Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.792164

51 (2013) 7025–7035
November

Taylor & Francis
Taylor & Francis Group

Treatment of cotton printing and dyeing wastewater by supercritical water oxidation

Qi Wang[a,b], Yongkang Lv[a], Rong Zhang[c], Jicheng Bi[c,*]

[a]*College of Chemistry and Chemical Engineering, Taiyuan University of Technology, No.79, West Yingze Avenue, Taiyuan, Shanxi 030024, China*
[b]*School of Chemical and Biological Engineering, Taiyuan University of Science and Technology, No.264, Section 2, Jinci Road, Taiyuan, Shanxi 030021, China*
[c]*State Key Laboratory for Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, No.27, Taoyuan Nan Road, Taiyuan, Shanxi 030001, China*
Tel./Fax: +86 351 4072379; email: bijc@sxicc.ac.cn

Received 1 June 2012; Accepted 12 February 2013

ABSTRACT

The cotton printing and dyeing wastewater obtained from a printing and dyeing mill was treated by supercritical water oxidation (SCWO) in a continuous-flow reactor. The experiments were operated between 400 and 600˚C, 25 MPa was selected as a suitable pressure, hydrogen peroxide (H_2O_2) was used as an oxygen source, and excess oxygen varied from 0 to 300%. The studies indicate that the total organic carbon (TOC) degradation efficiency is over 99.7% when the temperature increases to 600˚C at 300% excess oxygen. The influence of oxidants on TOC conversion is obvious at a lower temperature and then evidently weakens with temperature. The ammonia nitrogen (NH_3–N) removal by the SCWO reaction from the dyeing wastewater was also discussed. The result shows that a high temperature and the right amount of oxidizing agent are required to achieve a good effect on removing NH_3–N. A salt separator was applied for the separation of salts contained in the wastewater and to prevent the reactor block. The desalination rate of the separator during the SCWO reaction process was also discussed. The studies show that the removal efficiency of the total dissolved solids (TDS) can be up to 95.8% when the temperature reaches 647˚C. The TDS in effluent after treatment increases with initial TDS concentration rather than remaining unchanged at a certain temperature. It is probable that the changes of one or the total salt concentration in the salt solution influence the salt solubility in SCW, which results in the variations of the salt precipitation rate.

Keywords: Cotton printing and dyeing wastewater; SCWO; Thermal degradation; TOC; NH_3–N; Desalination

1. Introduction

The cotton printing and dyeing wastewater mainly comes from pretreatment, mercerizing, dyeing, and finishing processes of cotton fabric processing. The major pollutants contained in the wastewater are dyestuff, auxiliaries, surfactant, fluorescent brightener sodium sulfate, sodium hydroxide, and so on. Because of the characteristics of the wastewater, such as large

---

*Corresponding author.

water volume, high concentration of organic pollutant, deep chromaticity, high alkalinity, changeable water quality, and complex ingredient, it is difficult to treat wastewatwer. The treatment methods of dyeing wastewater mainly include physical [1,2], chemical [3–5], and biochemical methods [6]. At present, a combination of physicochemical and biochemical methods has been widely used in the treatments of dyeing wastewater because the biochemical process is low in cost. However, although some new technology, such as wet air oxidation, catalytic wet air oxidation [7], Sequencing Batch Reactor, Upflow Anaerobic Sludge Blomket Process, have already been developed and used for dyeing wastewater treatment, these methods still suffer disadvantages such as sludge generation; incomplete degradation and decolorization; and adsorbent regeneration and secondary pollution caused by by-products.

Supercritical water oxidation (SCWO) seems to be a prospective alternative method for the treatment of textile wastewater. SCWO technology was proposed by Professor Modell in 1982 [8], it received great attention, because this technology treated organic wastewater using advanced oxidation processes, and the structure of an organism could be destroyed thoroughly. Supercritical water ($t > 374$°C, $p > 22.1$ MPa) is an excellent medium for the rapid destruction of organic wastes by oxidation, because organics and oxygen can easily dissolve in supercritical water to form a homogeneous phase. At a typical operating temperature and pressure (450–600°C, 24–28 MPa), SCWO process can rapidly achieve high destruction efficiency (>99.99%) of organics in a short residence time (<1 min). The main products of this process are water, carbon dioxide, and molecular nitrogen [8,9].

Söğüt and Akgün [9] researched the degradation of salt-free dyehouse wastewater in a continuous tube SCWO reactor, the total organic carbon (TOC) degradation rate of 100% was obtained at 550°C, 25 MPa, 10 s, and 675.56% excess oxygen. Veriansyah et al. [10] discussed SCWO of the wastewater from a liquid crystal display manufacturing plant in a tubular flow reactor, 99.99% of the chemical oxygen demand (COD) conversion rate was achieved at 615.4°C, 25 MPa, 10 s, and 998% excess oxygen. Several studies [11–13] about SCWO of other artificial and industrial wastewater also have been conducted, but the data concerning SCWO of saline printing and dyeing wastewater have not been found.

The nitrogen present in the dyeing wastewater usually consists of organic nitrogen; the content of inorganic nitrogen, such as ammonia, and so on, is relatively rare. Organic nitrogen can be transformed to ammonia under certain conditions [14]. The organic nitrogen in dyeing wastewater is derived from the dyes with nitrogenous substituting groups, such as azo group, amino group, nitro group or N-containing heterocycle, and urea used as cellulose printing auxiliary. The functions of urea during the application of reactive dyes have been found to be an increase in the solubility of dye in the reaction medium, dye disaggregation, retardation of water evaporation during drying and swelling of cotton, thereby facilitating the dye–fiber reaction [15]. However, the use of urea has caused ecological problems associated with the high nitrogen content in the printing effluent. Therefore, the studies for reducing or eliminating urea from the printing paste formulation have been carried out [16], but so far the ammonia removal from dyeing wastewater is still an urgent problem to protect the environment.

Salt deposition is one of the severe problems facing the SCWO process. Because salts have low solubility in supercritical water, they precipitate and block the reactor or the transport lines. Many researches on fundamental principles and pertinent to the precipitation of salts and scale control found in an SCWO reactor [17] have been performed, and several specific reactor designs and operating techniques are used to control salt precipitation and solids buildup in SCWO systems [18] have also been developed, but not one design or method has proven itself to be clearly superior to the others and most of these techniques have not been applied commercially due to the complexity of technology and operation. So, the continued research on salt precipitation in SCWO systems is needed for further better separation technology applications.

