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Supercritical water oxidation of N-phenylglycinonitrile wastewater

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ABSTRACT

N-phenylglycinonitrile wastewater was treated with supercritical water oxidation (SCWO), at temperatures ranging from 375 to 550℃, a pressure of 25 MPa, residence times ranging from 5 to 60 s, and initial reactant concentrations ranging from 2,400 to 24,400 mg O_2/L in terms of chemical oxygen demand (COD). Results showed that when the initial COD of the wastewater was low and the oxidant was abundant, the temperature and residence time had significant effect on COD removal, while the initial COD concentration and oxidant dose did not show significant effects. A global rate expression was regressed from the complete set of data. An assumed pseudo-first-order global rate expression was determined with activation energy of 52.9(±2.9) kJ mol^{-1} and a preexponential factor of $3.6(\pm1.4)\times10^2\,\mathrm{s}^{-1}$.

Keywords: *N*-phenylglycinonitrile; Chemical oxygen demand (COD); Supercritical water oxidation (SCWO); Pseudo-first-order global rate

1. Introduction

Supercritical water oxidation (SCWO) is a process that uses water above the critical point (374℃ and 22.1 MPa) as a reaction medium to oxidize organic compounds [1,2]. Organic pollutants can be rapidly converted to mainly CO_2, H_2O, and inorganic salts by SCWO in a short time [3–5]. As a promising method, SCWO can be used for decomposing harmful organic compounds, especially wastes containing refractory organics of high concentration [6–8] and toxic substances, such as polychlorinated biphenyls [9–11] and methylphosphonic acid [12]. Nitrogen-containing organic compounds, such as aniline, nitrobenzene, pyridine, and methylamine, have also been reported to have been successfully decomposed in SCWO [8,13–16]. Dying wastewater has imposed serious environmental problems because of its high chemical oxygen demand (COD) concentration and potential toxicity [17,18]. Large efforts have been made to try to find ways of treating dying wastewater at reasonable cost and without generation of hazardous by-products [19–22]. *N*-phenylglycinonitrile is the intermediate product in the production of indigo, which is one of the most important materials of industrial dyestuff [23]. The production process of *N*-phenylglycinonitrile usually uses a water solution of aniline and hydroxy acetonitrile as raw materials, and polymerizes them by heating. In this process, wastewater with hazardous organics of high concentrations is produced, with the major products including aniline, methanol, cyanide, hydroxy acetoni-

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trile, and *N*-phenylglycinonitrile [24]. Currently, the reported treatment methods of *N*-phenylglycinonitrile wastewater, including combined oxidation of bentonite modified by cross-linking modification of iron and H_2O_2 [25], solvent extraction [26], and reverse osmosis [27], have only achieved a COD removal efficiency of 50–80%. The facultative aerobic method can remove over 90% COD [28], but amino compounds continuously accumulate and tend to cause the death of microorganism and failure of this process.

In this paper, the SCWO of *N*-phenylglycinonitrile wastewater was studied over a wide range of different temperatures, residence times, initial COD concentrations, and initial oxygen–COD ratios. Based on the experimental data, an assumed pseudo-first-order global rate expression was established.

2. Materials and analytical methods

2.1. Apparatus and procedure

The experiments were performed on a continuous-flow SCWO reactor (Fig. 1). The major parts of the apparatus included five modules: pumps, preheaters, reactor, cooling devices, and separator.

The feed and H_2O_2 solutions were first pumped by two separate electric-driven liquid pumps into the preheaters. The pumps were double entry liquid ring pumps with a supply flow of 0.05–2 kg/h. The preheaters were high-pressure tubing about 360 cm length, 0.6 cm inner diameter, and 1.5 cm outer diameter, made of Swagelok Stainless Steel (SS) 316 L. The temperatures of all stream in the outlet of the preheaters were measured using PT100 resistance thermometers (from −200 to 500°C). The heating devices in the preheating section were resistance wires. The H_2O_2 was completely decomposed to H_2O and O_2 in the preheater. A detailed explanation of H_2O_2 conversion is given in Section 2.2.

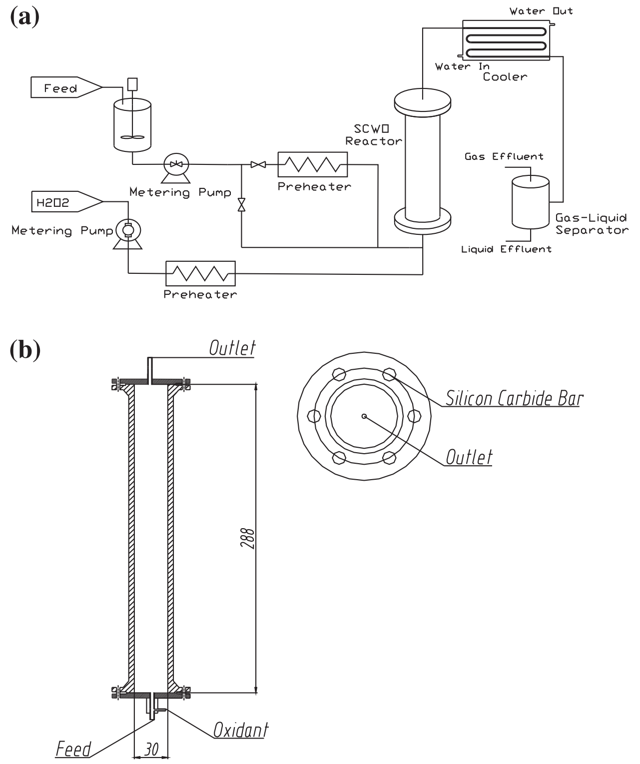

Fig. 1. Schematic flow diagram of SCWO continuous-flow reactor system. (a) SCWO system and (b) reactor.

