wang, Z. P. Zhang, Y. Shi, *Water Res.* **2008**, *42*, 3385.
- [9] J. A. Melero, F. Martínez, J. A. Botas, R. Molina, M. I. Pariente, *Water Res.* **2009**, *43*, 4010.
- [10] P. J. Cyr, R. P. Suri, E. D. Helmig, *Water Res.* **2002**, *36*, 4725.
- [11] X. Zhou, Z. Zhang, Y. Li, *Can. J. Chem. Eng.* **2017**, *95*, 432.
- [12] Z. Zhou, Y. Ma, Y. Liu, S. Lu, Z. Ren, *Can. J. Chem. Eng.* **2017**, *95*, 290.
- [13] X. Xiao, Y. Sun, W. Sun, H. Shen, H. Zheng, Y. Xu, J. Zhao, H. Wu, C. Liu, *Can. J. Chem. Eng.* **2017**, *95*, 1245.
- [14] M. J. Dietrich, T. L. Randall, P. J. Canney, *Environ. Prog.* **1985**, *4*, 171.
- [15] S. K. Bhargava, J. Tardio, J. Prasad, K. Föger, D. B. Akolekar, S. C. Grocott, *Ind. Eng. Chem. Res.* **2006**, *45*, 1221.

- [16] K. Fajerweg, J. N. Foussard, A. Perrard, H. Debellefontaine, *Water Sci. Technol.* **1997**, *4*, 103.
- [17] L. Lei, X. Hu, P. L. Yue, *Water Res.* **1998**, *9*, 2753.
- [18] B. Weber, A. Chavez, J. Morales-Mejia, S. Eichenauer, A. Stadlbauer, R. Almanza, *J. Environ. Manage.* **2015**, *161*, 137.
- [19] Y. Pu, X. Wen, Y. Li, D. Wang, N. R. Foster, J.-F. Chen, *Powder Technol.* **2017**, *305*, 125.
- [20] Y. Pu, Y. Li, D. Wang, N. R. Foster, J. Wang, J.-F. Chen, *Powder Technol.* **2017**, *308*, 200.

---

*Manuscript received January 29, 2017; revised manuscript received March 20, 2017; accepted for publication March 22, 2017.*