Desalination and Water Treatment
www.deswater.com

26 (2011) 131–138
February

1944-3994/1944-3986 © 2011 Desalination Publications. All rights reserved
doi: 10/5004/dwt.2011.2122

The treatment of wastewaters by supercritical water oxidation

Onur Ömer Söğüt*, Ekin Kıpçak Yildirim, Mesut Akgün

Chemical Engineering Department, Yıldız Technical University, Davutpaša Campus, No. 127, 34210 Esenler, Istanbul, Turkey
Tel. +90 (212) 3834764; email: sogutonur@yahoo.com

Received 22 November 2009; Accepted 9 June 2010

ABSTRACT

In this study, the treatment performance of SCWO process is evaluated on various industrial wastewaters such as textile dyehouse effluent; pesticide containing model wastewater; olive mill wastewater and cheese whey. These wastewaters have significant pollution potentials due to their high organic loads. The experiments were made under sub- and supercritical conditions in a continuous flow reactor, using H_2O_2 as the oxygen source. The removal efficiencies are evaluated in terms of total organic carbon concentrations (TOC). The results demonstrate that at various experimental conditions, SCWO provides high organic conversion yields up to 100% in very short reaction times within 30 s for each wastewater sample.

Keywords: Supercritical water oxidation; Hydrothermal; Olive mill wastewater; Textile wastewater; Whey; Pesticide; Water reuse

1. Introduction

Amount of organic and toxic wastes produced is increasing every year, while the discharge limitations and environmental regulations on treatment standards are getting more stringent. Some technologies such as adsorption, biological oxidation, chemical oxidation, incineration and land-based solutions such as land filling, deep well injection and lagooning have their own disadvantages by organics contaminated water treatment. Land-based solutions are not about removing the organic content; they bring the risk of contamination of toxic organics into soil, groundwater and even air, if volatile organics exist in the waste mixture. It may be foreseen that land disposal will be prohibited in following years.

Oxidation-based destruction methods include activated carbon treatment, biological treatment, incineration, wet air oxidation (WAO) and supercritical water oxidation (SCWO). Activated carbon treatment and biological treatment usually require the wastewater to be very dilute with a maximum organics concentration of 1%. Incineration of dilute wastewaters is not economically favorable, because the energy balance requires a minimum organic content of 20% in order to minimize the supplemental fuel costs. This method has also the disadvantage of high investment costs of separation units for removal of stack gases from the exhaust streams.

Wet air oxidation systems are usually operated in a temperature range of 150–350 °C and pressure range of 2–20 MPa, with residence times between 15–120 min. The chemical oxygen demand (COD) removal is typically between 75% and 90%. Remaining COD content usually consists of volatile acids such as acetic acid, thus this method may require to be supported with another treatment system in order to remove the remaining organics which are potentially harmful for the nature. Oxidation under more severe conditions can be seen as the key to reach nearly complete destruction of various organics in very short residence times [1]. Water, the most important solvent in nature, has very important characteristics as a reaction solvent under supercritical conditions. Above its critical point (374.8 °C and 22.1 MPa),

*Corresponding author.

Presented at the International workshop on urbanisation, land use, land degradation and environment (ULE 2009), 28 September – 1 October 2009, Denizli, Turkey

water exhibits unique physicochemical properties that make it an effective reaction medium. Therefore, supercritical water offers a control mechanism depending on solubility, a low viscosity, excellent transport properties based on its high diffusion ability and new reaction possibilities for hydrolysis or oxidation.

SCWO brings together an oxidant such as fed air, oxygen or hydrogen peroxide as an oxygen source and organic compounds to be oxidized in the presence of huge amount of water at high temperatures (400–600 °C) and pressures (25–30 MPa). These temperature and pressure values are higher than the critical conditions of water (374 °C, 22.1 MPa), which can be seen as the reaction media, thus the reaction occurs in the supercritical phase. Under these conditions, waste organics can function as a fuel in the oxidation reaction and organic carbon oxidized to CO_2 and hydrogen atoms to H_2O. Up to 99.9% degradation of organic constituents in the wastewater is typically achieved within reaction times between a few seconds to a few minutes depending on the reaction temperature [2]. With these destruction efficiencies, treated wastewater streams can be discharged without any further treatment [3]. Obtaining the severe operational conditions may seem expensive, but the operational costs can be minimized with a precise energy integration of the SCWO plant [4]. The potential of industrial reuse of odorless, colorless and transparent reactor effluents with very low organic residues provides advantages to the SCWO process in economical aspects as well.

