



Supercritical water oxidation of wastewater from acrylonitrile manufacturing plant

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ABSTRACT

The wastewater from an acrylonitrile manufacturing plant, which is difficult to biodegrade, was decomposed in subcritical and supercritical water. Experiments were carried out at temperature ranging from 299 to 552 °C and a pressure of 25 MPa. The initial total organic carbon (TOC) of acrylonitrile wastewater was set from 0.27 to 2.10 mol L⁻¹ with residence times ranging from 3 to 30 s. 30 wt.% H₂O₂ solution was used as an oxidant with the stoichiometric ratios of O₂ based on the initial TOC concentration ranging from 0.5 to 2.5. TOC conversion increased with increasing reaction temperature and residence time, however, beyond the stoichiometric oxygen–TOC ratio of 1:1, TOC conversion was barely affected by excess oxygen. The initial TOC concentration of acrylonitrile wastewater also had a negligible effect on TOC conversion. An assumed pseudo-first-order global rate expression was determined with an activation energy of 53.48(±33.57) kJ mol⁻¹ and a pre-exponential factor of 5.22(±1.74) × 10² s⁻¹. By considering the dependence of the reaction rate on TOC and O₂ concentration, a global rate expression was regressed from the complete set of 64 data points. The resulting activation energy was 66.33(±5.87) kJ mol⁻¹; the pre-exponential factor was 6.07(±6.89) × 10³ mol^{-0.26} s⁻¹; and the reaction orders for initial TOC and O₂ concentration were 1.26(±0.15) and 0.00(±0.15), respectively.

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1. Introduction

Supercritical water oxidation (SCWO) is an effective, eco-friendly technology for treating hazardous industrial wastes, discharging pure water, inorganic matters, CO₂, and N₂ [1–6]. Even though this technology suffers from corrosion and salt precipitation, SCWO has been a breakthrough for the decomposition of toxic, refractory wastewater [7–9].

World production of acrylonitrile exceeded 3.2 million tonnes for application in butadiene rubber and ABS polymer in 1988. In spite of the long production history of acrylonitrile, difficulties remain in treatment of the wastewater from acrylonitrile manufacturing plants. Wyatt and Knowles reported that the wastewater from such plants contains eight major organic components: acrylonitrile, acrylamide, acrylic acid, acrolein, cyanopyridine, fumaronitrile, succinonitrile, and maleimide [10]. This acrylonitrile wastewater has mainly been treated with microbial degradation, despite the fact that it is difficult to biodegrade. In order to increase

susceptibility to microbial attack, the concentrated feed from the plants should be diluted. Ramakrishna et al. pointed out that with the biological treatment by the powered activated carbon-activated sludge process, about 70–75% of the organic components in acrylonitrile wastewater are removed [11].

Studies of the application of SCWO for the treatment of wastewater from acrylonitrile manufacturing plants have yet to be published. In this work, the oxidation of acrylonitrile wastewater was carried out to consider the effect of reaction temperature, residence time, and initial total organic carbon (TOC) and O₂ concentration on TOC conversion. Experimental results were analyzed in detail to obtain the rate law for oxidation of acrylonitrile wastewater at supercritical conditions.

2. Experimental

The configuration of the continuous-flow SCWO system is shown in Fig. 1. The experimental apparatus consists of pumps, a wastewater pre-heater, an oxidant pre-heater, a tubular reactor, a cooler, a filter, a back-pressure regulator, and a separator. All wetted parts of the system were made of 1/8 in. 316 SS, except hot regions that were made of 1/8 in. Inconel 625. The oxidant and