In this work, the SCWO and degradation of the cotton printing and dyeing wastewater containing inorganic salts obtained from a printing and dyeing mill are studied. The aim is to investigate the effects of reaction conditions, such as temperature, excess oxygen, residence time, and initial concentration on the destruction of pollutants (includes TOC and NH_3–N) in the wastewater and provide fundamental information for the further SCWO scale-up design and operation. A salt separator was designed to remove inorganic salts dissolved in the wastewater and to prevent the reactor block. The seperation efficiency of the separator during the reaction process was also discussed for investigating the effects of desalination conditions on the the salt separation efficiency and further optimizing salt precipitation control methods.

2. Experimental

2.1. Apparatus and procedure

SCWO experiments were conducted in a continuous-flow reactor system as schematically shown in Fig. 1. The pilot apparatus includes the coiled tubular reactor (1,330 cm length × 4 mm i.d.), the oxidant preheater (400 cm × 4 mm i.d.), the wastewater preheater (800 cm × 4 mm i.d.), and the salt separator. The salt separator is a cylinder (30 cm × 40 mm i.d.) with an open at the bottom, an inlet, and an outlet line (4 mm i.d.) are on the top of it. All the wetted sections of the apparatus were made of stainless steel (310S). The reactor, the preheaters, and the salt separator were placed, respectively, into electric heating furnaces connected to an automatic temperature control system for regulating the working temperature. After the reactor temperature reached the set value (±5℃), the dyeing wastewater and the hydrogen peroxide solution were fed into lines by two high-pressure pumps and then separately preheated. The volume flowrate of oxidant and wastewater ranged from 8 to 40 and 15 to 85 mL/min, respectively, at each pumping condition. After preheating, the wastewater flowed into the salt separator to desalinate. In order to keep the pipeline from clogging, the temperature of the wastewater preheater was maintained at subcritical values (350–370℃) and the salt separator (see Fig. 1) was installed between the wastewater preheater and the reactor to remove most of the inorganic salts before the reaction. Both the reactor and salt separator's maximum working temperatures were 650℃. Then the two liquids were mixed at the reactor inlet. While leaving the reactor, the fluid was cooled rapidly by heat exchanger. Then the particulate matter was filtered out by a filter before the effluent was depressurized. The system pressure was maintained at 25 ± 1 MPa by a back-pressure regulator. Maximum working pressure of the back-pressure regulator was 30 MPa. The product stream was then separated into liquid and vapor phases in the gas-liquid separator. The gas products were gathered in an air trap, whereas the liquid ones were collected in a flask.

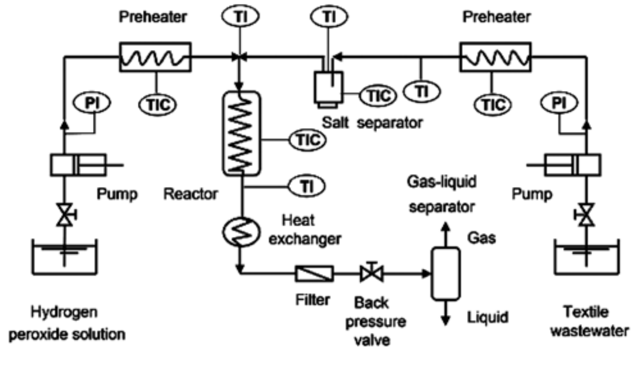

Fig. 1. Schematic diagram of continuous-flow SCWO reactor system.

2.2. Materials and analytical methods

The dyeing wastewater was obtained from a cotton printing and dyeing mill and used without filtering or diluting. Hydrogen peroxide solution was prepared by diluting a 30% (w/w) solution of H_2O_2 with deionized water to desired concentrations. The wastewater was obtained from the drainage pool of the mill, there were many dyestuff (reactive dyes, vat dyes, etc.), auxiliaries (sodium sulfate, sodium carbonate, sodium chloride, surfactant, etc.), and domestic sewage in it. The composition and proportion of the wastewater are unknown. Table 1 shows the properties of the wastewater.

The concentrations in the wastewater and the effluent after treating them by SCWO are characterized by analyzing TOC concentrations. TOC was determined by using a water quality analyzer (Analytik jena multi N/C 2100/2100S, Germany). COD of the wastewater was determined by using a microanalyzer (ET99718, Germany). The total dissolved solids (TDS) are used to specify salt concentration of the wastewater. Electrical conductivity and TDS concentration of the wastewater were checked by a conductivity meter (DDSJ-308A). NH_3–N was analyzed by distillation and titration method. Determination of colority and suspended solids (SS) of the wastewater was performed by multiple dilution and gravimetric methods. The concentrations of metallic ions in the wastewater were determined by inductively coupled plasma atomic emission spectrometry (Atomscan16, TJA). A pH meter (PHSJ-3F) was used to determine the pH values of the wastewater. The color of the wastewater was determined by naked eye detection. In the gaseous products, H_2, O_2, N_2, CO, CO_2, and CH_4 were analyzed by GC-TCD, and low molecular weight hydrocarbons (C_2–C_6) were analyzed by GC-FID.The reactor and salt separator residence time is expressed as:

$$\tau = \frac{V_R}{F_T} \times \frac{\rho_{s(T,P)}}{\rho_0} \tag{1}$$

where V_R is the reactor and salt separator volume, ml, $\rho_{s(T,P),}$ and ρ_0 are the fluid densities under reaction conditions and at normal temperature and pressure conditions, respectively, g/ml. F_T is the additive volumetric flow rate of both the wastewater and the oxidant streams, ml/s. Since the studies were carried

Table 1
Properties of the wastewater and comparison of the effluent with the first grade discharge standard of China and recommended reuse standard

Parameter	Raw wastewater	Effluent[a]	The first grade discharge standard of China	Recommended reuse standard [20] of the wastewater
Total organic carbon (TOC) (mg/L)	1350.25	11.34	–[b]	–
Chemical oxygen demand (COD_{cr}) (mg/L)	2,190	18.16	100	60
Total dissolved solids (TDS) (mg/L)	4,220	352	–	–
Electrical conductivity (μs/cm)	8,440	704	–	$\leqslant$1,500
NH_3–N (mg/L)	4.136	23.16	15	–
Colority (Times)	256	8	40	$\leqslant$25
Suspended solids (SS) (mg/L)	440.0	13.0	70	$\leqslant$30
Fe (mg/L)	8.0	<0.1	–	0.2–0.3
Mn (mg/L)	0.1	<0.1	–	$\leqslant$0.2
Na (mg/L)	1,740	27.3	–	–
Hardness (as $CaCO_3$) (mg/L)	218.78	133.69	–	$\leqslant$450
pH	9.09	8.45	6.0–9.0	6.0–9.0
Colour	Blue	Clear and colorless	–	–

[a] The wastewater was treated by SCWO at 500℃, 25 MPa, 20 s and 300% excess oxygen.

