Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.21494

99 (2017) 309–314
December

Continuous measurement of total organic carbon based on supercritical water oxidation

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Received 20 December 2016; Accepted 27 September 2017

ABSTRACT

A new instrument based on supercritical water oxidation (SCWO) and non-dispersive infrared (NDIR) detection was constructed. The investigation for the continuous measurement of the total organic carbon (TOC) of wastewater was carried out. 2-naphthol was selected as a typical organic pollutant. The linear relationship between TOC concentration of wastewater sample and NDIR signal value was established which showed that the continuous measurement of TOC detection with instrument constructed based on SCWO-NDIR technique is practical. The TOC detecting conditions such as feed flow (or residence time), oxidant multiple, and temperature of SCWO were tested. The results showed that residence time between 150 and 200 s was long enough to ensure the thorough decomposition of organics; when the suitable feed flow was 1.5–2.0 mL/min, the detection rate of 99% or higher could be obtained; the oxidant multiple more than nine was needed and the temperature of SCWO could be set at 440°C–460°C to obtain a satisfactory detection rate. The accuracy and precision of the instrument were also tested and the relative standard deviation of the measurement data was 0.92% and 1.59% respectively. The detection rate range of the simulated wastewater samples was 99.7%–101.2% for the instrument constructed. There was no obvious difference compared with the detection rates by Shimadzu TOC analyzer (VCPH).

Keywords: Supercritical water oxidation; Continuous measurement; Total organic carbon; 2-naphthol

1. Introduction

Supercritical water oxidation (SCWO) technology was proposed by American scholar Modell [1,2] at the beginning of 1980s. Water in the state above its critical point (374.3°C and 22.12 MPa) is known as supercritical water (SCW). SCW is more conducive to the formation of free radicals than normal water and substances dissolved in SCW show abnormal partial molar behavior, which can greatly improve the reaction rate and allow refractory organics to be oxidized to CO_2, H_2O and other non-toxic small-molecule compounds in a short period of time [3,4]. Because of the above advantages of SCW, the treatment of wastewater by SCWO has been widely studied [5–16]. In recent years, the United States, some European countries (e.g., Germany, Britain, and France), Japan, South Korea and other developed industrial countries have built a series of small pilot plants based on SCWO and have achieved satisfactory results under the cooperation of government, company, university and other research institutions. The processing objects are mainly wastewater containing polychlorinated biphenyls, phenol, nitrophenol, acrylonitrile [17–21] and other non-biodegradable toxic waste [22]. Therefore, these studies and applications are mainly focused on the technology of wastewater treatment.

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Total organic carbon (TOC) is a comprehensive indicator of the total amount of organic carbon in water, which represents the sum of the organics contained in the wastewater [23,24]. It not only directly reflects the content of organic pollutants but also is a high accurate measurement. Now TOC has been widely used to monitor the quality of surface water and wastewater. The basic principle of TOC measurement includes the oxidation of organic carbon to CO_2 and the detection of CO_2. The current method for organic oxidation used high-temperature combustion or wet catalytic oxidation. These methods either require high temperatures or need catalysts. Furthermore, there exist salt clogging problem when wastewater contains inorganic salt. Fortunately SCWO, because of its characteristics of fast reaction speed and complete oxidation, can be used as the oxidation method in the TOC detection process. In this case, no catalyst or high temperature is needed, and more importantly, there is no salt clogging problem because pure water was used as the mobile phase and the inorganic salts (if exist) would flow out with the water. The instrument could be cleaned by pure water flow after sample detection. Therefore, SCWO is expected to be a new method for TOC detection which achieved great attention. On the other hand, the current TOC analyzer was generally used to test individual water sample. TOC concentration of the sample could be calculated by the linear relationship between the TOC concentration of the standard sample and CO_2 peak area. However, the above-mentioned linear relationship was no longer suitable for the calculation when TOC concentration of the wastewater needs to be detected continuously. In this paper, a new instrument based on SCWO and non-dispersive infrared (NDIR) detection was constructed. 2-Naphthol is an important organic intermediate and widely used in dye and pharmaceutical industry. In addition, it is a common refractory organic pollutant; hence, it was chosen as the model pollutant. The investigation for the continuous measurement of TOC of wastewater was carried out.