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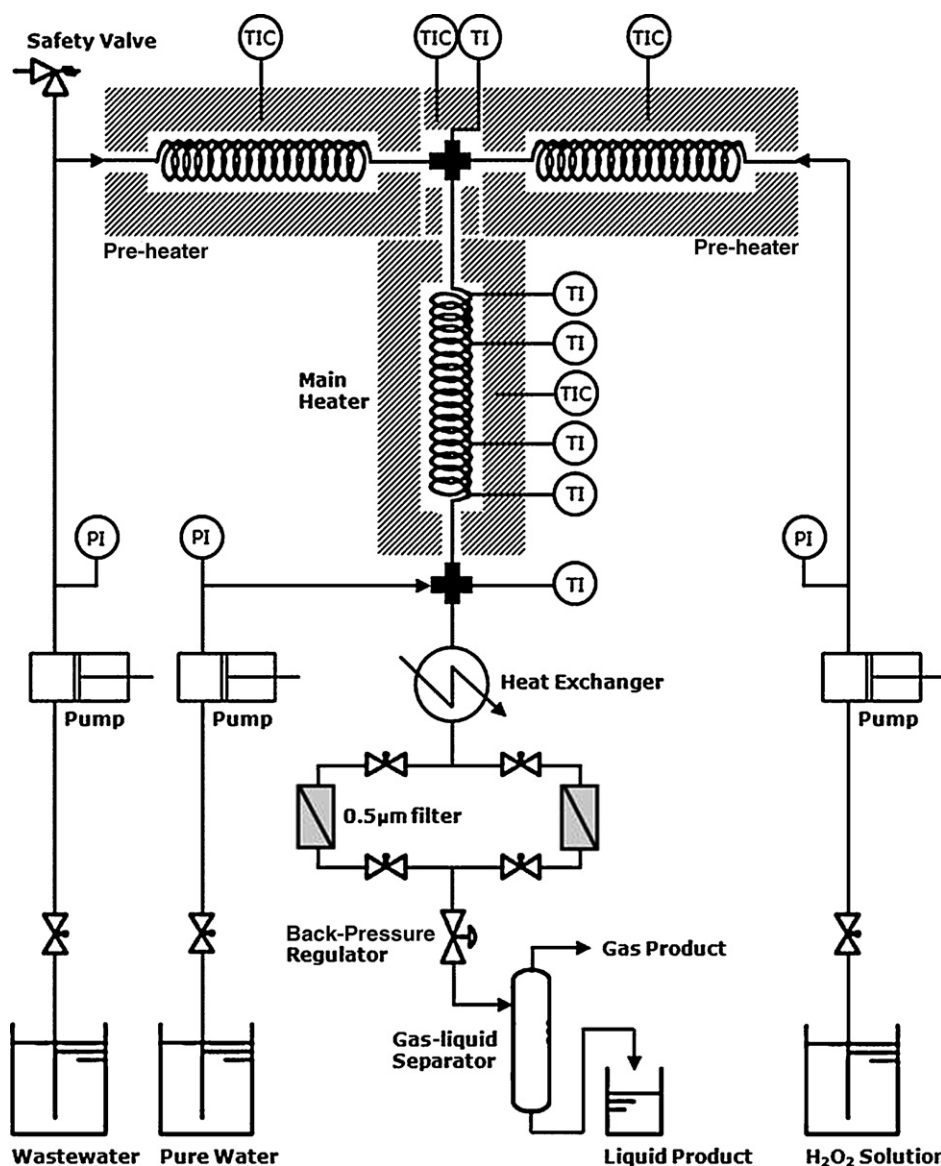


Fig. 1. Diagram of the continuous supercritical water oxidation (SCWO) system. All wetted parts of the system were made of 316 SS, except hot regions that were made of Inconel 625. The cross-piece at the reactor inlet was precisely designed to enhance the mixing efficiency for oxidant and wastewater.

wastewater streams were pressurized by two high-pressure pumps and then separately pre-heated to the reaction temperature. The H_2O_2 solution was used as the oxidant, decomposing to O_2 and H_2O completely in the oxidant pre-heater before being mixed with the wastewater at the reactor inlet. After exiting the reactor, the effluent was passed through the cooler and the $0.5 \mu\text{m}$ inline filter. The product stream was then depressurized by the back-pressure regulator and separated into liquid and vapor phases. The flow rate of the H_2O_2 solution ranged from 0.24 to 3.96 mL min^{-1} , and the flow rate of wastewater from 2.05 to $19.16 \text{ mL min}^{-1}$. Monitoring of the volumetric flow rates of liquid products was achieved through the time interval measurement.