[b] Not covered by the standard.

out with wastewater and hydrogen peroxide solution, and no density data of the reaction system were acquirable under reaction conditions, the fluid density at the reaction conditions was assumed to be the density of pure water and determined using the NIST Standard Reference Database [19].

TOC conversion X is defined as follows:

$$X = \frac{[\mathrm{TOC}]_0 - [\mathrm{TOC}]_f}{[\mathrm{TOC}]_0} \tag{2}$$

Here $[\mathrm{TOC}]_0$ is the initial concentrations in feed and $[\mathrm{TOC}]_f$ is the residual TOC concentrations in the effluent after the reaction, mol/L.

Excess oxygen is calculated using the following equation:

$$\text{Excess } O_2(\%) = \frac{[O_2]_a}{[O_2]_s} \times 100 \tag{3}$$

where $[O_2]_a$ represents the actual concentration of O_2 from the complete destruction of hydrogen peroxide fed into the reactor, mmol/L, $[O_2]_s$ represents the stoichiometric requirement concentration of O_2 based on $[\mathrm{TOC}]_0$ of the wastewater, mmol/L.

TDS removal efficiency Y is defined as follows:

$$Y = \frac{[\mathrm{TDS}]_0 - [\mathrm{TDS}]_f}{[\mathrm{TDS}]_0} \tag{4}$$

Here $[\mathrm{TDS}]_0$ is the initial TDS concentration in feed and $[\mathrm{TDS}]_f$ is the TDS concentration in effluent, mg/L.

3. Experimental results and discussion

3.1. Oxidation and degradation

3.1.1. Effect of temperature

The effect of temperature on the TOC removal from the dyeing wastewater by SCWO is illustrated in Fig. 2. The experiments were conducted in a temperature range of 400–600℃ keeping a constant pressure of 25 MPa and residence time of 20 s, while the excess oxygen varied from 0 to 300%. As shown in Fig. 2, TOC degradation efficiency increases from 86.48 to 99.79% as the temperature increases from 400 to 600℃ at 300% excess oxygen, while that increases from 79.9 to 99.15% with increasing the temperature from 400 to 550℃ at 100% excess oxygen. We can see the TOC degradation varies significantly with temperature. Besides, the variety of TOC degradation is high at temperatures ranging from 400 to 500℃ and then slight when the temperature is higher than 500℃, more than 98.9% TOC is already destructed at 500℃. The results suggest that the printing and dyeing wastewater can be easily destructed at moderate temperatures by SCWO. This point can be confirmed by the example of Söğüt et al. [9]. They studied the

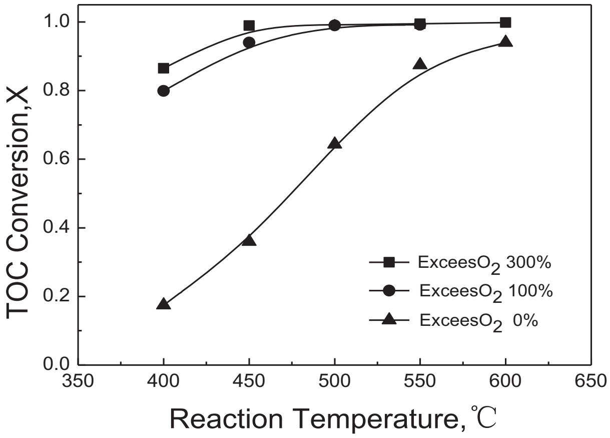

Fig. 2. Effect of temperature on TOC degradation efficiency at 25 MPa and 20 s.

reactivity of salt-free dyehouse wastewater in supercritical water, TOC degradation efficiency increased from 93.43 to 100%, when the temperature increased from 400 to 600℃ at 25 MPa, 10 s, and 675.56% excess oxygen, and the transformation rate of TOC exceeded 97% at 500℃. From Table 1, we can see when the temperature is above 450℃ at 20 s and 300% excess oxygen, the COD in effluent is lower than 34.83 mg/L, the value that already meets the national discharge standard of Class I.

To better understand the SCWO process of dyeing wastewater, an investigation on thermal degradation of the wastewater in supercritical water (SCW) was carried out. The experiments were conducted in the same system without the oxidant (0% excess oxygen). The results show that only 17.46% of TOC in the wastewater is degraded at 400℃, 0% excess oxygen, but 86.48% of TOC conversion can be obtained at the same temperature, and 300% excess oxygen. This is because organics and oxygen dissolved in supercritical water can form a homogeneous phase during SCWO reaction, a single supercritical phase reaction medium is one where higher concentrations of reactants can often be attained and that there are no interphase mass transport processes to hinder reaction rates [21].

From Fig. 2 we can see that, when compared with 100 or 300% excess oxygen, the effect of temperature on the TOC thermal degradation is very noticeable at 0% excess oxygen, and the TOC degradation efficiency varies from 17.46 to 93.98% with the temperature increasing from 400 to 600℃, although it is very low at 400℃ due to no oxygen. It is very difficult to find out the reaction mechanism of our thermal degradation reactions because of complicated constitutions in the wastewater, but we know TOC in SCW can decompose or convert to other compounds via pyrolysis, hydrolysis, condensation reactions, and others [21–23]. It is the rate of above reactions increasing with the temperature that results in a tremendous raise in TOC conversion of the thermal degradation reaction since the richer TOC concentration are remained, while there is limited scope for the increment of TOC conversion in SCWO because there is already a high level of TOC conversion at low temperature. The refractory organics after the thermal degradation reaction may be condensates of organic compounds in the wastewater or unknown hydrocarbons.

Table 2 shows the gas-phase product composition and their changes of thermal degradation and oxidation reaction in SCW. We can see the main gas-phase products of SCWO reaction are N_2, CO_2, and a small quantity of H_2, CH_4. The disappearance of H_2, CH_4, and the rise of N_2 contents shows that the TOC oxidation reactions gradually get complete. The main gases of thermal degradation reactions in SCW are H_2, N_2, CO_2, CH_4, C_2–C_6. As the contents of N_2 increase, the hydrocarbons of lower molecular weight C_2–C_6 disappear and CO, CH_4 can be ignored as the temperature shows the degradation or transformation of TOC.

It can also be seen from Fig. 2 that the removal of TOC in the dyeing wastewater by SCWO greatly increases with the addition of oxidant, but the changes of TOC conversion are not big as the excess oxygen increases from 100 to 300%, and the influence of oxidant on TOC conversion is obvious at a lower temperature and then evidently weakens with temperature. So a higher temperature can be used to cut down the oxygen consumption on the TOC destruction.