2. Materials and methods

2.1. Instrumentation

Fig. 1 is the diagram of TOC measuring instrument with continuous sample introduction, continuous oxidation under supercritical water condition, and continuous detection by NDIR, consisting of a sampling unit, SCWO reaction unit, separation unit, and NDIR detection unit. First, a certain concentration of 2-naphthol (Shanghai Jinshan Tingxin Chemical Reagent Company (Jinshan District, Shanghai), >98% purity) solution, ultrapure water and oxidant solution (H_2O_2, 30% wt) were mixed proportionally through a low-pressure gradient mixer and then pumped continuously into the helical reactor made of stainless steel tube (length 30 m, o.d. 1/8", i.d. 1.5 mm) by the high-pressure constant-flow pump. The 2-naphthol in liquid was sufficiently oxidized continuously under the supercritical water. After the reaction, the pressure was lowered by the back pressure valve and the liquid after cooling flows into the gas–liquid separation cell (placed in a thermostat water bath pot) where the CO_2 was continuously blown off by high-purity N_2 (200 mL/min). The wet CO_2 gas was dried by an electronic dehumidifier and then detected continuously by the NDIR detection unit. The TOC of the sample was proportional to the concentration of CO_2 in the gas flow; that is, the signal of NDIR. Therefore, the organic carbon content of the tested water samples can be analyzed according to the signal of NDIR. The whole process with continuous sample introduction, continuous reaction, and continuous detection was achieved. Meanwhile, the TOC of samples was also detected by a Shimadzu TOC analyzer

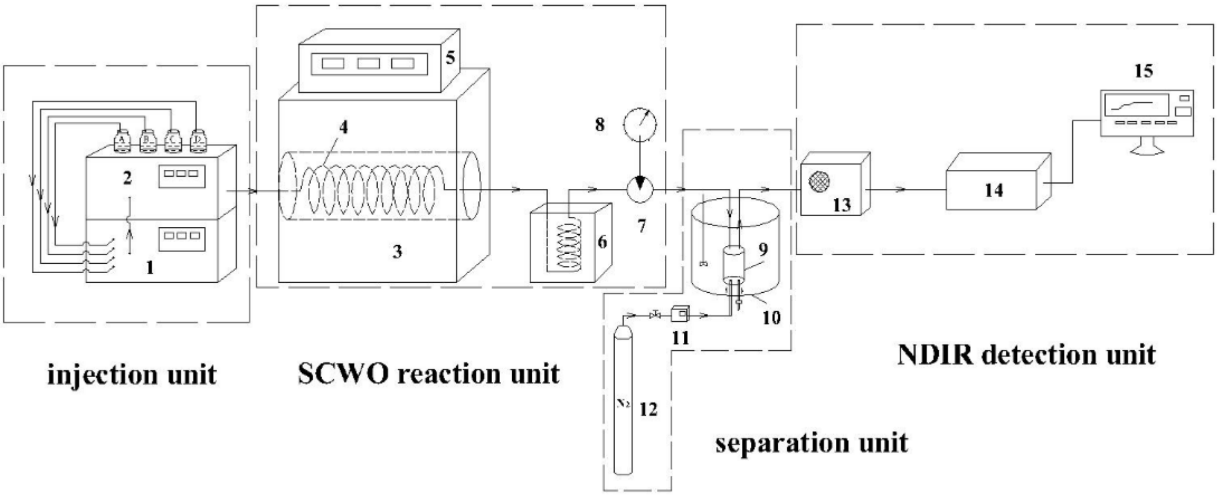

Fig. 1. Diagram of the analysis equipment for TOC detection by SCWO-NDIR; (1) low-pressure gradient mixer, (2) high pressure constant flow pump, (3) furnace, (4) tube reactor, (5) PID temperature controller, (6) cooling tank, (7) back pressure valve, (8) pressure gauge, (9) gas–liquid separation cell, (10) thermostat water bath, (11) mass flowmeter, (12) nitrogen cylinder, (13) electronic dehumidifier, (14) NDIR detector, and (15) computer.