This study is focused on the treatment of four different wastewater samples: a textile dyehouse effluent, a water sample contaminated with a pesticide used in agricultural production, olive mill wastewater (OMW) and cheese whey by using SCWO. Removal of organic contents in these wastewater samples are investigated in terms of TOC concentration.

2. Experimental

SCWO experiments were performed in a continuous-flow reactor system as described in a previous work [5]. The oxidant feed stream consists of diluted hydrogen peroxide (H_2O_2) in deionized water. A second feed vessel was loaded with wastewater sample. Both of the feed liquids were pumped into the furnace to be preheated in separate lines. During preheating, hydrogen peroxide decomposes completely into oxygen and water [6]. After preheating to reaction temperature, both streams unite passing through a mixing tee and the oxidation reaction occurs in the following part of the pipeline. Upon exiting the reactor, the effluent was cooled rapidly through a heat exchanger. The solid particles, which would be formed presumably, were filtered out by an inline filter, before the stream was depressurized by a back pressure regulator used to keep the reactor under 25 MPa pressure. The product stream was then separated into liquid and vapor phases. The liquid products were collected and analyzed for remaining TOC concentrations.

3. Analytical methods

The wastewater and liquid phase reactor effluent concentrations were characterized by the analyses of the TOC contents. TOC analyses were performed by total organic carbon analyzer (HACH-LANGE IL550 TOC-TN), which is based on combustion catalytic oxidation method, using a highly sensitive multi-channel non-dispersive infrared detector (NDIR). Standard solutions for the calibration were prepared by using potassium hydrogen phthalate (Acros). All the reagents were pure for analytical use. In order to provide precise data, the samples were analyzed in triplicate, and the averages are reported as results. COD of the wastewater was measured by using NanoColor® test tubes according to Standard Method 5220 D [7].

3.1. Brief information on SCWO kinetics

Organics removal in supercritical water media takes place in two simultaneous incidents: hydrothermal degradation (or decomposition) and oxidation. Those two reactions are shown in two terms in the model equation. A typical SCWO reaction rate model equation is as follows [6]:

$$\frac{-d[\mathrm{TOC}]}{dt} = k_{Th}[\mathrm{TOC}]^a[\mathrm{H_2O}]^b + k_{Ox}[\mathrm{TOC}]^c [\mathrm{O_2}]^d[\mathrm{H_2O}]^e \quad (1)$$

Here, [TOC], [H_2O] and [O_2] represent the concentrations of TOC, water and oxygen in the reaction media, respectively. The terms a and b represent the reaction orders for TOC and water at hydrothermal degradation reaction; and the terms c, d and e represent the reaction orders for TOC, oxygen and water at oxidation reaction, respectively. k_{Th} and k_{Ox} are the reaction rate constants of thermal degradation and oxidation, respectively.

Rate constant (k) for any chemical reaction is defined in Arrhenius form as:

$$k = k_0 \cdot e^{-\frac{E}{RT}} \quad (2)$$

Here, k_0 is the pre-exponential factor and E_a is the activation energy (J mol^{-1}) specific for a given reaction. R and T are the universal gas constant and absolute temperature, respectively.

There is no consensus about the effect of water concentration on reaction rates. The reaction media mainly (~98%) consists of water, thus the water terms can be eliminated. Oxygen is used in excess at oxidation reactions and the changes in its concentration can be omitted. Thus, the equation takes the form shown below:

$$\frac{-d[\mathrm{TOC}]}{dt} = k_{Th,0}\cdot e^{-\frac{E_{a,Th}}{RT}}[\mathrm{TOC}]^a + k_{Ox,0}\cdot e^{-\frac{E_{a,Ox}}{RT}}[\mathrm{TOC}]^c[\mathrm{O_2}]_0^d \quad (3)$$

The terms $k_{Th,0}$, $k_{Ox,0}$, $E_{a,Th}$, and $E_{a,Ox}$ represent the pre-exponential factors and activation energy values of thermal degradation and oxidation, respectively. $[O_2]_0$ is the initial oxygen concentration in the reaction media.