The removal of NH_3–N after the above-mentioned SCWO reactions is also discussed. The effect of temperature on the NH_3–N removing from the dyeing wastewater is illustrated in Fig. 3. As shown in Fig. 3, NH_3–N concentration in effluent decreases from 55.42 to 3.31 mg/L at 300% excess oxygen as the temperature increases from 400 to 600℃. It can be seen that the temperature has a great effect on NH_3–N degradation when using excessive oxidant, which is concordant with other researchers' work. Du et al. [12] studied the decomposition of NH_3–N in coking wastewater in supercritical water at 25 MPa, 300% excess oxygen. It was found that NH_3–N was very stable at 500℃ and when the temperature increased from 550 to 575℃, its conversion increased dramatically from 14 to 76%. An interesting phenomenon that can be found from the experiment result is that the NH_3–N concentration after the reaction is higher than the initial NH_3–N concentration (4.14 mg/L) in feedstock. The NH_3–N concentrations in effluent increase largely because ammonia is a major SCWO intermediate

Table 2
Gas-phase product compositions and their changes of thermal degradation and oxidation reaction in SCW

Temperature		Molar fraction of gas component									
		H_2	O_2	N_2	CO	CO_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8
Oxidization	450℃	0.009	0.763	0.023	–	0.20	0.005	–	–	–	–
	600℃	–	0.816	0.034	–	0.15	–	–	–	–	–
Pyrolysis	450℃	0.405	0.038	0.055	0.008	0.31	0.158	0.013	0.007	0.005	0.001
	600℃	0.335	0.002	0.371	0.001	0.29	0.0003	–	–	–	–

product of nitrogenous organic compounds (Azo dyes, heterocyclic dye, urea, etc.) degradation in the wastewater and NH_3 oxidation process is usually considered as the control step of the reaction. This point is illustrated by some experiments. Benjamin et al. [14] examined the reactivity of methylamine in SCW. They found the major products measured are ammonia and methanol. Savage [21] pointed out that when nitrobenzene and 4-nitroaniline were degraded in SCW in the absence of oxygen, NH_3, CO, CO_2 and N_2 were among the products formed, while in the presence of oxygen, most of the nitrogen appeared as N_2 in the reaction products.

We can see from Fig. 3, in the absence of oxygen (excess $O_2 = 0$), the NH_3–N after the treatment increases from 53.77 to 62.39 mg/L when the temperature increases from 400 to 600℃, while NH_3–N in effluent decreases from 58.31 to 29.57 mg/L as the temperature varies from 400 to 550℃ at 100% excess oxygen. That is to say that the NH_3–N in effluent increases with temperature rather than decreases in the absence of oxygen even if the temperature reaches 600℃, but there has been some decrease in NH_3–N concentrations with adding stoichiometric oxygen. The studies by Segond et al. [24] and Al-Duri et al. [25] are the case in point. Segond et al. found that the conversion of ammonia was only 2% at 600℃, 24.5 MPa and 120 s, 0% excess oxygen. Al-Duri et al. investigated the SCWO of N-containing hydrocarbons (1, 8-diazobicyclo[5.4.0] undec -7- ene) and DMF (dimethyl formamide) at oxidant stoichiometric ratio, it was found that ammonia was still abundant at 650℃ because of its recalcitrant nature.

This indicates that ammonia is stable within the temperature range of 400–600℃ in the absence of oxidants and when adding a certain amount of oxidant

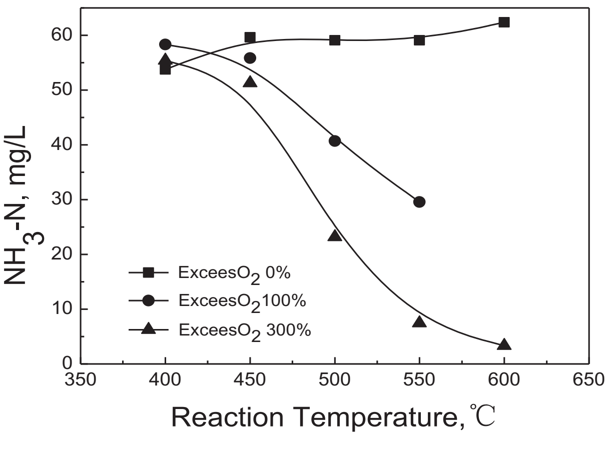

Fig. 3. Effect of temperature on NH_3–N concentration at 25 MPa and 20 s.

will promote the degradation of NH_3–N. The influence of oxidant on the degradation of NH_3–N becomes more obvious when the reaction temperature is higher than 500℃ and the degradation of NH_3–N increases gradually with the excess oxygen increasing from 100 to 300%. So, in order to obtain high conversion of NH_3–N in SCWO reaction, a high enough temperature and the right amount of oxidizing agent are required, if taking the cost of the oxidizing agent into account.

3.1.2. *Effect of residence time*

Fig. 4 shows the variation trend of TOC removal with residence times at the temperatures of 400, 450, and 500℃, 0 and 300% excess oxygen, respectively. Due to the destruction of TOC in the wastewater requiring a relatively moderate temperature, the experiments on TOC degradation were carried out at lower temperatures (400, 450℃), a higher value of excess oxygen (300%), a higher temperature (500℃), and 0% excess oxygen. As the excess oxygen is 300%, TOC conversion increases from 85.88 to 94.93% at 400℃ and from 98.09 to 98.65% at 450℃ within the same residence time range of 15–45 s. Obviously, with the extension of residence time, high temperature curve becomes more gentler. This is because most of the TOC content is removed earlier and fewer TOC concentrations remain in the wastewater; and at high temperature, the course of the reaction slows down. Sánchez-Oneto et al. [13] studied SCWO of the semi-synthetic cutting oil wastewater using pure oxygen as oxidant, a similar trend of changes in TOC conversion was obtained at 400–500℃, 25 MPa, residence time of 20–100 s, oxygen excess coefficient varied from 60% of stoichiometric oxygen to 20% oxygen excess.

In the absence of oxidants (0% excess oxygen), TOC conversion in effluent increases from 58.2 to 90.6% at 500℃ with the residence time increasing from 15 to 45 s. Experiments on the dyeing wastewater appear that TOC conversion is lower at 15 s, 500℃, and 0% excess oxygen, but the residence time has greater influence on the TOC degradation than that at 400℃ and 300% excess oxygen. This may be because the extension of residence time is helpful to the residual unreacted chemical substance decomposing at 500℃. In contrast, long residence time is not necessary for the SCWO of TOC because higher conversion has been achieved at the short residence time.