After preheating, the two lines were then mixed at the reactor inlet by a mixing tee. The reactor vessel consisted of stainless steel 321, with an outer and inner diameter of 50 and 30 mm, respectively. The reaction chamber was 200 mL and 288 mm long. Six silicon carbide bars packed around the reactor (Fig. 1(b)) were used to provide heat. It was insulated with materials containing asbestos to minimize heat loss and allow isothermal operation of the flow reactor. A type K multipoint thermocouple (0–1,000°C) was inserted through the top port of the mixing tee into the reactor to measure the stream temperature in the reactor inlet section. Another similar thermocouple was inserted in the end of the reactor to determine the effluent temperature.

Then, the effluent was cooled to ambient temperature by passing through a water-cooled, counter-flow heat exchanger. The cooled products then passed into the separator where gaseous and liquid effluents were removed for collection and/or analysis.

The pressures of all stream were adjusted using pressure reducing valves (TESCOM, 44–1100 Series), and were then measured by pressure gauges and pressure transducers (0–40 MPa). The flow rates of all streams were adjusted by plunger stroke (SLPMMV26V), and were measured by Coriolis-type mass flow meters.

To study the effect of residence time, initial COD concentrations, and O_2 concentrations on COD removal efficiency, a set of SCWO experiments were conducted in an isothermal, isobaric tubular reactor. The reaction was conducted over a temperature range of 375–550°C, with the residence time from 5 to 60 s, at a fixed pressure of 25 MPa. The initial COD concentrations in the reactor ranged from 655.1 to 81.9 $\mathrm{mmol\,O_2\,L^{-1}}$. The initial O_2/COD ratio ranged between 0.5 and 2.5. The experimental parameters and results are listed in Table 2.

2.2. Materials

A H_2O_2 solution (H_2O_2, 30 wt.%) was used to supply O_2 as an oxidant in the experiments. It was

Table 1
Properties of *N*-phenylglycinonitrile wastewater

Terms	*N*-phenylglycinonitrile wastewater
Glycolonitrile (wt.%)	1.5
Aniline and *N*-phenylglycinonitrile (wt.%)	1.5
BOD_5 ($mg\,L^{-1}$)	4,500
COD_{Cr} ($mg\,O_2\,L^{-1}$)	24,400
TOC ($mg\,L^{-1}$)	7,450
Total N ($mg\,L^{-1}$)	1,500
pH	4.9

very important to determine the complete conversion of H_2O_2 to O_2 for the reliability of the experimental results. We also conducted an analysis of the liquid in the preheater. After the preheating process began, about 2 s later, no H_2O_2 was detected. The conversion of H_2O_2 was estimated according to the study of Takagi and Ishigure [29]. The estimation process was as follows. When temperatures were up to 280°C, the decomposition of H_2O_2 in liquid density water had an Arrhenius behavior with a first-order rate constant of $0.24\,s^{-1}$ at 280°C. Based on this behavior, when the temperature was 380°C, the rate constant was $2.64\,s^{-1}$. Then, it was estimated that the shortest preheating time in our experiments was 10 s, which was far longer than the time that is needed for complete conversion of H_2O_2.

N-phenylglycinonitrile wastewater was obtained from an *N*-phenylglycinonitrile manufacturing plant in China. The production process of *N*-phenylglycinonitrile in this plant adopted polymerization of aniline and hydroxy acetonitrile by heating. The process flow diagram of *N*-phenylglycinonitrile production is shown in Fig. 2, which suggests that the effluent contains lots of organic compounds, such as aniline, cyanide, hydroxy acetonitrile, *N*-phenylglycinonitrile, methanal, anilino acid, and methanol. The properties of *N*-phenylglycinonitrile wastewater are shown in Table 1.

2.3. Analytical methods

The COD concentrations of wastewater and liquid phase reactor effluents were analyzed by a COD analyzer (5B-3C, Lianhua Company, China) and Standard Method 5220D [30]. The biochemical oxygen demand (BOD) of the wastewater was analyzed with EPA Method 405.1 [31]. Total nitrogen of the wastewater was analyzed according to the standard methods issued by the Ministry of Environmental Protection, China [32].

The gas products were analyzed by Thermo ISQ Single Quadrupole GC–MS and Perkin Elmer Clarus