3.1.1. Oxidation reaction

For oxidation reaction, the rate equation in terms of conversion ratio can be written as:

$$-[\mathrm{TOC}]_0\frac{d(1-X)}{d\tau} = k_{Ox,0}e^{-E_a/RT}[\mathrm{TOC}]_0^a(1-X)^a[\mathrm{O_2}]_0^b \quad (4)$$

Here, the term τ is residence time in the pipe reactor and X is organics conversion ratio which can be defined as:

$$X = 1-\frac{[\mathrm{TOC}]}{[\mathrm{TOC_0}]} \quad (5)$$

With initial condition of $X = 0$ at $\tau = 0$, the rate equation can be arranged as follows:

$$X = 1-\left[1+(a-1)10^{k_0}e^{-E_a/RT}[\mathrm{TOC}]_0^{a-1}[\mathrm{O_2}]_0^b\,\tau\right]^{1/(1-a)} \quad \text{for } a\neq 1 \quad (6)$$

3.1.2. Hydrothermal degradation reaction

With zero reaction order for TOC concentration, the reaction rate equation for hydrothermal degradation in absence of oxidant can be written as follows:

$$\frac{-d[\mathrm{TOC}]}{dt} = k_{Th,0}\cdot e^{-\frac{E_{a,Th}}{RT}}[\mathrm{TOC}] \quad (7)$$

Which can be arranged in terms of TOC conversion ratio:

$$-[\mathrm{TOC}]_0\frac{d(1-X)}{d\tau} = k_0 Exp(-E_a/RT)[\mathrm{TOC}]_0(1-X) \quad (8)$$

$$-[\mathrm{TOC}]_0\frac{d(1-X)}{d\tau} = k_0\cdot e^{(-E_a/RT)}[\mathrm{TOC}]_0(1-X) \quad (9)$$

For initial condition $X = 0$ at $\tau = 0$, final rate equation for hydrothermal degradation reaction becomes:

$$X = 1-e^{k_0\tau\cdot e^{-E_a/RT}} \quad (10)$$

4. Results and discussion

4.1. Textile dyehouse wastewater treatment

Textile industry wastewater generally contains undesirable components which are toxic and/or mutagenic to aquatic life [8]. Textile industries produce a huge amount of wastewater, which cause "money waste" if it is discharged instead of being reused after a proper treatment [9].

SCWO treatment of an original textile dyehouse wastewater sample has been investigated. In order to avoid precipitation of inorganic matter, a non-salty wastewater sample obtained from a synthetic fibers dyehouse was chosen for this study. Substances such as sodium acetate, acetic acid, imidazolyne based softener, C.I. Basic Yellow 13, C.I. Basic Red 46, C.I. Basic Blue 3, C.I. Basic Blue 41, C.I. Basic Blue 159 containing wastewater with an unknown composition was obtained from a textile factory located in Yalova, Turkey. Because the composition is unknown, the organic matter content has been evaluated in terms of TOC. The visually inspected color of the wastewater was dark violet. Fig. 1 shows the untreated wastewater sample together with a reactor effluent sample after SCWO in 550 °C. Table 1 shows the properties of the wastewater.

Fig. 1. Untreated textile dyehouse wastewater sample and reactor effluent after SCWO (550 °C).

Table 1
Properties of dyehouse wastewater

Parameter	Value
COD	1467 mg l^{-1}
TOC	744.5 mg l^{-1}
TN	109.4 mg l^{-1}
pH	4.92

By hydrothermal degradation of dyehouse wastewater, the TOC content in the liquid effluent drops even in the absence of oxidant, so it is obvious that the organics leave the system in gas phase by transforming into gaseous hydrocarbons. By increasing the temperature from 450 °C to 650 °C, conversion ratios in terms of TOC increase from 15% to 70.5%. Experimental results are graphically shown on Figs. 2 and 3. Fig. 2(a) shows the TOC removal without using oxidant and (b) with oxidant at various reaction temperatures. Considering the final TOC intervals on the Figures, it is obvious that the presence of oxidant increases the conversion ratios.