The variation trend of NH_3–N removal with increasing residence times in the above-mentioned reaction temperature and excess oxygen are displayed in Fig. 5. The concentration of NH_3–N in effluent varies from 54.59 to 49.62 mg/L as the residence time increases from 10 to 45 s at 450℃, 300% excess oxygen, while the content of NH_3–N changes from 59.13 to 60.34 mg/L at 500℃, 0% excess oxygen, and same residence time. All experiment data exhibit that the residence time has little effects on the destruction of NH_3–N at 400 or 450℃, 300% excess oxygen and 500℃, 0% excess oxygen. Heiling and Tester [26] generalized a conclusion from SCWO of ammonia that it was very difficult to oxidize below 540℃ at residence times of 6–13 s. The study conducted by Du et al. [12] showed that NH_3–N was very stable at 500˚C, only about 5% ammonia degraded at 300% excess oxygen and 24 s. Therefore, only by increasing the temperature while adding adequate oxidant can increase NH_3–N conversion available and prolonging the residence time has little effect on the destruction of NH_3–N at lower temperatures.

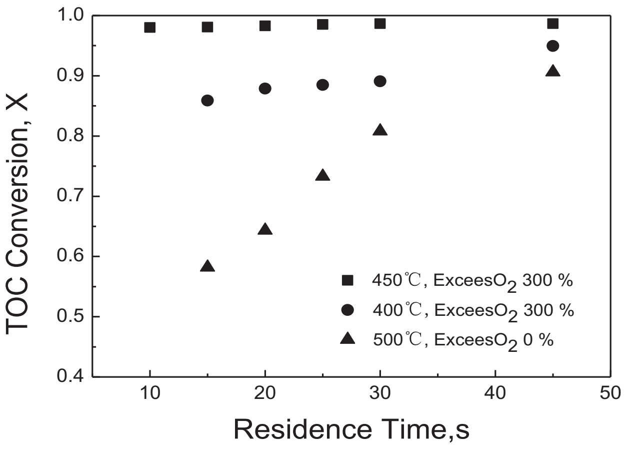

Fig. 4. Effect of residence time on TOC degradation efficiency at 25 MPa.

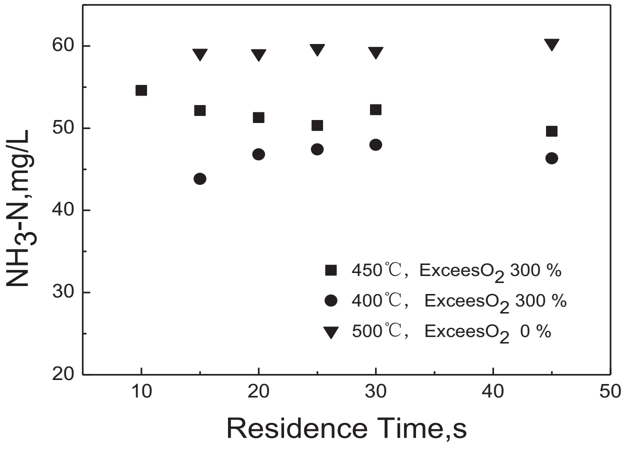

Fig. 5. Effect of residence time on NH_3–N concentration at 25 MPa.

3.1.3. *Effect of initial concentration*

The effect of initial concentration in feedstock on TOC degradation efficiency and NH_3–N concentration after SCWO treatment is illustrated in Fig. 6. The lower concentration wastewater was prepared by diluting raw water with deionized water to desired concentration. It can be seen that the initial concentration has no effect on TOC degradation efficiency. The NH_3–N concentration in the effluent, grow basically in step with TOC initial concentration in feedstock. So the initial concentration has no effect on the NH_3–N conversion, too. Because of a relatively low TOC concentration in feedstock, the effect of initial TOC concentration in the wastewater on thermal degradation of pollutants in SCW has not been discussed.

Some investigators pointed that the increase of water density led to an increase of SCWO reaction rate [27,28]. Al-Duri et al. [25] drew a conclusion that pressure affected conversion in the sub- and near-critical conditions but not in the supercritical region. Qi et al. [29] found that the destruction efficiency of aniline by SCWO increased with pressure at 400℃, while the pressure effect disappeared at 450℃. According to the arrenitus equation, the rate of SCWO reaction mainly depends on the reaction temperature. Therefore, compared with temperature, the influence of pressure on SCWO is less significant. In consideration of equipment investment at high operating pressure and maximum the back-pressure regulator working pressure, 25 MPa is selected as an suitable pressure in our SCWO experiments.

3.2. *Desalination*

The salt separator in the SCWO reaction system is a reverse flow vessel, the working principle of which is similar to a reverse flow tank reactor [18], salts were precipitated directly to the bottom of the vessel by gravity, inertia, and forced convection because of a recirculation flow pattern. Desalination in the salt separator was conducted at the temperature range of 422–647℃ and 25 MPa, most of the salts contained in dyeing wastewater were effectively removed after desalting process. In the previous experiments without salt separator, obvious pressure fluctuations occurred. No plugging or pressure fluctuations were observed in experiments after desalination.

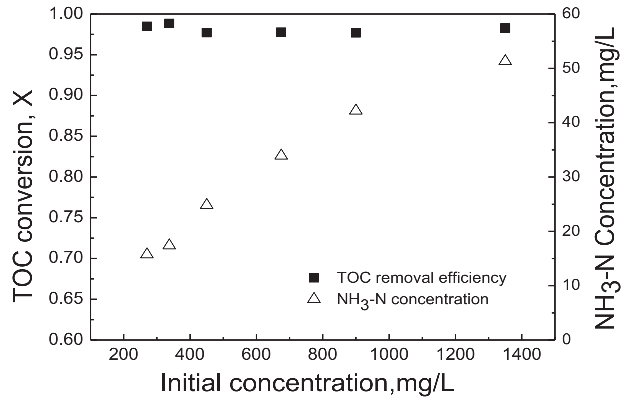

Fig. 6. Effect of TOC initial concentration in feedstock on degradation efficiency and NH_3–N concentration in effluent at 450℃, 25 MPa, exceeds O_2 of 300%, and 20 s.