$30 \text{ wt.}\% \text{H}_2\text{O}_2$ solution (J.T. Baker) was used as a source of oxygen, without further dilution. Acrylonitrile wastewater was supplied from an acrylonitrile manufacturer in Korea. The properties of the acrylonitrile wastewater are shown in Table 1. The organic concentration of wastewater and liquid products were characterized by analyzing the total organic carbon. TOC and total N analyses were performed using Tekmar–Dohrmann Model Apollo 9000 HS. Triplicate runs were made on each sample to provide overall data

precision. The standard deviations of TOC concentrations were less than 1.8% with the averages used to calculate TOC conversion.

TOC decomposition was used to evaluate the extent of oxidative decomposition of acrylonitrile wastewater, X , defined as follows:

$$X = \frac{[\text{TOC}]_0 - [\text{TOC}]_t}{[\text{TOC}]_0} \quad (1)$$

Table 1
Properties of concentrated acrylonitrile wastewater

Description	Acrylonitrile wastewater
TOC (mg L^{-1})	27,240
Total N (mg L^{-1})	11,995
pH	5.40
Fe (mg L^{-1})	12.59
Ni (mg L^{-1})	1.55
Cr (mg L^{-1})	2.83
Mo (mg L^{-1})	0.24
Na (mg L^{-1})	53.97

where $[\text{TOC}]_0$ is the initial TOC concentration calculated when the feed of the wastewater storage tank is mixed with water generated from the H_2O_2 solution at the reactor inlet (mol L^{-1}). $[\text{TOC}]_t$ is the residual TOC concentration of the liquid product after reaction (mol L^{-1}). The stoichiometric ratio of oxygen, based on the initial TOC concentration, is defined as

$$\text{Stoichiometric ratio of } \text{O}_2 = \frac{[\text{O}_2]}{[\text{TOC}]_0} \quad (2)$$

where $[\text{O}_2]$ is the oxygen concentration (mol L^{-1}) generated from the 30 wt.% H_2O_2 solution. The total residence time in the reactor is calculated using the following equation:

$$\tau = \frac{V_{\text{Reactor}} \times \rho_{\text{Fluid}}(P, T)}{M_{\text{Fluid}}} \quad (3)$$

where V_{Reactor} is the reactor volume; $\rho_{\text{Fluid}}(P, T)$ is the fluid density at the reaction pressure and temperature (g mL^{-1}); and M_{Fluid} is the fluid mass flow rate at the reactor inlet. The fluid density at

Table 2
Summary of oxidation experiments for acrylonitrile wastewater conducted in the continuous tubular reactor

Reaction temperature ($^{\circ}\text{C}$)	Reaction pressure (MPa)	Initial TOC (mol L^{-1})	O_2 (mol L^{-1})	Stoichiometric ratio of O_2	Residence time (s)	TOC conversion (%)
549	25	0.54	0.27	0.5	15	77
552	25	0.51	0.51	1.0	15	95
551	25	0.49	0.74	1.5	15	95
551	25	0.47	0.94	2.0	15	96
552	25	0.45	1.13	2.5	15	97
501	25	0.54	0.27	0.5	15	77
505	25	0.51	0.51	1.0	15	85
503	25	0.49	0.74	1.5	15	85
503	25	0.47	0.94	2.0	15	86
504	25	0.45	1.13	2.5	15	85
450	25	0.54	0.27	0.5	15	54
450	25	0.51	0.51	1.0	15	58
450	25	0.49	0.74	1.5	15	60
450	25	0.47	0.94	2.0	15	63
451	25	0.45	1.13	2.5	15	67
401	25	0.54	0.27	0.5	15	39
401	25	0.51	0.51	1.0	15	40
401	25	0.49	0.74	1.5	15	39
401	25	0.47	0.94	2.0	15	40
400	25	0.45	1.13	2.5	15	43
350	25	0.54	0.27	0.5	15	31
350	25	0.51	0.51	1.0	15	26
350	25	0.49	0.74	1.5	15	27
350	25	0.47	0.94	2.0	15	27
350	25	0.45	1.13	2.5	15	25
550	25	0.26	0.39	1.5	15	95
550	25	0.27	0.27	1.0	15	94
400	25	0.26	0.39	1.5	15	39
400	25	0.27	0.27	1.0	15	40
550	25	0.87	1.30	1.5	15	97
551	25	0.94	0.94	1.0	15	95
401	25	0.87	1.30	1.5	15	43
399	25	0.94	0.94	1.0	15	43
551	25	1.16	1.74	1.5	15	94
551	25	1.30	1.30	1.0	15	94
401	25	1.16	1.74	1.5	15	46
397	25	1.30	1.30	1.0	15	47
551	25	1.40	2.10	1.5	15	94
551	25	1.60	1.60	1.0	15	94
402	25	1.40	2.10	1.5	15	44
399	25	1.60	1.60	1.0	15	45
550	25	0.49	0.74	1.5	30	97
551	25	0.49	0.74	1.5	10	89
550	25	0.51	0.51	1.0	30	96
550	25	0.51	0.51	1.0	10	88
401	25	0.49	0.74	1.5	30	51
397	25	0.49	0.74	1.5	10	37
400	25	0.51	0.51	1.0	30	54
397	25	0.51	0.51	1.0	10	37
550	25	0.49	0.74	1.5	6	82
550	25	0.51	0.51	1.0	6	85
550	25	0.51	0.51	1.0	3	71
400	25	0.49	0.74	1.5	6	28
400	25	0.51	0.51	1.0	6	23
400	25	0.51	0.51	1.0	3	23
300	25	0.54	0.27	0.5	15	16
301	25	0.51	0.51	1.0	15	13
299	25	0.49	0.74	1.5	15	18
300	25	0.47	0.94	2.0	15	18
301	25	0.45	1.13	2.5	15	21
530	25	0.54	0.27	0.5	15	77
544	25	0.54	0.27	0.5	15	76