Fig. 3 shows the SCWO reaction results by variable oxidant concentrations at 500 °C and 550 °C temperatures. Increasing oxidant concentrations make the SCWO reactions more effective, but repeating the same reactions with only 50 °C higher temperature increases the conversions even more dramatically than the increasing oxidant concentrations do. This comparison on magnitudes of temperature and oxidant concentration effects on SCWO applies also to the other wastewater samples discussed in this work.

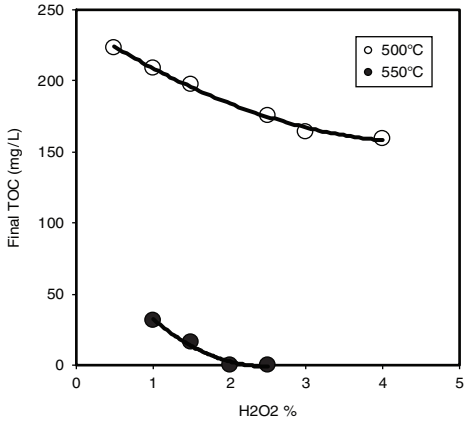

Fig. 3. Effect of oxidant concentration on TOC removal under 500 °C and 550 °C temperatures with 8 s residence time.

4.2. Olive mill wastewater treatment

Olive mill wastewater (OMW) is a dark–colored byproduct of olive oil industry which has highly polluting characteristics. It contains high amounts of polyphenols, volatile acids, polyalcohol, nitrogen compounds, pectin, oil and tannin [10]. Toxic phenolic ingredients of the OMW require to be removed prior to biological treatment, which can be considered as an additional cost [11,12]. The OMW mentioned in this work was obtained from an olive oil production plant near Aydın, Turkey. Some of the properties of the OMW are shown in Table 2.

A roughly filtered OMW sample with an initial TOC concentration of 19,100 mg l^{-1}, which was supplied from an olive oil factory, has been treated using SCWO. As expected, temperature and oxidant concentrations both

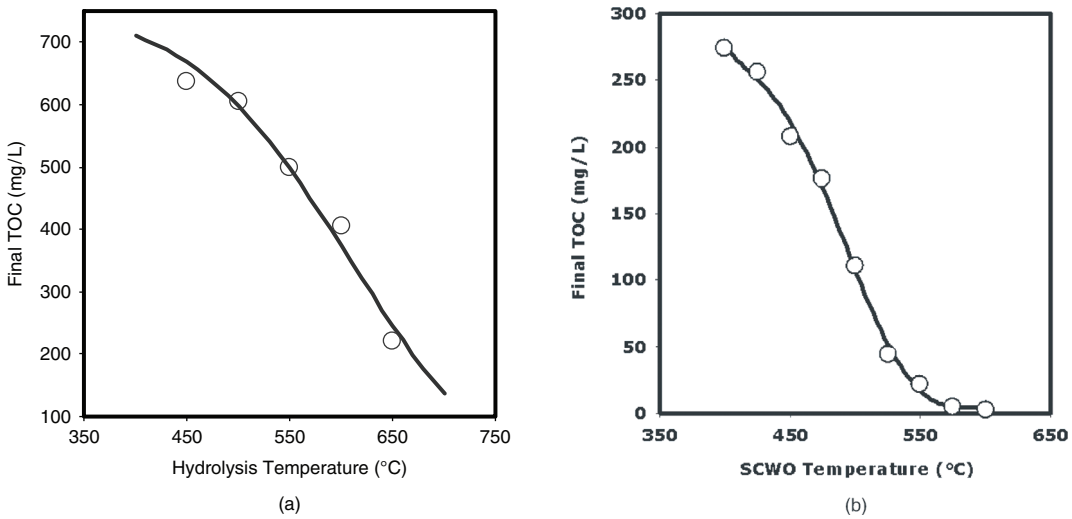

Fig. 2. (a) Effect of temperature on textile wastewater hydrolysis in absence of oxygen. Residence time: 10.6 s. (b) Effect of temperature on SCWO efficiency using 2% H_2O_2 solution with 8 s residence time.

Table 2
Properties of the OMW

Parameter	Value
COD	55,000 mg l^{-1}
TOC	19,100 mg l^{-1}
TN	395.6 mg l^{-1}
pH	5.37

affect the result, and temperature is more essential than high oxidant concentrations.