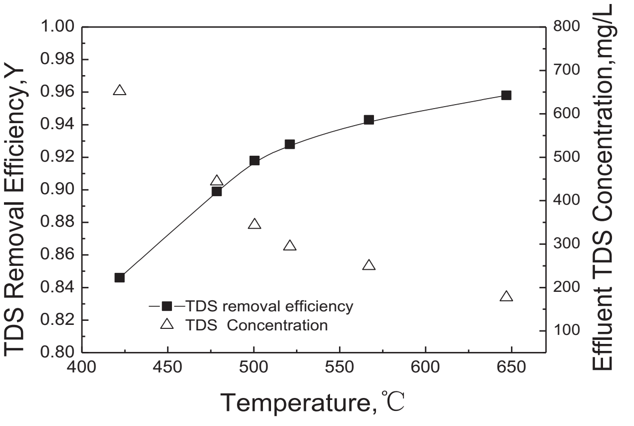

Fig. 7. Effect of temperature on the TDS removal efficiency at 25 MPa and 67.7 s, volume flowrate 21.7–43.3 ml/min.

3.2.1. *Effect of temperature*

The TDS contained in the dyeing wastewater is 4,220 mg/L. The major components of the salts are sodium sulfate, sodium carbonate, sodium chloride, and so on. All the desalination conditions, including temperature, pressure, residence time, and wastewater flow-rate are the operating parameters of the separator during the above SCWO reaction. The effect of temperature on the TDS removal efficiency for the dyeing wastewater is illustrated in Fig. 7. It can be seen that when temperature increases from 422 to 647℃, TDS in effluent decreases from 651.75 to 177 mg/L and the removal efficiency of TDS can be up to 95.8% at 647℃. These data are consistent with the findings obtained from studies on salt separation from the coking wastewater [12] and the solubility of sodium sulfate and sodium chloride in supercritical water [30,31]. Hodes et al. pointed out [17] that the order of magnitude drop in density of SCW dramatically decreases the number and strength of hydrogen bonds present in water, causing it to exhibit nonpolar behavior similar to that of many organic compounds. Since SCWO is highly compressible, density itself is mainly affected by temperature and pressure at the conditions found in an SCWO reactor. That is to say, with the raise in temperature, the decrease in density of water in the SCWO reactor leads to the decrease in the solubility of inorganic salts in the SCWO or increase in the removal efficiency of them during the SCWO reaction. Therefore, higher temperature is an important factor to improve the salt separation efficiency.

3.2.2. Effect of residence time

The effect of residence time on the TDS removal efficiency for the dyeing wastewater is illustrated in Fig. 8. It can be seen that the residence time has no effect on the TDS removal efficiency at 422 and 478℃, as the residence time increases from 50.76 to 152.3 s (due to the limitation of experimental conditions). Armellini et al. [31] studied the precipitation of NaCl and Na_2SO_4 in water from sub- to supercritical conditions. They calculated that 1 μm Na_2SO_4 particles would be formed within a very short time of 10 ms at 385℃ and 25 MPa based on a mass transfer limited growth model and concluded that primary sodium sulfate particle diameters were typically between 1 and 3 μm, while some aggregates reached diameters up to about 20 μm. Armellini et al. [32] also examined, sodium chloride solubility at temperatures of 450, 500, and 550℃ and pressure ranging from 100 to 250 bar. Water flow rates varied from 0.2 to 3.0 g/min, which corresponded to water–salt contact times in the tube from 10–200 s. Throughout the experiments, the dependence of the measured concentrations on flow-rate was tested, but no uniform dependence of concentration on flow-rate was observed.

It can be concluded from above results, that Na_2SO_4 particles would be formed within a very short time (<200 ms) in water from sub- to supercritical conditions and the water flow rate (water–salt contact times) have no effect on NaCl solubility in sub- and supercritical water at the residence time of 10–200 s, although the saturated concentration of NaCl are different under every experimental temperature and pressure. Because about 87 and 89% of inorganic salts have been removed at 422 and 478℃ separately, and the concentration and removal efficiency of salts in the effluent do not vary with residence time in our experiments, so we can infer from above results that most of the inorganic salts contained in the dyeing wastewater may have already separated crystals out within the minimum residence time of the separator (50.76 s) and it is inefficacious to obtain more inorganic salt precipitation from saturated aqueous solution in a supercritical phase by prolonging residence time at a constant temperature and pressure in our experiments.

3.2.3. Effect of initial concentration

The effect of initial TDS concentration on the TDS removal efficiency for the dyeing wastewater was investigated at 478℃ and 67.7 s of residence time. The results are shown in Fig. 9. In these experiments, the TDS removal efficiency increases from 74.94 to 89.48% as initial TDS increases from 844 to 4,220 ml/L. Interestingly, the content of TDS in effluent also increases with the initial TDS concentration rather than remain unchanged at a certain temperature. Armellini et al. [31] concluded from the results of previous researches, that sodium sulfate solubility in high temperature aqueous sodium chloride solution increased with sodium chloride concentration. DiPippo et al. [33] investigated phase equilibria in the NaCl-Na_2SO_4-H_2O system at 200 and 250 bar for total salt concentrations

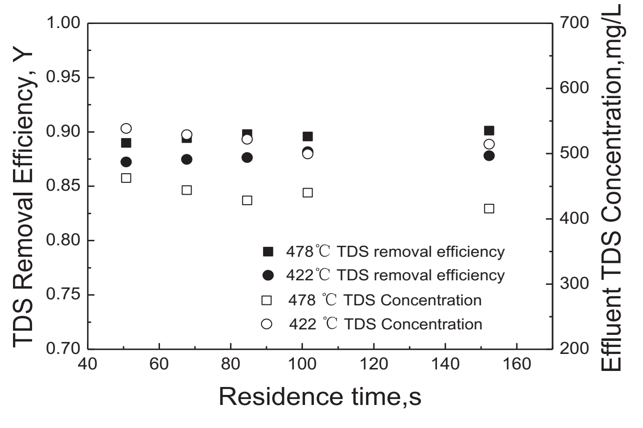

Fig. 8. Effect of residence time on the TDS removal efficiency at 25 MPa, volume flowrate 19.3–59.9 ml/min at 422℃, volume flowrate 14.3- 43.0 ml/min at 478℃.