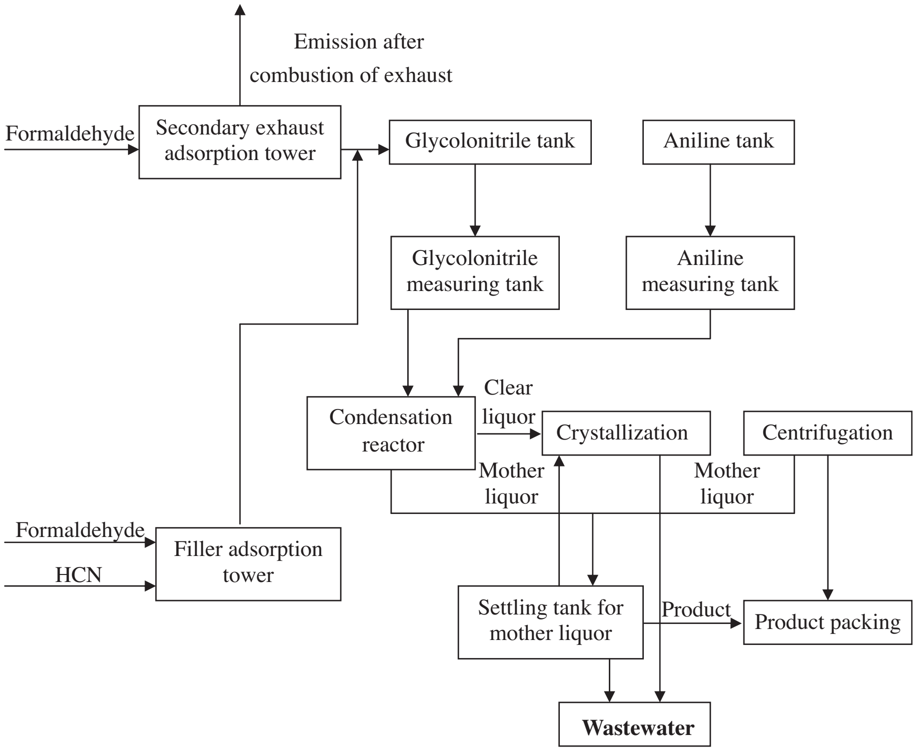

Fig. 2. Process flow diagram of *N*-phenylglycinonitrile production.

Table 2
Summary of wastewater oxidation experiments conducted in the flow reactor

T (°C)	P (MPa)	Initial COD (mol L^{-1} 10^{-3})	Initial O_2/COD ratio	Residence time (s)	Effluent COD (mol $L^{-1}10^{-3}$)	COD removal(%)
375	25	655.1	1	30	392.4	40.1
375	25	655.1	1.2	30	378.0	42.3
376	25	655.1	1.5	30	363.6	44.5
400	25	655.1	1	30	286.9	56.2
400	25	327.6	1.2	30	136.6	58.3
400	25	655.1	1.5	30	297.4	54.6
401	25	655.1	1.2	5	435.0	33.6
400	25	655.1	1.2	10	408.1	37.7
400	25	655.1	1.2	15	337.4	48.5
401	25	655.1	1.2	60	233.9	64.3
451	25	655.1	0.5	60	280.4	57.2
450	25	655.1	0.75	60	136.9	79.1
450	25	655.1	1	60	38.7	94.1
452	25	655.1	1.2	60	24.9	96.2
452	25	655.1	1.5	60	21.0	96.8
451	25	655.1	2	60	15.7	97.6
450	25	655.1	2.5	60	17.0	97.4
450	25	655.1	1	30	133.6	79.6
450	25	655.1	1.2	30	122.5	81.3
450	25	327.6	1.2	30	64.9	80.2
450	25	163.8	1.2	30	33.1	79.8
450	25	81.9	1.2	30	17.0	79.2
450	25	327.6	1.5	30	65.2	80.1
450	25	163.8	1.5	30	34.2	79.1
450	25	81.9	1.5	30	16.8	79.5
452	25	655.1	1.5	30	127.7	80.5
452	25	655.1	1.2	10	303.3	53.7
450	25	655.1	1.2	5	372.1	43.2
451	25	655.1	1.2	15	227.3	65.3
550	25	655.1	1	30	14.4	97.8
550	25	655.1	1.2	30	15.1	97.7
550	25	655.1	1.5	30	13.8	97.9
500	25	655.1	1	30	44.5	93.2
501	25	655.1	1.2	30	41.9	93.6
501	25	655.1	1.5	30	43.2	93.4
502	25	327.6	1.2	30	19.0	94.2
500	25	163.8	1.2	30	8.8	94.6
500	25	81.9	1.2	30	4.3	94.8
501	25	655.1	1.2	5	176.2	73.1
502	25	655.1	1.2	10	112.7	82.8
500	25	655.1	1.2	15	93.7	85.7
500	25	655.1	1.2	60	21.0	96.8
501	25	327.6	1.5	30	18.0	94.5
502	25	163.8	1.5	30	9.7	94.1
500	25	81.9	1.5	30	4.0	95.1

580 GC. In the liquid product, the total organic carbon (TOC) and inorganic carbon (IC) contents were measured with a TOC analyzer (Shimadzu TOC-5000A TOC analyzer), and the ammonia nitrogen (NH_3–N) and nitrate ion NO_3^- were analyzed with a Shimadzu UV-2450 UV–VIS spectrophotometer.

The major components of *N*-phenylglycinonitrile wastewater was analyzed by gas chromatography/mass spectroscopy (GC–MS). The organic compounds were identified by using a Thermo DSQ II gas chromatograph with TRACE GC Ultra with mass spectrometer (Thermo Company, USA). The analysis procedure was according to the following conditions: column, a DB-5 fused silica capillary (30 m long, 0.25 mm ID), held at 50°C for 3 min, and then increased to 170°C at a rate of 10°C /min and held for 1 min. The injector, transfer line, and ion source were kept at 250, 250, and 200℃, respectively, while helium, with a flow rate of 1 mL/min, was used as the carrier gas. When chromatographic separation was finished, the samples were identified by mass spectrometry.