Figs. 4a and 4b represent the effect of varying oxidant concentrations under constant temperature, and varying temperatures with constant oxidant concentration on TOC removal with SCWO, respectively. As seen on the Figures, the final TOC values change more consequently with changing temperatures than with changing oxidant concentrations.

The visual results of the OMW treatment are shown in Fig. 5 with two examples. Fig. 5 shows samples of reactor effluents after treatment under 500 °C and 550 °C temperatures with an untreated OMW sample. The slightly yellowish color observed at the sample obtained from SCWO under 500 °C was completely removed in 550 °C.

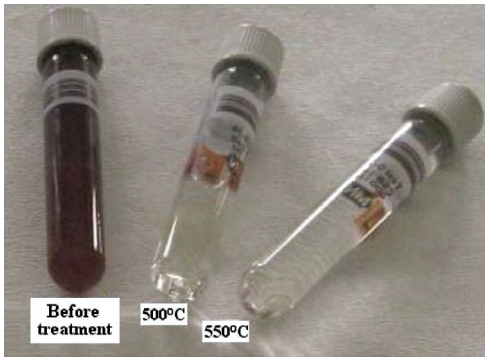

Fig. 5. Untreated OMW sample with 500°C and 550°C reactor effluent samples.

Table 3
Properties of the cheese whey

Parameter	Value
COD	102,000 mg l^{-1}
TOC	56,000 mg l^{-1}
TN	610 mg l^{-1}
pH	4.06

4.3. Cheese whey treatment

Even dairy wastewater generally does not contain toxic chemicals, it has to be treated because of its organic content and decomposition of which result also an inconvenient odor [13]. Whey is the liquid residue of milk after separation of casein and fat. It contains lactose, soluble non–casein proteins, vitamins, minerals and traces of milk fat. Those organics result characteristically in a COD concentration of 50,000–70,000 mg l^{-1}, therefore it cannot be discharged and requires to be processed even it may be economically unbeneficial [14,15]. A homemade cheese whey sample was treated by SCWO. Table 3 shows the properties of the untreated cheese whey sample. A photograph of an untreated

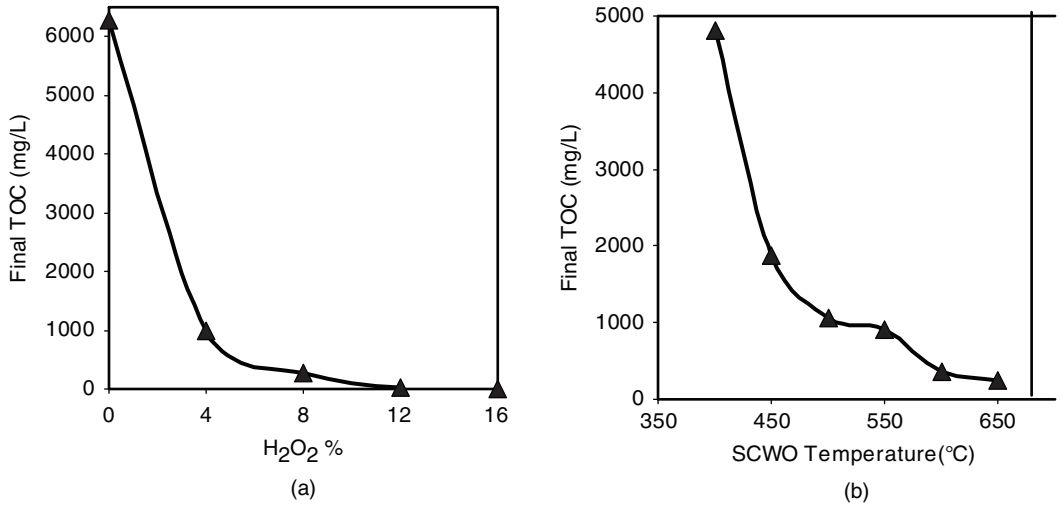

Fig. 4. (a) Effect of oxidant concentration on SCWO of OMW at 600 °C. Res. time: 10 s. (b) Temperature effect on SCWO of OMW. H_2O_2 concentration: 8%. Res. time: 10 s.