the reaction conditions is assumed to be that of pure water and is calculated based on the Peng–Robinson–EoS [12].

3. Results and discussion

Sixty-four oxidation experiments were carried out in an isothermal, isobaric tubular reactor to investigate the effect of residence time and concentration of initial TOC and O₂ on TOC conversion. There was no salt plugging during experiments due to the low concentration of Na in the acrylonitrile wastewater as shown in Table 1. Table 2 shows the experimental conditions and results obtained. The reaction conditions ranged from temperatures of 299 to 552 °C, and the residence time from 3 to 30 s, at a fixed pressure of 25 MPa. The reactor volume was varied between 3 and 15 cm³ depending on the residence time. The initial TOC and O₂ concentrations at the reactor inlet ranged from 0.27 to 2.10 mol L⁻¹, with the stoichiometric ratios of O₂ based on the initial TOC concentration ranging from 0.5 to 2.5. TOC conversion obtained ranged from 13 to 97% in various oxidation conditions.

Fig. 2 shows the effect of the O₂ stoichiometric ratio on TOC conversion at a fixed reaction pressure (25 MPa) and TOC concentration of the wastewater storage tank (0.57 mol L⁻¹). The initial TOC and O₂ concentrations at the reactor inlet were varied by changing the flow rates of wastewater and H₂O₂ solution to keep the residence time at a constant value of 15 s. It was found that TOC conversion increased significantly with increasing in reaction temperature [13–16]. However, as can be seen in Fig. 2, the ratio of O₂ does not have a significant effect on TOC conversion compared to the reaction temperature, indicating that the global reaction order for O₂ is almost zero when it exists in excess. Fig. 2 also shows there is little difference in TOC conversion between the reaction temperature of 501 and 549 °C at an O₂ stoichiometric ratio of 0.5. This constant TOC conversion is considered a consequence of oxygen deficiency.

The influence of the residence time on the TOC conversion was considered at a fixed reaction pressure (25 MPa). The residence time was varied by changing the length of reactor or the flow rates of wastewater and H₂O₂ solution. The TOC conversion increased with increasing residence time as shown in Fig. 3, indicating a linear relationship between TOC conversion and residence time in the low TOC conversion region. Fig. 4 shows the effect of initial TOC concentration on TOC conversion at a fixed reaction pressure (25 MPa) and residence time (15 s), whereby the TOC conversion remains unchanged with varying initial TOC concentrations between 0.26