2.4. Calculations

2.4.1. Residence time

Because the density of supercritical water varies with different temperatures and pressures, the residence time of reactants was calculated according to the density of supercritical water, reactor volume, and feed flow. The experimental data of certain residence times can be gained by adjusting the flow rate of feed. The system can be regarded as a pure water system for wastewater with a low organic concentration (≤5%). So, the residence time was calculated by:

$$\mathrm{t} = \frac{V_r \times \rho_w}{F \times \rho_0} \tag{1}$$

where t is the residence time (s) of reactants, V_r is the reactor volume (m^3), $\rho_w$is the water density under reaction conditions ($kg\,m^{-3}$), F is the wastewater flow ($m^3\,s^{-1}$), and ρ_0 is the water density at normal temperature and pressure ($kg\,m^{-3}$). The density of supercritical water was obtained from the study of Akiya and Savage [33].

2.4.2. Initial concentration of reactants

The initial concentration of reactants was calculated as follows:

$$[\mathrm{COD}]_0 = \frac{[\mathrm{COD}]_r \times F_r}{F_r} \tag{2}$$

$$[\mathrm{O_2}]_0 = \frac{[\mathrm{H_2O_2}]_r \times F_r}{F_r} \tag{3}$$

where $[\mathrm{COD}]_r$ is the COD concentration of the reactant feed ($mmol\,O_2\,L^{-1}$), F_r is the reactant feed flow rate ($kg\,h^{-1}$), F_T is the total feed flow rate, and $[O_2]_0$ is the initial concentration of O_2 ($mmol\,L^{-1}$).

2.4.3. COD removal efficiency

The COD removal efficiency was used to evaluate the extent of oxidative decomposition of *N*-phenylglycinonitrile wastewater, X, as defined in the following equation:

$$X = \frac{[\mathrm{COD}]_0 - [\mathrm{COD}]_f}{[\mathrm{COD}]_0} \tag{4}$$

where $[\mathrm{COD}]_f$ is the residual COD concentration of the liquid product effluent when the reaction is completed.

3. Results and discussion

3.1. SCWO of N-phenylglycinonitrile

3.1.1. Effect of oxidant dosage

The major reaction product containing nitrogen was reported to be N_2 [6,34,35], and thus the oxidation reaction of the major compounds in the *N*-phenylglycinonitrile wastewater can be expressed as:

$$C_8H_8N_2 + 10O_2 \rightarrow 8CO_2 + 4H_2O + N_2 \tag{5}$$

$$C_6H_7N + 7.75O_2 \rightarrow 6CO_2 + 3.5H_2O + 0.5N_2 \tag{6}$$

$$C_2H_3NO + 3O_2 \rightarrow 2CO_2 + 1.5H_2O + 0.5N_2 \tag{7}$$

Experiments studying the effect of oxidant dose were conducted as shown in Fig. 3. The COD removal showed a linear increase with increasing O_2/COD ratio under certain conditions. When the O_2/COD ratio was 1.2, COD removal reached a value of 96.2%. When the O_2 dose continued to increase, the increase rate of COD removal efficiency slowed down. This indicated that the oxidant was abundant when the O_2/COD ratio was above 1.2.

3.1.2. Effect of reaction temperature

Three sets of experiments were conducted to examine the effect of temperature on COD removal, at

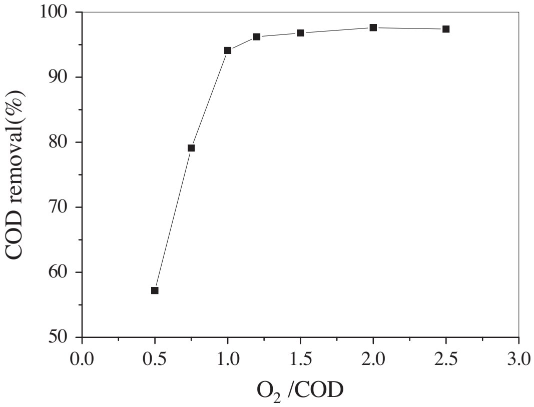

Fig. 3. Effect of initial O_2/COD ratio on COD removal at fixed reaction pressure and residence time ($T = 450$℃, $p = 25$ MPa, and residence time = 60 s).

O_2/COD ratios of 1.0, 1.2, and 1.5. The reaction pressure was 25 MPa, and residence time was 30 s. The results are shown in Fig. 4. As temperature increased, COD removal showed a rising tendency. The decomposition rate of *N*-Phenylglycinonitrile wastewater in a low temperature range temperature was markedly lower than in a high temperature range, but the decomposition rate increased more rapidly than that in the high temperature range. When the temperature increased from 375 to 450°C, COD removal rose from 40.1 to 81.3%, but when reaction temperature increased from 500 to 550°C, COD removal only rose from 94.2 to 97.9%. The temperature behavior can be analyzed from two aspects. First, the oxidation of organic pollutants is an irreversible process, and therefore, with increasing temperature, an increased reaction rate resulted in increasing the decomposition rate. Second, under fixed pressure, with increasing temperature, the density of supercritical water decreased while reactant concentration and reaction rate decreased.

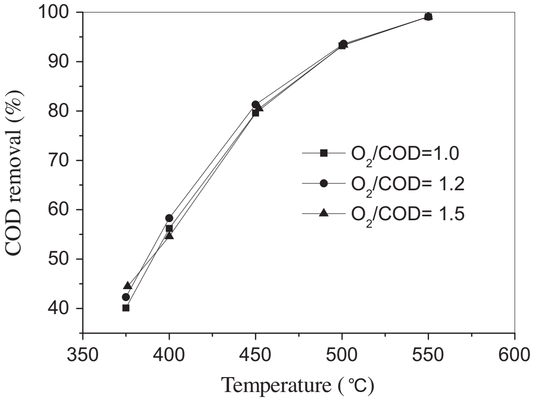

Fig. 4. Effect of reaction temperature on COD removal at fixed reaction pressure and residence time ($p = 25$ MPa and residence time = 30 s).