Fig. 6. Untreated cheese whey sample (left) and the 550 °C reactor effluent sample after SCWO.

cheese whey sample together with an SCWO–treated reactor effluent sample is shown in Fig. 6.

From a 1/10 diluted cheese whey with an initial TOC concentration of 5600 mg l^{-1}, TOC removal efficiencies between 87.06% and 99.76% were obtained in various experimental conditions within 6–21 s residence times. Fig. 7 shows results of oxidant concentration (a) and temperature (b) dependent TOC removal experiments, respectively.

4.4. Agricultural pesticide contaminated wastewater treatment

Pesticides generally are chemically stable and resistant to biodegradation. They are water soluble and can contaminate the ground water [16]. Traditional oxidation processes with limited organics conversions form mutagenic compounds, which are still dangerous for the aquatic life [17].

SCWO treatment of an agricultural pesticide (o,o–dimethyl–2, 2–dichloro vinyl phosphate) contaminated model wastewater sample has been investigated. Pesticide sample (Didifos® 55EC) is obtained from its producer (Hektaş Co., İstanbul). Initial TOC concentration of the sample was 54.71 mg l^{-1}. TOC removal efficiencies between 70.4%–100% have been achieved under various conditions within reaction times of 7–21 s.

Fig. 8 shows the effect of oxidant concentration (a) and of temperature (b) on TOC removal from pesticide contaminated wastewater.

4.5. Kinetic evaluation for hydrothermal and oxidative treatment of the pesticide in supercritical water

The unknown parameter values in Eqs. (6) and (10) can be determined after statistical analysis. As an example, after statistical analysis from experimental data obtained by the treatment of pesticide containing model wastewater, the overall model equation for hydrothermal degradation and supercritical water oxidation become:

For SCWO,

$$-\frac{d[\mathrm{TOC}]}{dt} = 1.954(s^{-1})e^{\frac{-19.425\,\frac{kJ}{mol}}{\mathrm{RT}}}\cdot[\mathrm{TOC}] + 0.628(mmol^{-0.35}L^{0.35}S^{-1})e^{\frac{-36.084\,\frac{kJ}{mol}}{\mathrm{RT}}}\cdot[\mathrm{TOC}]^{1.15}\cdot[0_z]^{0.2} \quad (11)$$

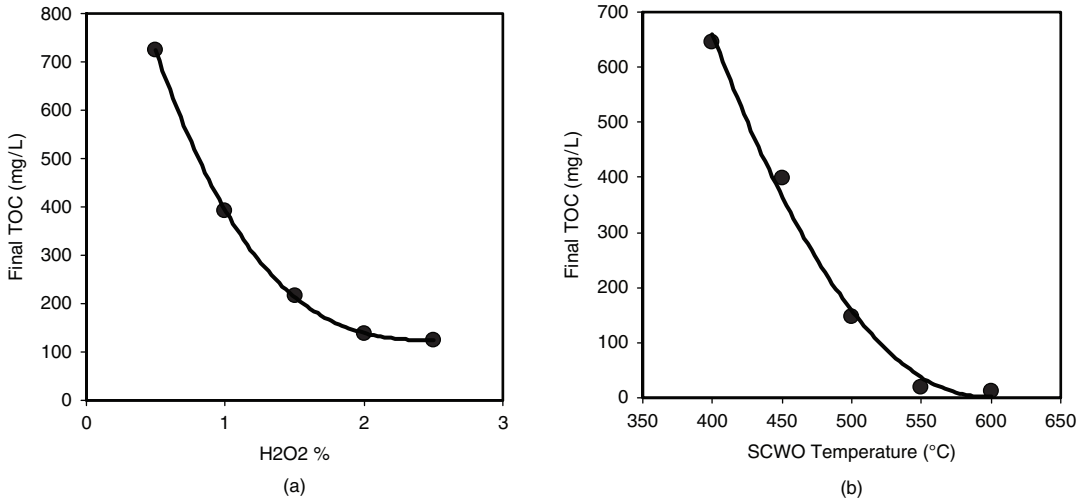

Fig. 7. (a) Effect of oxidant concentration on SCWO of cheese whey with 8 s residence time, at a temperature of 500 °C. (b) Effect of temperature on SCWO of cheese whey with 8 s residence time.