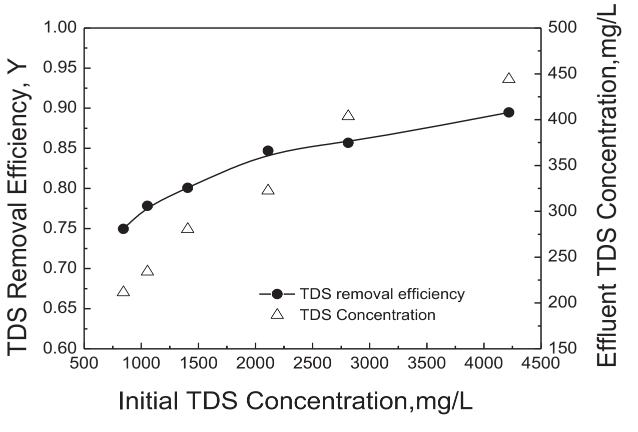

Fig. 9. Effect of initial TDS concentration on the TDS removal efficiency at 478℃, 25 MPa, and 67.7 s, volume flowrate 32.2 ml/min.

ranging from 5 to 20 wt.% over temperatures ranging from 320 to 400℃. They found that while increasing the total salts concentration from 5 to 10 wt.% it appeared to have produced a large change in the location of the invariant point where liquid, solid salt, and vapor are in equilibrium.

Due to the complexity of the inorganic salts composition in our dyeing wastewater, it is difficult to exactly explain the causes of our experimental phenomena. It can be seen from above studies that the ternary mixture of NaCl, Na_2SO_4, and water exhibits solubility of Na_2SO_4 in SCW is affected by the concentration of NaCl, and the triple point of $NaCl–Na_2SO_4–H_2O$ system changes with the total salt concentration at 200 and 250 bar. That is to say, concentration changes of one salt or total salts in the salt solution may influence the solubility of the salts in SCW that leads to a change in the salt precipitation rate. From experiments, we can see that at the supercritical condition, the assumption that the greater the initial salt concentration of the wastewater, the better the removal effect of salts does not hold. Besides, Schubert et al. [34] concluded that it is not possible to predict the separation performance of a given salt mixture by just knowing the separation performance of the corresponding single salt solution. At present, more experiments about desalination of dyeing wastewater in SCWO should be taken to get more information as possible for performing SCWO of the wastewater and to find a better desalination technology under SCWO conditions.

Table 1 shows, the composition of the dyeing wastewater and the first grade discharge standard of China and reuse the standards. It can be seen from Table 1 that when the reaction temperature is 500℃, 25 MPa, 20 s, and 300% excess oxygen, the effluent COD_{cr}, NH_3–N, TDS, and conductivity of the wastewater is 18.16, 23.16, 352, and 704 mg/L, respectively. The COD_{cr} is far below the first grade discharge standard of China and the recommended standard of reuse, but the NH_3–N exceeds the first grade discharge standard of China. In order to meet the State's discharge standard, a higher NH_3–N degradation temperature is needed. The TDS and conductivity in effluent completely comply with the standard of reuse water proposed by the Donghua University [20] (national standard has not yet promulgated). In addition, suspended solid is 13.0 mg/L, Fe < 0.1 mg/L, Mn < 0.1 mg/L, hardness is 133.69 mg/L and pH is 8.45 in effluent, which are lower than the pollutant discharge standards of stipulated by government and the proposed reuse standards. The maximal limitation for COD and SS in the national effluent standards applied in Japan in protecting the living environments are 120 and 150 mg/L [35]. Mattioli et al. [36] reported the quality of wastewater reclamation for textile finishing in the Prato textile area, which was the concentration of SS, COD, and conductivity below 22, 53 mg/L, and 1,636 μs/cm, separately. These values can be met by our cotton printing and dyeing wastewater after SCWO treatment (Table 1). This information may provide help for research on the reuse technology of cotton printing and dyeing wastewater.

4. Summary and conclusion

The dyeing wastewater was treated by SCWO and thermal degradation in SCW in a lab scale tubular reactor. The experimental results demonstrate that TOC can be easily destructed in SCWO process. The conversion of TOC is over 99.7% when the temperature increases further to 600℃ at 300% excess oxygen. The influence of oxidant on TOC conversion is obvious at a lower temperature and then evidently weakens with increasing temperature.

The NH_3–N degradation is mainly affected by the reaction temperatures and the amount of oxidant in SCWO reaction. Ammonia is recalcitrant within the temperature range of 400–600℃ in the absence of oxidant. Adding a certain amount of oxidant will significantly promote the degradation of NH_3–N and the influence of oxidant on degradation of NH_3–N becomes more obvious when the reaction temperature is higher than 500℃.

A salt separator was designed and installed between the wastewater preheater and the reactor. The salt separator is a reverse flow vessel. The removal efficiency of TDS can be up to 95.8% at 647℃. The TDS removal efficiency increases from 74.94 to 89.48% as initial TDS concentration increases from 844 to 4,220 mg/L, in the meantime, the TDS in effluent increases with initial TDS concentration rather than remaining unchanged. So, the assumption that the higher the initial salt concentration of the wastewater, the better the removal effect of salts does not hold at the supercritical condition.

The COD, saltness, suspended solid, and so on in effluent by SCWO can meet not only the Chinese national discharge standard of Class I, but also the standards of reuse water proposed by the Donghua University (national standard has not yet promulgated) when the temperature is above 500℃, except NH_3–N. A higher reaction temperature is needed in order to achieve higher effective removal of NH_3–N and meet national discharge standard.

Salt plugging seems to be the most severe problem that hinders the industrial scale-up of SCWO process so far. The oxygen costs are considered as one of the major costs [37]. Now, more research addressing such questions needs to be done. The investigation in this work about the effect of reaction conditions on the removal of pollutants in the wastewater might be beneficial to reduce oxygen consumption and to control salt precipitation.