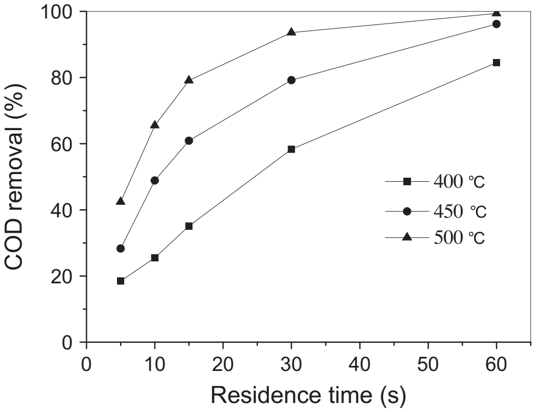

Fig. 5. Effect of residence time on COD removal at a fixed reaction pressure ($p = 25$ MPa and $O_2/COD = 1.2$).

3.1.3. Effect of residence time

The effect of residence time on COD removal was studied at an initial COD/O_2 ratio of 1.2, and temperatures of 400, 450, and 500℃. The results indicated that residence time has a significant effect on decomposition rate of organic pollutants (Fig. 5). Under certain conditions, the decomposition rate of *N*-Phenylglycinonitrile wastewater increased with increasing residence time, and the rate of increase was first fast and became slower in the later stage. In the beginning period of residence time from 5 to 15 s, the decomposition rate rapidly increased. At a residence time over 30 s, the decomposition rate of organics relatively modestly increased. At this time, the effect of residence time on decomposition efficiency was not significant.

3.1.4. Effect of initial COD concentration

To study the effect of initial COD concentration on COD removal, four sets of experiments were performed. Different initial COD concentrations were obtained by dilution of the *N*-phenylglycinonitrile wastewater with deionized water. The results are shown in Fig. 6. It was observed that with increasing concentration of organic pollutants, a rapidly increasing rate of decomposition was gained, but the oxidation rate (or COD removal) did not significantly change. Maybe, it was because of the relatively lower COD. For the organic pollutants decomposed by SCWO in our experiments, the COD removal obtained at a low concentration was not found to be higher than that obtained at a high reactant concentration. Therefore, for high COD removal under different reactant concentrations, it is suggested that SCWO is suitable for decomposition of high concentration organic wastes. Thus, the effect of temperature on COD removal was concluded to be great. This can be

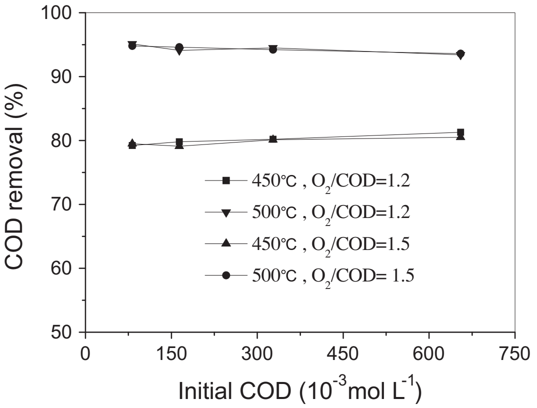

Fig. 6. Effect of initial COD concentration at the reactor inlet on COD removal at a fixed reaction pressure and residence time ($p = 25$ MPa and residence time = 30 s).

interpreted in that SCWO is a fast reaction, and in the residence time of 30 s, the reaction reached equilibrium, and the initial reactant concentration had little effect on the equilibrium. Additionally, COD decomposition is a pseudo-first-order reaction, and the reaction rate constant is not concerned with the initial reactant concentration [36].

3.2. Carbon balances and nitrogen balances analysis

Carbon balances (mole%) were defined by the total carbon content in the gas and liquid products with respect to the feed carbon content introduced within *N*-phenylglycinonitrile wastewater. In the same way, nitrogen balances were defined as the total nitrogen output related to the total nitrogen input.

To conduct the carbon and nitrogen balance analysis, the gaseous products and the major component of liquid products were analyzed. The original wastewater had a TOC of 7,450 mg L^{-1}, and TN of 1,500 mg L^{-1}. It was determined that the carbon and nitrogen-containing gas products were CO_2, CO, N_2, and N_2O. For the liquid products, the IC, TOC, dissolved organic nitrogen (DON) NO_3^-, and NH_3–N were analyzed. The carbon and nitrogen distributions with temperature were analyzed, and the results are listed in Figs. 7 and 8. The errors in the carbon and nitrogen recovery rates were 0.3–4.2% and the typical error was 0.8%. And, it was calculated that the carbon balances were 97–102.4%, and the nitrogen balances were 98.5–104.2%.

As a whole, with increasing temperature, the TOC percentage rapidly decreased, whereas the production of CO_2 and IC quickly increased. It can be seen that the most abundant species of all products was CO_2, with a yield of about 86.4% at 550°C. The proportion of CO decreased as temperature rose. This was because of the increasing oxidation degree caused by increasing temperature. When temperature rose, the oxidation tended to be more and more complete, so as the incomplete oxidation product, CO yields decreased.