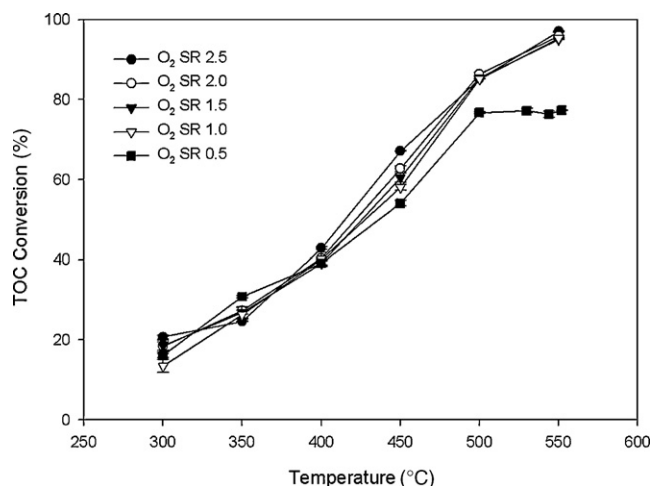


Fig. 2. Effect of reaction temperature on TOC conversion at fixed reaction pressure (25 MPa) and residence time (15 s).

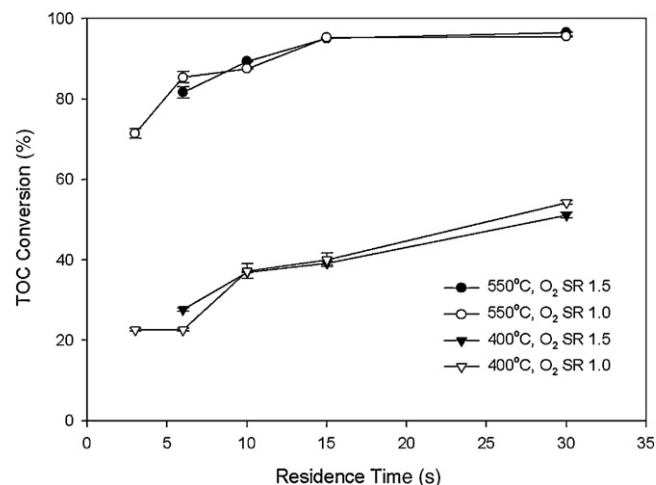


Fig. 3. Effect of residence time on TOC conversion at a fixed reaction pressure (25 MPa).

and 2.10 mol L⁻¹ when other operation variables are kept the same. This is the indication of the fact that the global reaction order for TOC concentration is one, as the decomposition rate of the initial TOC is constant regardless of initial TOC concentration when reaction pressure, reaction temperature, and the O₂ stoichiometric ratio are fixed. Fig. 4 also shows that the stoichiometric ratio of O₂ does not have a significant effect on TOC conversion compared to the reaction temperature shown in Fig. 2.

In order to develop a reliable reaction rate expression, only 26 experimental data points were considered, obtained at supercritical conditions in case the O₂ concentration was above the stoichiometric ratio of 1.5. These experiments were designed to evaluate the effect of wastewater and O₂ concentration on the organic disappearance rate. Usually water is a reactant in SCWO process and its concentration affects the reaction rate constant. However, the reaction order for water was considered zero in the point of view that the reaction medium always consisted of more than 99% of water and its impact on the TOC disappearance rate was to be avoided. So the global reaction rate can be described as follows:

$$-\frac{d[\text{TOC}]_t}{d\tau} = A \exp\left(\frac{-E_a}{RT}\right) [\text{TOC}]_t^a [\text{O}_2]^b \quad (4)$$

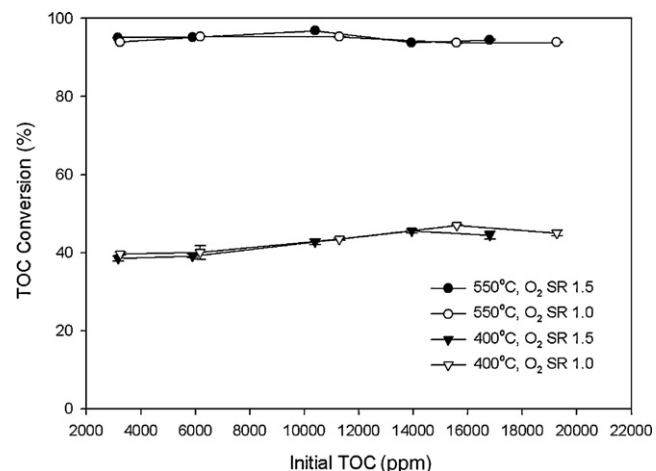


Fig. 4. Effect of initial TOC concentration at the reactor inlet on TOC conversion at a fixed reaction pressure (25 MPa) and residence time (15 s).