References

[1] S. Chowdhury, P.D. Saha, Scale-up of a dye adsorption process using chemically modified rice husk: Optimization using response surface methodology, Desalin. Water Treat. 37 (2012) 331–336.
[2] G. Ciardelli, L. Corsi, M. Marcucci, Membrane separation for wastewater reuse in the textile industry, Resour. Conserv. Recycl. 31 (2001) 189–197.
[3] S. Meric, H. Selcuk, V. Belgiorno, Acute toxicity removal in textile finishing wastewater by Fenton's oxidation, ozone and coagulation-flocculation processes, Water Res. 39 (2005) 1147–1153.
[4] G. Ciardelli, N. Ranieri, The treatment and reuse of wastewater in the textile industry by means of ozonation and electroflocculation, Water Res. 35 (2001) 567–572.
[5] S.M. Lam, J.C. Sin, A.Z. Abdullah, A.R. Mohamed, Degradation of wastewaters containing organic dyes photocatalysed by zinc oxide: A review, Desalin. Water Treat. 41 (2012) 131–169.
[6] M.T. Sulak, H.C. Yatmaz, Removal of textile dyes from aqueous solutions with eco-friendly biosorbent, Desalin. Water Treat. 37 (2012) 169–177.
[7] S.K. Bhargava, J. Tardio, J. Prasad, K. Folger, D.B. Akolekar, S.C. Grocott, Wet oxidation and catalytic wet oxidation, Ind. Eng. Chem. Res. 45 (2006) 1221–1258.
[8] M. MODELL, Using supercritical water to destroy tough waters, Chem. Week 4 (1982) 21–26.
[9] O. Ö Söğüt, M. Akgün, Treatment of dyehouse waste-water by supercritical water oxidation: A case study, J. Chem. Technol. Biotechnol. 85 (2010) 640–647.
[10] B. Veriansyah, T.J. Park, J.S. Limb, Y.W. Lee, Supercritical water oxidation of waste-water from LCD manufacturing process: Kinetic and formation of chromium oxide nanoparticles, J. Supercrit. Fluids 34 (2005) 51–61.
[11] Y.H. Shin, N.C. Shin, B. Veriansyah, J. Kim, Y.W. Lee, Supercritical water oxidation of wastewater from acrylonitrile manufacturing plant, J. Hazard. Mater. 163 (2009) 1142–1147.
[12] X. Du, R. Zhang, Z. Gan, J. Bi, Treatment of high strength coking wastewater by supercritical water oxidation. Fuel, (2010), doi:10.1016/j.fuel.2010.09.018
[13] J. Sánchez-Oneto, F. Mancini, J.R. Portela, E. Nebot, F. Cansell, E.J. Martínez de la Ossa, Kinetic model for oxygen concentration dependence in the supercritical water oxidation of an industrial wastewater, Chem. Eng. J. 144 (2008) 361–367.
[14] K.M. Benjamin, P.E. Savage, Hydrothermal reactions of methylamine, J. Supercrit. Fluids 31 (2004) 301–311.
[15] N.S.E. Ahmed, Y.A. Youssef, R.M. El-Shishtawy, A.A. Mousa, Urea/alkali-free printing of cotton with reactive dyes, Color. Technol. 122 (2006) 324–328.
[16] J.R. Provost, Effluent improvement by source reduction of chemicals used in textile printing, J. Soc. Dyers Colour. 108 (1992) 260–264.
[17] M. Hodes, P.A. Marrone, G.T. Hong, K.A. Smith, J.W. Tester, Salt precipitation and scalecontrol in supercritical water oxidation-Part A: Fundamentals and research, J. Supercrit. Fluids 29 (2004) 265–288.
[18] P.A. Marrone, M. Hodes, K.A. Smith, J.W. Tester, Salt precipitation and scale control in supercritical water oxidation-part B: Commercial/full-scale applications, J. Supercrit. Fluids 29 (2004) 289–312.
[19] A.H. Harvey, A.P. Peskin and S.A. Klein, NIST/ASME Steam Properties, NIST Standard Reference Database 10, Version 2.2. Gaithersburg, MD: National Institute of Standard and Technology (2000).
[20] C.Y. Ma, Study on advanced treatment and reuse technology of printing and dyeing wastewater. PhD thesis. Donghua University, Shanghai, Chinese (2007).
[21] P.E. Savage, Organic Chemical Reactions in Supercritical Water, Chem. Rev. 99 (1999) 603–621.
[22] L.A. Torry, R. Kaminsky, M.T. Klein, M.R. Klotz, The effect of salts on hydrolysis in supercritical and near-critical water: Reactivity and availability, J. Supercrit. Fluids 5 (1992) 163–168.
[23] S.H. Townsend, M.A. Abraham, G.L. Huppert, M.T. Klein, S.C. Papsek, Solvent effects during reactions in supercritical water, Ind. Eng. Chem. Res. 27 (1988) 143–149.
[24] N. Segond, Y. Matsumura, K. Yamamoto, Determination of Ammonia Oxidation Rate in Sub- and Supercritical Water, Ind. Eng. Chem. Res. 41 (2002) 6020–6027.
[25] B. Al-Duri, L. Pinto, N.H. Ashraf-Ball, R.C.D. Santos, Thermal abatement of nitrogen-containing hydrocarbons by non-catalytic supercritical water oxidation (SCWO), J. Mater. Sci. 43 (2008) 1421–1428.
[26] R.K. Heiling, J.W. Tester, Oxidation of simple compounds and mixtures in supercritical water: Carbon monoxide, ammonia, and ethanol, Environ. Sci. Technol. 22 (1988) 1319–1324.
[27] T.D. Thornton, P.E. Savage, Phenol oxidation in supercritical water, J. Supercrit. Fluids 3 (1990) 240–248.
[28] M. Koo, W.K. Lee, C.H. Lee, New reactor system for supercritical water oxidation and its application on phenol destruction, Chem. Eng. Sci. 52 (1997) 1201–1214.
[29] X.H. Qi, Y.Y. Zhuang, Y.C. Yuan, W.X. Gu, Decomposition of aniline in supercritical water, J. Hazard. Mater. 90 (2002) 51–62.
[30] S.N. Rogak, P. Teshima, Deposition of sodium sulfate in a heated flow of supercritical water, AIChE J. 45 (1999) 240–247.
[31] F.J. Armellini, J.W. Tester, Precipitation of sodium chloride and sodium sulfate in water from sub-to supercritical conditions: 150 to 550°C, 100 to 300 bar, J. Supercrit. Fluids 7 (1994) 147–158.
[32] F.J. Armellini, J.W. Tester, Solubility of sodium chloride and sulfate in sub- and supercritical water vapor from 450–550°C and 100–250 bar, Fluid Phase Equilib. 84 (1993) 123–142.
[33] M.M. DiPippo, K. Sako and J.W. Tester, Ternary phase equilibria for the sodium chloride-sodium sulfate-water system at 200 and 250 bar up to 400°C. Fluid Phase Equilib. 157 (1999) 229–255.
[34] M. Schubert, J.W. Regler, F. Vogel, Continuous salt precipitation and separation from supercritical water. Part 2. Type 2 salts and mixtures of two salts, J. Supercrit. Fluids 52 (2010) 113–124.
[35] http://www.env.go.jp/en/water/wq/nes.html
[36] D. Mattioli, F. Malpei, G. Bortone, A. Rozzi, Water minimization and reuse in the textile industry, In: P. Lens, L. Hulshoff Pol, P. Wilderer, T. Asono (Eds), Water recycling and resource recovery in industry, IWA, London, pp. 545–584, 2002.
[37] P. Kritzer, E. Dinjus, An assessment of supercritical water oxidation (SCWO): Existing problems, possible solutions and new reactor concepts, Chem. Eng. J. 83 (2001) 207–214.