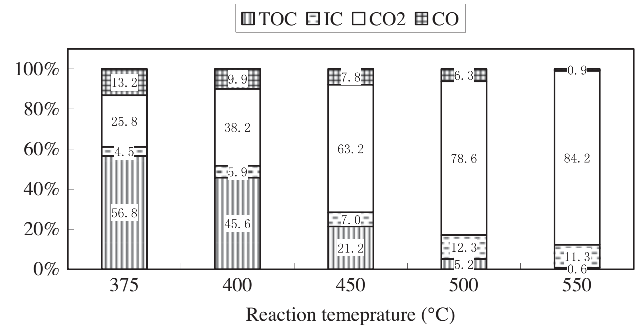

Fig. 7. Dependence of carbon distribution on temperature ($p = 25$ MPa, residence time = 60 s and O_2/COD = 1.2).

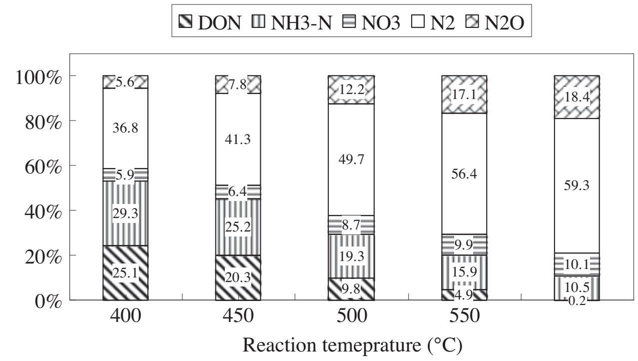

Fig. 8. Dependence of nitrogen distribution on temperature ($p = 25$ MPa, residence time = 60 s and O_2/COD = 1.2).

Fig. 8 illustrates the nitrogen distribution dependence on temperature. The reaction was greatly promoted by temperature, as can be seen by the phenomenon of the rapid decrease of DON. N_2 was the major nitrogen product of *N*-phenylglycinonitrile wastewater oxidation in supercritical water. When temperature increased, the content of N_2 rapidly increased with the proceeding of the SCWO reaction, and accounted for 59.3% at a temperature of 550℃.

The increasing temperature also favored the production of N_2O, with the production of N_2O at 550℃ being double that at 400℃. Nitrite ions only showed a slightly difference when temperature changed, which inferred that their production was independent of the temperature.

3.3. Global kinetics for oxidation of N-phenylglycinonitrile wastewater

Because the products of organic pollutants decomposed by SCWO are complex, it is difficult to get the elementary reaction model. Here, we used the exponential function to describe the kinetics. The reaction of organics decomposition in SCWO was related to temperature, reactant concentration, and oxygen concentration. In the decomposition experiments of complex wastewater, COD was used to describe the reactant concentration. We used the data obtained from the experiment at 823 K, which represent the worst case for employing the plug-flow idealization in this work, to calculate the values of characteristic times and nondimensional numbers pertinent to the tubular flow reactors. Our results show that on the whole, the values of the nondimensional groups in our study can meet the theoretical criteria of plug flow condition [37]. This indicates that the experimental data obtained from the performance of our reactor can be safely analyzed in the plug-flow idealization. So, the global reaction rate can be described as Eq. (8), and the data in the equation was gained by the above experiments (the data was not included in the equation when O_2/COD ratio was lower than 1):

$$-\frac{d[\mathrm{COD}]}{dt} = A\exp\left(\frac{-E_a}{RT}\right)[\mathrm{COD}]^a[\mathrm{O}_2]^b \tag{8}$$

where t is reaction time (s), A is the Arrhenius constant specific for the reaction, E_a represents the activation energy ($\mathrm{J\,mol^{-1}}$), R is gas constant ($8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}$), T is the reaction temperature (K), [COD] is the reactant concentration ($\mathrm{mol\,L^{-1}}$), $[\mathrm{O}_2]$ is oxygen concentration ($\mathrm{mol\,L^{-1}}$), and a and b are the reaction orders of reactant and oxygen, respectively.

Rearranging Eq. (8) with respect to the COD removal X defined by Eq. (4), the following equation can be obtained:

$$-\frac{d(1-X)}{dt} = A\exp\left(\frac{-E_a}{RT}\right)[\mathrm{COD}]_0^{a-1}(1-X)^a[\mathrm{O}_2]^b \tag{9}$$

As shown in Figs. 3 and 5, COD removal slightly changed with changes of O_2 concentration and initial COD concentration during the experimental process. Therefore, the global reaction rate can be considered a pseudo-first-order reaction with respect to the initial COD concentration, assuming a zero order for O_2 concentration. If Eq. (9) is rearranged with respect to the COD removal, using the initial condition of $X=0$ at residence time $t=0$, it can be solved analytically to provide Eq. (10):

$$X = 1 - \exp\left[-At\exp\left(\frac{-E_a}{RT}\right)\right]. \tag{10}$$

Based on the experimental data, Gauss–Newton was used to conduct nonlinear regression analysis (Matlab V6.5). The pseudo-first-order reaction rate predicted is

$$-\frac{d[\mathrm{COD}]}{dt} = (3.6 \pm 1.4)\times 10^2\mathrm{s}^{-1} \times \exp\left(\frac{-(52.9 \pm 2.9)\mathrm{kJ{\cdot}mol^{-1}}}{RT}\right) \times [\mathrm{COD}] \tag{11}$$

The final predicted value of Arrhenius kinetics parameters, A and E_a, are, respectively, $(3.6 \pm 1.4) \times 10^2\,\mathrm{s}^{-1}$ and $(52.9 \pm 2.9)\,\mathrm{kJ\,mol^{-1}}$. All the parameters were estimated in a 95% confidence interval on the predicted response (Fig. 9).