(VCPH) with combustion oxidation so as to make a comparison with SCWO and NDIR detection.

2.2. Control of conditions

The concentrations of organic pollutant and oxidant could be controlled by regulating the proportionality. The experimental range was covered with a feed solution of 1,000 mg/L of 2-naphthol, hydrogen peroxide (H_2O_2) solution, and ultrapure water. The residence time could be varied by adjusting the feed flow (1.0–2.5 mL/min). The 2-naphthol and H_2O_2 contents were very low and could be neglected. Therefore, the physical properties of pure water were used to describe the phase behavior of the mixed reacting system. τ, the residence time of mixed substances in the reactor was calculated by the following equation:

$$\tau(\mathrm{s}) = \frac{V_R \cdot \rho_{p,T}}{q_m} \tag{1}$$

where V_R was the reactor volume (cm^3), $\rho_{\mathrm{p,T}}$ was the water density at reaction pressure and temperature ($\mathrm{g/cm}^3$), and q_m was the mass flow (g/s). The density of SCW was calculated via the p-V-T relation of SCW [25,26], and values are listed in Table 1. The residence time ranged from 115 to 309 s depending on the mass flow, temperature 460°C–480°C and pressure 24.0 MPa.

2.3. Definition of the oxidant multiple and the detection rate X

2-Naphthol in the sample could be oxidized by H_2O_2 to produce CO_2 during SCWO and H_2O_2 dosage is an important parameter that affect the organic carbon conversion. However, it is not easy to determine theoretically the amount of H_2O_2 needed because of its unstability and the complexity of the oxidation reaction. Hence, it is necessary to define an oxidant multiple (*n*), the ratio of H_2O_2 dosage to the theoretical oxygen demand, according to the following stoichiometric equation and to obtain the suitable value by experiment.

$$C_{10}H_8O + 23H_2O_2 \rightarrow 10CO_2 + 27H_2O \tag{2}$$

The detection rate *X* could be calculated by the following equation:

$$X = \frac{\mathrm{TOC}_m}{\mathrm{TOC}_t} \times 100\% \tag{3}$$

Table 1
The density of supercritical water under different temperature and pressure (g/mL)

P (MPa)	*T* (°C) 24.0
380	0.399
400	0.154
420	0.122
440	0.107
460	0.0972
480	0.0901

where $\mathrm{TOC_m}$ was the measured TOC (mg/L) value of the sample detected by the NDIR signal and $\mathrm{TOC_t}$ was the theoretical value of TOC (mg/L).

3. Results and discussion

3.1. Establishment of the relationship between TOC concentration and NDIR signal

The current TOC analyzer was generally used to test individual water sample. The sample first entered a catalytic combustion unit and the organic carbon was oxidized to CO_2 at high temperature; then CO_2 in gas–liquid mixture was blown off by high purity N_2 and the wet gas was dried by an electronic dehumidifier; finally, CO_2 in the gas was detected by the NDIR detector to gain the corresponding CO_2 peak area. TOC concentration of the sample could be calculated by the linear relationship between the TOC concentration of the standard sample and CO_2 peak area. However, the above mentioned linear relationship was no longer suitable when TOC concentration of the wastewater needs to be detected continuously. Therefore, the new relationship between TOC concentration of standard sample and NDIR signal value should be established for the continuous measurement of TOC by the new equipment constructed on the base of SCWO. According to the knowledge of gas–liquid equilibrium and thermodynamics, the amount of CO_2 generated via the oxidation of organic carbon from the continuous water sample stream was in direct proportion to the CO_2 concentration of gas phase, as long as temperature and pressure of the gas–liquid separator maintained constants, and then the NDIR detector had a corresponding signal value at this moment. Hence, there was a certain relationship between TOC concentration of the continuous water sample flow and NDIR signal, meanwhile the NDIR signal would change with the variation of TOC concentration in continuous water samples. Attempts were made to realize the continuous measurement of TOC in water samples by establishing the relationship between TOC concentration of continuous standard sample and NDIR signal value.