where $[\text{TOC}]_t$ is the residual TOC concentration of the liquid product after reaction (mol L^{-1}), $[\text{O}_2]$ the oxygen concentration (mol L^{-1}), τ the residence time in reactor, and a and b are the reaction orders of $[\text{TOC}]_t$ and $[\text{O}_2]$, respectively. E_a and A represent the activation energy and the pre-exponential factor for the reaction. Rearranging Eq. (4) with respect to the TOC conversion, X , defined by Eq. (1), the relationship obtained is

$$-\frac{d(1-X)}{d\tau} = A \exp\left(\frac{-E_a}{RT}\right) [\text{TOC}]_0^{a-1} (1-X)^a [\text{O}_2]^b \quad (5)$$

As shown in Figs. 2 and 4, changes in O_2 concentration and initial TOC concentration throughout the experiment have little effect on TOC conversion. Therefore, the global reaction rate can be considered a pseudo-first-order reaction with respect to the initial TOC concentration, assuming a zero-order for the O_2 concentration. Since all of the experiments were carried out at short residence times, between 3 and 30 s, the method of initial rates can be used. If Eq. (5) is rearranged with respect to the TOC conversion, X , using the initial condition of $X=0$ at residence time $\tau=0$, it can be solved analytically to provide the following equation:

$$X = 1 - \exp\left[-A\tau \exp\left(\frac{-E_a}{RT}\right)\right] \quad (6)$$

Fig. 5 shows the assumed first-order Arrhenius plot for acrylonitrile wastewater in supercritical water oxidation. Using a non-linear regression analysis, the best-fit values were calculated by minimizing the sum of the squared differences of the experimental and the predicted conversion for all data points. This provided estimates of a global activation energy of $53.48(\pm 33.57) \text{ kJ mol}^{-1}$ and a pre-exponential factor of $5.22(\pm 1.74) \times 10^2 \text{ s}^{-1}$ to a 95% confidence level. The resulting pseudo-first-order reaction rate predicted is

$$-\frac{d[\text{TOC}]_t}{d\tau} = 5.22(\pm 1.74) \times 10^2 \text{ s}^{-1} \exp\left[\frac{-53.48(\pm 33.57) \text{ kJ mol}^{-1}}{RT}\right] [\text{TOC}]_t \quad (7)$$

Conversely, the global reaction rate can differ from first-order for the initial TOC concentration and zero-order for the oxygen concentration. If the method of initial rates is applied to Eq. (5), with the initial condition $X=0$ at residence time $\tau=0$, it can be solved analytically to provide the following equation:

$$X = 1 - \left[1 - (1-a)A\tau \exp\left(\frac{-E_a}{RT}\right) [\text{TOC}]_0^{a-1} [\text{O}_2]^b\right]^{1/(1-a)} \quad (8)$$

A non-linear regression analysis was used to fit a , A , E_a , and b . The best-fit values were obtained by minimizing the sum of the squared

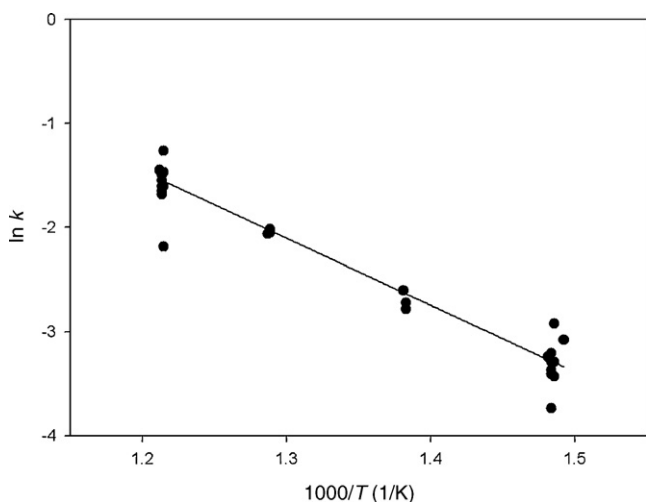


Fig. 5. Assumed first-order Arrhenius plot for acrylonitrile wastewater in supercritical water oxidation.