To explain the detailed kinetics of *N*-phenylglycinonitrile wastewater oxidation in SCW, comparison of the reaction orders and activation energy for wastewater in Eq. (11) with the study of textile wastewater (the major pollutant is Cl Disperse Orange 25, which was also refractory nitrogen-containing compound of high molecular weight) [38] was conducted. The two kinds of wastewater have the same reaction order for COD. The activation energies were $52.9 \pm 2.9\,\mathrm{kJ\,mol^{-1}}$ and $27.8 \pm 1.2\,\mathrm{kJ\,mol^{-1}}$ for *N*-phenylglycinonitrile waste water and textile wastewater, respectively. The Arrhenius pre-exponential factors for the two studies were $(3.6 \pm 1.4) \times 10^2\,\mathrm{s}^{-1}$ and $(34.3 \pm 1.5)\,\mathrm{s}^{-1}$, respectively. The comparison indicates that the oxidation process in supercritical water is very complex and significantly differs among various compounds, especially for complex wastewater, and different amounts and kinds of elementary steps are included in the process.

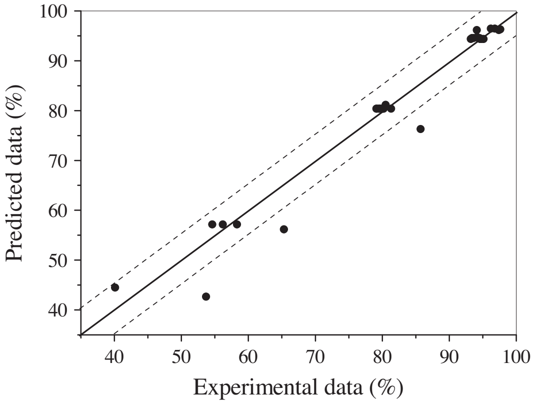

Fig. 9. Parity plot of the comparison of experimental and predicted COD removal.

4. Conclusion

Oxidation of *N*-phenylglycinonitrile wastewater was studied, using a continuous flow reactor with supercritical water. The results demonstrated that SCWO was an effective treatment method for *N*-phenylglycinonitrile wastewater. A high COD removal of up to 97.9% was obtained when pressure was 25 MPa, temperature was 550°C, the initial O_2/COD ratio was 1.5, and the residence time was 30 s. The global rate expression according to wastewater concentration with respect to the COD was regressed from the complete set of data. Assuming the reaction rate was pseudo-first-order for the initial COD concentration, reaction rate expression was determined with activation energy of (52.9 ± 2.9) kJ mol^{-1} and a pre-exponential factor of $(3.6 \pm 1.4) \times 10^2\ \text{s}^{-1}$ to a 95% confidence level.