2-Naphthol was chosen to be as the model organic to prepare the standard water sample with known concentration in this experiment. The analytical grade 2-naphthol was dried for 1 h at a temperature of 120°C and dissolved in 1 L of ultrapure water, preparing a standard solution with 1,000 mg/L of TOC. Samples with different concentrations diluted from the original standard solution were measured under SCWO conditions of temperature of 480°C, pressure of 24.0 MPa, an injection flow rate of 2.0 mL/min, and oxidant multiple $n = 20$. The advantageous conditions such higher temperature and larger oxidant multiple were set to assure 2-naphthol was oxidized completely.

Fig. 2 shows the linear relation between the initial TOC concentration of samples and the NDIR signal value. The organic carbon in 2-naphthol solution was completely oxidized to CO_2, whose concentration was in proportion to the NDIR signal value. The good linear relationship between the NDIR signal value and the concentration of organic substances in tested water samples indicated that TOC detection employing the SCWO-NDIR technique was practical.

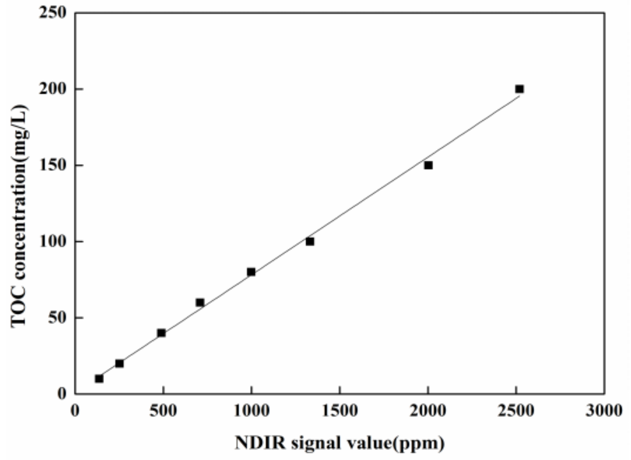

Fig. 2. The relationship between TOC concentrations and NDIR signal value reaction conditions: temperature 480°C, pressure 24.0 MPa, injection flow rate 2.0 mL/min, oxidant multiple $n = 20$.

3.2. Investigation of TOC testing conditions

Continuous measurement of TOC using the equipment constructed based on SCWO and NDIR detection would concern mainly with the feed flow rate or residence time of sample, oxidant multiple, temperature, and pressure of SCWO. The earlier report showed that the weak effect of pressure of SCWO on the decomposition of organics has been observed and 24.0 MPa was appropriate pressure for the SCWO system [26,27]. The feed flow rate or residence time of sample, oxidant multiple, temperature of SCWO will be discussed in the following sections.

3.3. Feed flow rate or residence time of sample

Generally, the residence time of SCWO system would largely affect the decomposition of the organics. In other words, in these experiments, the TOC detection rate X would be influenced by feed flow rate of sample obviously. The measured TOC and its corresponding detection rate X of samples under different feed flows (i.e., residence time) are listed in Table 2 for pressure of 24.0 MPa, oxidant multiple $n = 9$ and temperature of 460°C. Similar results at 480°C are also listed in Table 2. When the sample was fed at 2.5 mL/min, the TOC detecting rate was relative lower. That is to say when the residence time were relative shorter the organic carbon could not be converted to CO_2 completely. The reduction of feed flow rate, that is, the increase of residence time was conducive to improve the TOC detection rate. However, long residence time was unnecessary when the feed flow rate was less than 1.5 mL/min. The result showed that 150–200 s of residence time was long enough to ensure the thorough decomposition of organics. When the feed flow was 1.5–2.0 mL/min, the detection rate X of 99% or higher could be obtained.