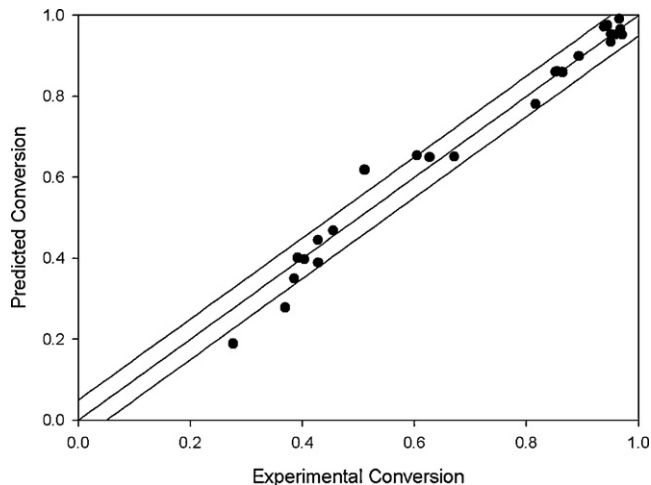


Fig. 6. Parity plot for the comparison of the experimental and the predicted conversion.

differences of the experimental and predicted conversions leading to reaction orders of $a = 1.26 \pm 0.15$ for the initial TOC concentration and $b = 0.00 \pm 0.15$ for the O_2 concentration. The values of the Arrhenius parameters, A and E_a , are $6.07(\pm 6.89) \times 10^3 \text{ mol}^{-0.26} \text{ s}^{-1}$ and $66.33 \pm 5.87 \text{ kJ mol}^{-1}$, respectively. The confidence level reported is 95%. The resulting rate expression for the oxidation of acrylonitrile wastewater is as follows:

$$-\frac{d[\text{TOC}]_t}{d\tau} = 6.07(\pm 6.89) \times 10^3 \text{ mol}^{-0.26} \text{ s}^{-1} \exp\left[\frac{-66.33(\pm 5.87) \text{ kJ mol}^{-1}}{RT}\right] \times [\text{TOC}]_t^{1.26 \pm 0.15} [\text{O}_2]^{0.00 \pm 0.15} \quad (9)$$

Fig. 6 shows a parity plot for the comparison of the experimental and the predicted conversions. The dashed lines indicate a deviation of $\pm 5\%$ conversion from the perfect match. This model fits the experimental data reasonably well.

4. Conclusion

Supercritical water oxidation was demonstrated as an effective treatment for acrylonitrile wastewater which is difficult to biodegrade. A TOC conversion greater than 97% was obtained within 15 s at a temperature of 552°C . A detailed study of the decomposition of acrylonitrile wastewater to evaluate the effect of experimental variables on TOC conversion revealed the correlation of TOC conversion with reaction temperature and residence time. Conversely, the initial TOC concentration and the oxygen stoichiometric ratio did not significantly influence TOC conversion.

Assuming the reaction rate is first-order for the initial TOC concentration and zero-order for oxygen, the estimated activation energy is $53.48(\pm 33.57) \text{ kJ mol}^{-1}$, and the pre-exponential factor is $5.22(\pm 1.74) \times 10^2 \text{ s}^{-1}$ to a 95% confidence level. By considering the dependence of the reaction rate on the TOC and O_2 concentration, a non-linear regression analysis led to $6.07(\pm 6.89) \times 10^3 \text{ mol}^{-0.26} \text{ s}^{-1}$ for the pre-exponential factor, $66.33 \pm 5.87 \text{ kJ mol}^{-1}$ for the activation energy, $1.26(\pm 0.15)$ for the reaction order of the initial TOC concentration, and $0.00(\pm 0.15)$ for the reaction order of the oxygen concentration.

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