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References

[1] P.E. Savage, Organic chemical reactions in supercritical water, Chem. Rev. 19 (1999) 603–622.
[2] G. Anitescu, L.L. Tavlarides, Oxidation of biphenyl in supercritical water: Reaction kinetics, key pathways, and main products, Ind. Eng. Chem. Res. 44 (2005) 1226–1232.
[3] A. Fourcault, B. García-Jarana, J. Sánchez-Oneto, F. Marias, J. R. Portela, Supercritical water oxidation of phenol with air: Experimental results and modeling, Chem. Eng. J. 152 (2009) 227–233.
[4] T.D. Thomas, P.E. Savage, Phenol oxidation pathways in supercritical water, Ind. Eng. Chem. Res. 31 (1992) 2451–2456.
[5] F. Zhang, S. Chen, C. Xu, G. Chen, J. Zhang, C. Ma, Experimental study on the effects of operating parameters on the performance of a transpiring-wall supercritical water oxidation reactor, Desalination. 294 (2012) 60–66.
[6] K.M. Benjamin, P.E. Savage, Supercritical water oxidation of methylamine, Ind. Eng. Chem. Res. 44 (2005) 5318–5324.
[7] B. Veriansyah, J. Kim, Supercritical water oxidation for the destruction of toxic organic wastewaters: A review, J. Environ. Sci. 19 (2007) 513–522.
[8] G. Zhang, I. Hua, Supercritical water oxidation of nitrobenzene, Ind. Eng. Chem. Res. 42 (2003) 285–289.
[9] G. Anitescu, L.L. Tavlarides, V. Munteanu, Decomposition of monochlorobiphenyl isomers in supercritical water in the presence of methanol, AIChE J. 50 (2004) 1536–1544.
[10] P.O. Christopher, C.T. Mark, A.B. David, Supercritical water oxidation of the PCB congener 2-chlorobiphenyl in methanol solutions: A kinetic analysis, Environ. Sci. Tech. 39 (2005) 6839–6844.
[11] V. Marulanda, G. Bolaños, Supercritical water oxidation of a heavily PCB-contaminated mineral transformer oil: Laboratory-scale data and economic assessment, J. Supercrit. Fluids. 54 (2010) 258–265.
[12] B. Veriansyah, E. Song, J. Kim, Destruction of methylphosphonic acid in a supercritical water oxidation bench-scale double wall reactor, J. Environ. Sci. 23 (2011) 545–552.
[13] M.D. Bermejo, F. Cantero, M.J. Cocero, Supercritical water oxidation of feeds with high ammonia concentrations: Pilot plant experimental results and modeling, Chem. Eng. J. 137 (2008) 542–549.
[14] N. Crain, S. Tebbal, L. Li, E. Gloyna, Kinetics and reaction pathways of pyridine oxidation in supercritical water, Ind. Eng. Chem. Res. 32 (1993) 2259–2268.
[15] M.J. Cocero, E. Alonso, R. Torio, D. Vallelado, F. Fdz-Polanco, Supercritical water oxidation in a pilot plant of nitrogenous compounds: 2-Propanol mixtures in the temperature range 500–750℃, Ind. Eng. Chem. Res. 39 (2000) 3707–3716.
[16] X. Qi, Y. Zhuang, Y. Yuan, W. Gu, Decomposition of aniline in supercritical water, J. Hazard. Mater. B90 (2002) 51–62.
[17] A. Gong, H. Tan, Study on pre-treatment experiment for *N*-phenylglycinonitrile organic wastewater, Shanxi Archit. 26 (2011) 19–25.
[18] Q. He, M. He, F. Ji, J. Qu, Study on *N*-phenylglycinonitrile wastewater treatment by anoxic-aerobic process, J. Chongqing Jianzhu Univ. 24 (2002) 49–52.
[19] T. Long, J. Mu, J. Fang, L. Chen, Study on the pretreatment of *N*-phenylglycinonitrile wastewater Fe-crosslinked betonite and H_2O_2 combined method, Water Supply Drain. 35a (2009) 325–329.
[20] C. Li, J. Xie, R. Lai, Test research on pre-treatment of wastewater extracted from *N*-phenylglycinenitrile, Chin. Environ. Prot. Ind. 11 (2007) 30–33.
[21] J. Qiu, Y. Fu, M. Yang, Y. Xiang, Utilization of reverse osmosis membrane for natural gas wastewater chemical wastewater separation, Sichuan Archit. 26 (2006) 163–164.
[22] Q. He, J. Li, H. Li, M. He, F. Ji, Treatment of *N*-phenylglycinonitrile wastewater by facultative-aerobic process, Chin. Water Wastewater. 20 (2004) 79–80.
[23] G. Gnanapragasam, M. Senthilkumar, V. Arutchelvan, T. Velayutham, S. Nagarajan, Bio-kinetic analysis on treatment of textile dye wastewater using anaerobic batch reactor, Bioresour. Technol. 102 (2011) 627–632.
[24] V. David, M.O. Juan, E. Eduardo, M. Vicente, A. Antonio, Electrochemical wastewater treatment directly powered by photovoltaic panels: Electrooxidation of a dye-containing wastewater, Environ. Sci. Tech. 44 (2010) 5182–5187.
[25] 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.
[26] A. Ojstrsek, D. Fakin, Colour and TOC reduction using biofilter packed with natural zeolite for the treatment of textile wastewaters, Desalin. Water. Treat. 33 (2011) 1–3.
[27] K.D. Evangelia, K.L. Nikolaos, Dyes removal from simulated and industrial textile effluents by dissolved-air and sispersed-air flotation techniques, Ind. Eng. Chem. Res. 47 (2008) 5594–5601.
[28] H. Samiha, A.O. Mehmet, O. Nihal, B. Nizar, D. Mohamed, Comparative mineralization of textile dye indigo by photo-Fenton process and anodic oxidation using boron-doped diamond anode, Desalin. Water Treat. 45 (2012) 297–304.
[29] J. Takagi, K. Ishigure, Thermal decomposition of hydrogen peroxide and its effect on reactor water monitoring of boiling water reactors, Nucl. Sci. Eng. 89 (1985) 177–186.
[30] A.D. Eaton, L.S. Clesceri, A.E. Greenberg, Standard methods for the examination of water and wastewater, American Public Health Association, Washington, DC, 1995, 5–15.
[31] Environmental monitoring and support laboratory, Office of research and development, US Environmental Protection Agency, Method 405.1. Methods for Chemical Analysis of Water and Waste. Cincinnati, OH, 1983, 441.
[32] Water quality-determination of total nitrogen-alkaline potassium persulfate digestion UV spectrophotometric method (HJ 636–2012), Ministry of Environmental Protection of The People's Republic of China, national standards for environmental protection in China, 2012.

[33] N. Akiya, P.E. Savage, Roles of water for chemical reactions in high-temperature water, Chem. Rev. 102 (2002) 2725–2750.

[34] K.M. Benjamin, P.E. Savage, Detailed chemical kinetic modeling of methylamine in supercritical water, Ind. Eng. Chem. Res. 44 (2005) 9785–9793.

[35] M.J. Cocero, E. Alonso, R. Torio, D. Vallelado, F. Fdz-Polanco, Supercritical water oxidation in a pilot plant of nitrogeneous compounds: 2-propanol mixtures in the temperature range 500–750˚C, Ind. Eng. Chem. Res. 39 (2000) 3707–3716.

[36] Y.H. Shin, N.C. Shin, B. Veriansyah, J. Kim, Y. Lee, Supercritical water oxidation of wastewater from acrylonitrile manufacturing plant, J. Hazard. Mater. 163 (2009) 1142–1147.

[37] A.H. Cutler, M.J. Antal, Jr., M. Jones, Jr. A Critical evaluation of the plug-flow idealization of tubular-flow reactor data, Ind. Eng. Chem. Res. 27 (1988) 691–697.

[38] O.Ö. Söğüt, M. Akgün, Treatment of textile wastewater by SCWO in a tube reactor, J. Supercrit. Fluids. 43 (2007) 106–111.