Table 2
Effect of feed flow on the detection result of TOC with different temperature

Temperature (°C)	Feed flow (mL/min)	τ (s)	TOC_m (mg/L)	X (%)
460	1.0	309	833.41	100.01
	1.5	206	833.24	99.99
	2.0	155	829.06	99.49
	2.5	124	813.30	97.60
480	1.0	286	833.06	99.97
	1.5	191	832.49	99.9
	2.0	143	826.41	99.17
	2.5	115	817.77	98.13

τ: the residence time, s.

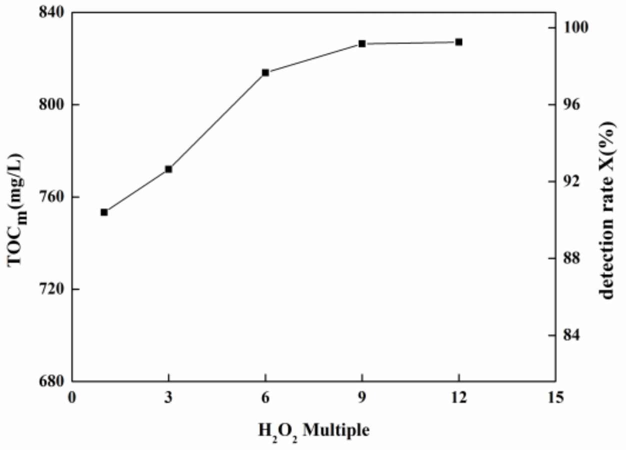

Fig. 3. Effect of H_2O_2 multiple on the detection result of TOC reaction conditions: temperature 400°C, pressure 24.0 MPa, injection flow rate 2.0 mL/min.

3.4. Oxidant multiple

The organic carbon is converted via the oxidation reaction so the oxidizer would play a crucial part in TOC detection. The aqueous H_2O_2 solution was used as the oxidant, and the effects of the oxidant multiple n on the detection result of TOC are shown in Fig. 3. The temperature, pressure of SCWO and feed flow of sample were maintained at 400°C, 24.0 MPa and 2.0 mL/min, respectively. Theoretically, the oxidant little more than stoichiometric equivalence is enough for the oxidation conversion of organic carbon. However, small excess of H_2O_2 (i.e., $n = 1–6$) did not lead to high TOC detecting rate which may be explained by the instability of H_2O_2 and the consequent loss of oxidant ability. The result demonstrated that the larger oxidant multiple more than nine was needed to obtain a satisfactory detection rate.

3.5. Temperature of SCWO

As everyone knows, temperature is an important condition for a reaction; temperature of SCWO is the indispensable parameter investigated for TOC detection. The TOC_m changed with reaction temperature under pressure of 24.0 MPa, feed flow of 2.0 mL/min, and $n = 9$ are shown in Fig. 4. TOC_m was significantly affected by temperature and the increase of temperature could promote the conversion of organic carbon and the detection of TOC. However, higher temperature also put forward severe requirement for SCWO reactor and cause higher energy consumption during the detection. The results showed that the temperature of SCWO could be set at 440°C–460°C to accomplish the TOC detection.

3.6. Accuracy and precision

Accuracy and precision are important indexes to estimate a new analysis method or equipment constructed. It is necessary to investigate the precision of the instrument and the accuracy of the method. The precision and accuracy were expressed by the relative standard deviation (RSD, %) and the detection rate (%) of samples respectively.

Under the same experimental conditions, one sample was measured with the instrument six times. The results are shown in Table 3. The RSD could be calculated by the following equation. The RSD of the measured data was 0.92% and the precision of the instrument was quite satisfactory.

At the same time, six samples with same TOC concentration were detected with the instrument under the same experimental conditions. The results are shown in Table 4 and the average TOC concentration of samples was 730.3 mg/L. The RSD of the measured data was 1.59%, which showed that the instrument have good reproducibility.