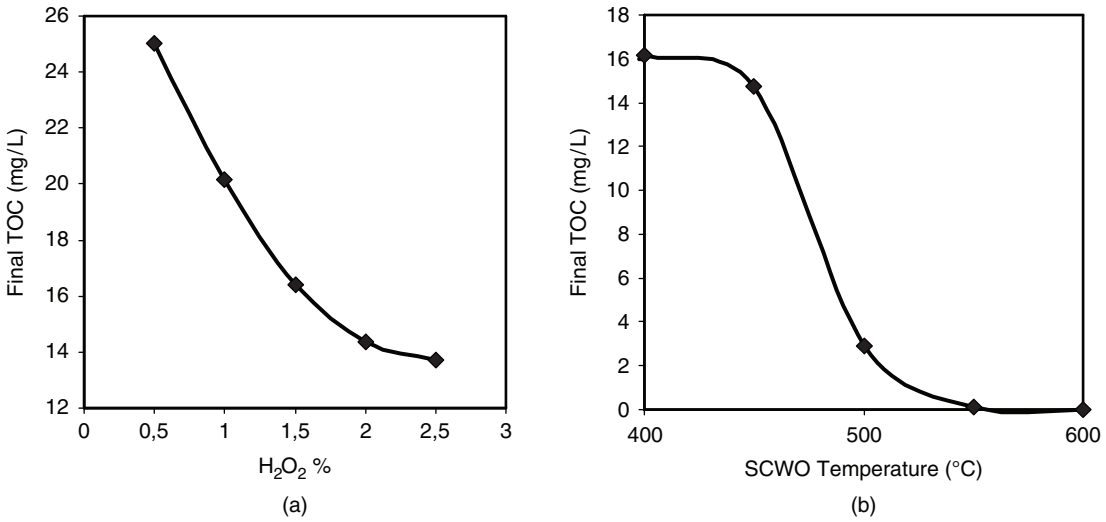

Fig. 8. (a) Effect of oxidant concentration on TOC removal from pesticide contaminated wastewater under 500 °C temperature with 8 s residence time. (b) Effect of temperature for the same wastewater. Residence time: 8 s. H_2O_2 concentration: 2%.

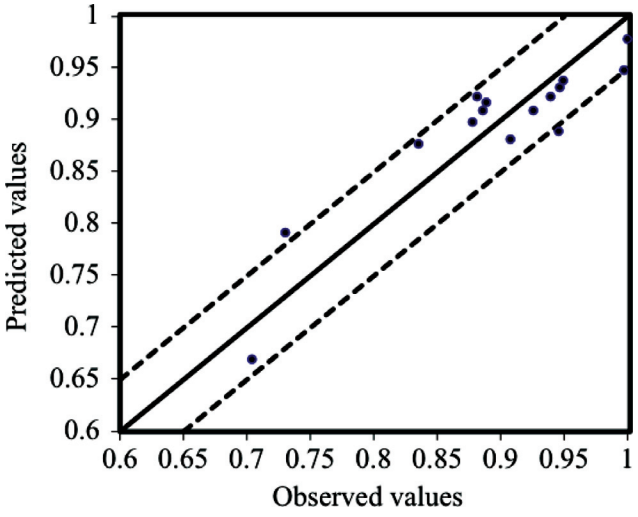

Fig. 9. Comparison of experimental and model results for SCWO of pesticide containing model wastewater.

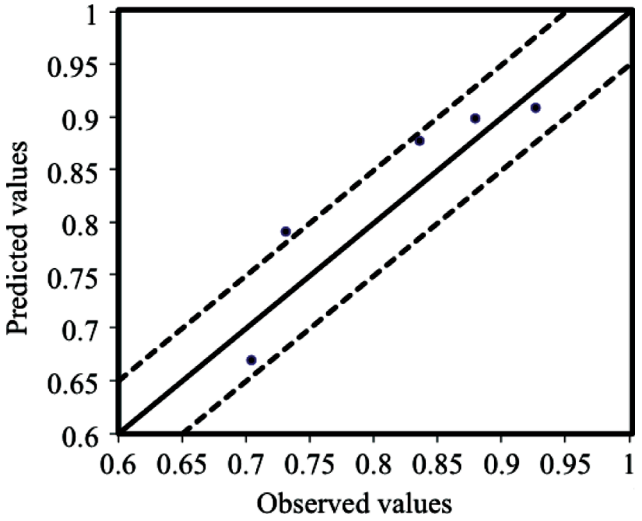

Fig. 10. Comparison of experimental and model results for hydrothermal degradation of pesticide containing model wastewater.

The results obtained by using the experimental conditions in the model equation were compared with the actual experimental data. Figs. 9 and 10 show this comparison of the experimental and model results for SCWO and hydrothermal degradation experiments, respectively. Predicted and observed values represent the model and experimental conversion results for each run, respectively.

5. Conclusion

SCWO treatment of four different wastewater samples containing various organics in a laboratory scale continuous flow pipe reactor was investigated in this work.

Degradation of organic content occurs in two simultaneous steps, thermal decomposition and oxidation. Thermal decomposition is the transformation of the organic substances in the wastewater into smaller gaseous hydrocarbons under high temperatures, even in absence of oxygen. In order to understand the role of thermal degradation in SCWO reactions, individual experiments under various temperatures were carried out without using hydrogen peroxide.

Because of the severe conditions in reaction media with minimized mass transfer limitations, SCWO reactions resulted with very rapid removal of TOC content for all types of samples. First, temperature and then

oxidant concentration in the reactor were the main variables affecting the TOC conversions by SCWO.

Achieving the severe conditions such as high pressure and temperatures sound expensive, but with a precise heat integration, this process could be even economically beneficial regarding the high conversion rates obtained in very short reaction times.

Acknowledgements

This work has been supported by The Scientific and Technological Research Council of Turkey (TUBITAK, project no. 104M214).

References

[1] V. Bambang and K.J. Duck, J. Environ. Sci., 19 (2007) 513–522.
[2] R.M. Serikawa, T. Usui, T. Nishimura, H. Sato, S. Hamada and H. Sekuno, Fuel, 81 (2002) 1147–1159.
[3] Giovanni Del Re, and Gabriele Di Giacomo, Desalination, 138 (2001) 61–64.
[4] M.J. Cocero, E. Alonso, M.T. Sanz and F. Fdz–Polanco, The J. Supercrit. Fluid., 24 (2002) 37–46.
[5] O.Ö. Söğüt and M. Akgün, The J. Supercrit. Fluid., 43 (2007) 106–111.
[6] E. Croiset, S.F. Rice and R.G. Hanush, AIChE J., 43 (1997) 2343–2352.
[7] A.D. Eaton, L.S. Clesceri and A.E. Greenberg, Standard Methods for the Esamination of Water and Wastewater, 19th ed., American Public Association, Washington, DC, 1995.
[8] A. Maljaei, M. Arami and N. Mohammad Mahmoodi, Desalination, 249 (2009) 1074–1078.
[9] Woei–Jye Lau and A.F. Ismail, Desalination, 245 (2009) 321–348.
[10] H. Erkonak, O.Ö. Söğüt and M.Akgün, The J. Supercrit. Fluid., 46 (2008) 142–148.
[11] Ezgi Oktav Akdemir and Adem Ozer, Desalination, 249 (2009) 660–666.
[12] Oliver Chedeville, Marie Debacq, and Catherine Porte, Desalination, 249 (2009) 865–869.
[13] Baisali Sarkar, P.P. Chakrabarti, A. Vijaykumar and Vicay Kale, Desalination, 195 (2006) 141–152.
[14] J.-C. Frigon, J. Breton, T. Bruneau, R. Moletta and S.R. Guiot, Bioresource Tech., 100 (2009) 4156–4163.
[15] M.S. Yorgun, I. Akmehmet Balcioglu and O. Saygin, Desalination, 229 (2008) 204–l216.
[16] Aida Kestaoui Abdesselam, Nizar Bellakhal, Nihal Oturan, Muhamed Dachraoui, Mehmet and A. Oturan, Desalination, 250 (2010) 450–455.
[17] M.I. Badawy, Monraser Y. Ghaly, Tarek and A. Gad–Allah, Desalination, 194 (2006) 166–175.