On the other hand, the simulated wastewater samples containing 2-naphthol were detected by a Shimadzu TOC analyzer and the instrument constructed in this paper respectively for comparison. The results are listed in Table 5 and the detection rate ranging with the instrument constructed was 99.7%–101.2%. Compared with the recoveries by Shimadzu TOC analyzer, there was not much difference. Therefore, the TOC detection instrument based on SCWO could be used to detect the TOC concentration of wastewater samples.

4. Conclusions

New instrument based on SCWO and non-dispersive infrared detection was constructed to investigate the continuous measurement of the TOC of wastewater. The TOC detecting conditions such as feed flow (or residence time), oxidant multiple, and temperature of SCWO were tested. The main conclusions were as follows:

- The linear relationship between TOC concentration of wastewater sample and NDIR signal value was established, and the continuous measurement of TOC detection with equipment constructed based on SCWO-NDIR technique was achieved.
- The result showed that 150–200 s of residence time was long enough to ensure the thorough decomposition of organics. When the suitable feed flow was 1.5–2.0 mL/min,

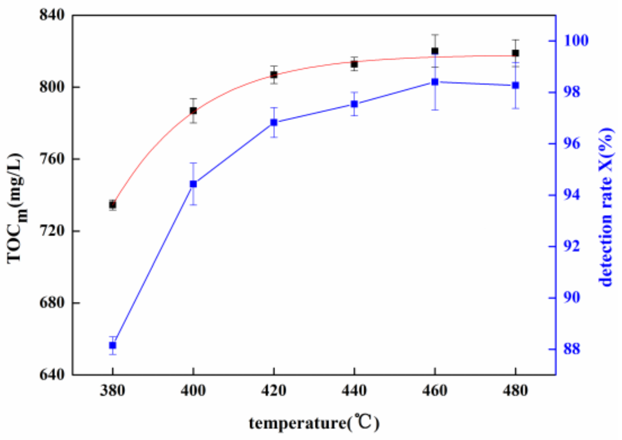

Fig. 4. The effect of temperature on the detection result of TOC reaction conditions: pressure 24.0 MPa, injection flow rate 2.0 mL/min, oxidant multiple $n = 9$.

Table 3
Results of precision experiments

Experimental conditions	Measuring NO.	TOC$_m$ (mg/L)	RSD (%)
$T = 380°C$	1	730.6	0.92
$P = 24.0$ MPa	2	736.8	
$n = 6$	3	728.1	
	4	720.9	
	5	732.2	
	6	740.0	

Table 4
Results of repeatability experiments

Experimental conditions	Sample NO.	TOC$_m$ (mg/L)	RSD (%)
$T = 380°C$	1	719.9	1.59
$P = 24.0$ MPa	2	718.9	
$n = 6$	3	740.8	
	4	720.2	
	5	740.2	
	6	741.6	
	Average	730.3	

Table 5
Comparison of TOC detection by the instrument constructed and Shimadzu TOC analyzer

	Sample NO.	1	2	3	4	5
TOC(mg/L)	Theoretical value	20.31	30.47	40.63	60.94	81.26
	By the instrument constructed	20.56	30.41	40.52	61.01	81.18
	By Shimadzu TOC analyzer	20.66	30.75	40.69	61.71	81.41
Detecting rate (%)	By the instrument constructed	101.2	99.8	99.7	100.1	99.9
	by Shimadzu TOC analyzer	101.7	100.9	100.1	101.3	100.2

the detection rate *X* of 99% or higher could be obtained. The oxidant multiple more than nine was needed and the temperature of SCWO could be set at 440°C–460°C to obtain a satisfactory detection rate.

- The RSD of the measurement data was 0.92% and 1.59%, respectively. There was no obvious difference between the recoveries of the simulated wastewater samples obtained by the instrument constructed in this paper and Shimadzu TOC analyzer.

Acknowledgments

This work was supported by the Science Foundation of Zhejiang Province (No. LY12B07009) and the Welfare Technology Research Projects of Zhejiang Province (No. 2013C33015).

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