Decomposition of aniline in supercritical water

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Abstract

The decomposition of aniline in supercritical water (SCW) was studied. Experiments were performed at various temperatures, pressures, residence times, dosage of oxidant H_2O_2 and initial aniline concentrations to investigate their effect on the destruction efficiency. Manganous sulfate and ferrous sulfate were screened out during the experiment to study the effect of the homogenous catalysts on destruction efficiency. The effect of pH was also studied. The experiments showed that the dosage of oxidant H_2O_2, experimental temperature, pressure, reaction residence time and even initial concentration of the aniline in wastewater have a significant affect on the TOC removal; manganous sulfate and ferrous sulfate improve the oxidation; TOC removal improves slightly with a decrease in the initial pH value. At a system temperature 450 °C, pressure 28 MPa, initial pH 4.0, residence time 46 s and K value 1.1, TOC removal can reach 100%. © 2002 Elsevier Science B.V. All rights reserved

Keywords: Aniline; Supercritical water; Oxidation; Catalysis oxidation; Hydrogen peroxide

1. Introduction

Aniline is a poisonous compound, which is used widely in the chemical industry as the raw material in the manufacture of dyes, rubbers, pharmaceutical preparation, plastic and paint. The amount of aniline produced in China is over 80,000 t per year. There are more than 150 kinds of down-stream products of aniline. The analogs of aniline are environmental priority control pollutants, which are strictly controlled in industrial drainage. Aniline and most of its derivatives are difficult to biodegrade [1]. They are not decomposed completely by the activated sludge process, and they inhibit the biodegradation of the other chemicals. Traditionally, aniline wastewater is treated by using photodecomposition [2,3], electrolysis [4], resin adsorption [5], oxidation by ozone [6], biodegradation [1,7,8] and some other processes. These processes can decompose or remove aniline in wastewater to some extent, but aniline is very difficult to decompose completely. Aniline may form some intermediate

Nomenclature

D	destruction efficiency of aniline
K	dose ratio of actual added to stoichiometric H_2O_2
P	pressure of reaction
t	residence time of reaction
T	temperature of reaction
TOC	total organic carbon concentration of aniline-containing wastewater
$[TOC]_e$	TOC value of aniline detected in effluent
$[TOC]_i$	TOC value of aniline in influent

products such as *p*-methyl phenol and carboxyl acid. [2]. The question then is how can aniline be decomposed completely? In this study, the oxidation behavior of aniline with supercritical water oxidation (SCWO) process was studied.

SCWO technology is a novel waste treatment process developed since 1980. The SCWO process takes advantage of the fact that above the critical point of water (374 °C and 22.1 MPa), organic compounds as well as oxidants such as oxygen, air and hydrogen peroxide are completely miscible with water due to the static dielectric constant of supercritical water (SCW) corresponding to those of apolar organic liquids like *n*-hexane, and consequently there is no possibility of interface mass transfer limiting the reaction rate. On the basis of these solvating characteristics of SCW, the oxidation of organic compounds is expected to proceed rapidly in a single oxygen-rich phase [9]. Since the oxidation temperature is much lower than in incineration, oxides of nitrogen such as NO and NO_2 are not formed. The high destruction efficiency of a number of hazardous organic compounds in SCW has been demonstrated [10–19]. In these studies, oxygen played a dominant role as the oxidant. Generally, these SCWO processes have utilized a high temperature that can be decreased by changing the oxidant. As a result, there will be a reduction in energy usage as well as yielding a more favorable choice of material for the reactors.

Some researchers have compared the efficiencies of hydrogen peroxide and oxygen as the oxidant for the destruction of 3-chlorobiphenyl under SCW condition in the range of 473–723 K using a batch-reactor system. The results showed that the conversion utilizing hydrogen peroxide was significantly higher than that utilizing oxygen; the highest conversion using hydrogen peroxide was greater than 99.999%, while the conversion using oxygen was only 14.3% under the same chosen conditions [20]. Thus, hydrogen peroxide was chosen in our work to study the affects of variables such as temperature, pressure and residence time on the TOC removal from aniline. The effects of some homogeneous catalysts on the destruction of aniline were also studied.

2. Experimental

The experiments were conducted in a laboratory-scale continuous-flow SCWO reactor system. The major components of the system were a feed tank, high pressure metering pumps, preheater, sand bath reactor, manometers, thermocouples, cooler, gas–liquid
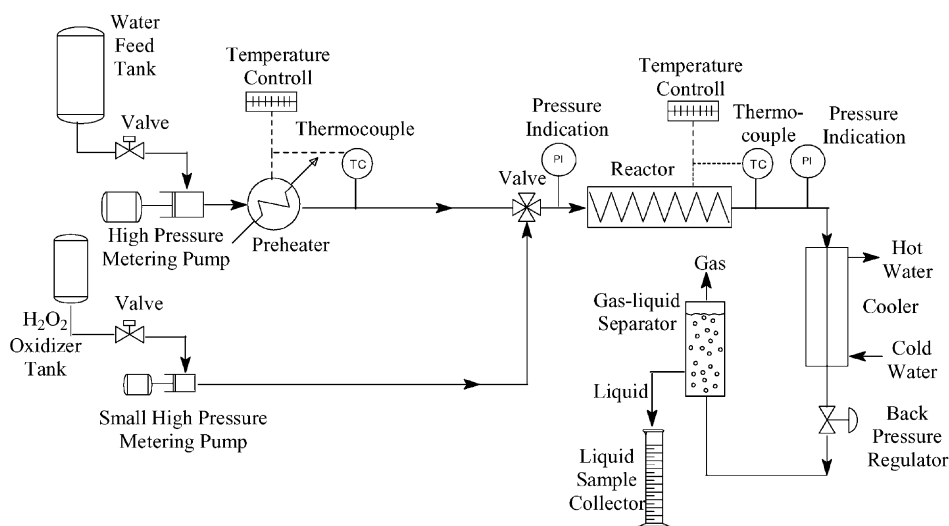
Fig. 1. Schematic diagram of the SCWO experimental apparatus.

separator and back pressure regulator. The internal volume of the reactor was 28 ml. All wetted parts of the system were made of 316 SS. The SCWO apparatus and process are shown in Fig. 1. This equipment has been described in detail previously [21].

In a typical test, the preheater was heated initially to 200 °C, the feed solution of aniline was pumped with a high pressure metering pump through preheater tubing before mixing with oxidant hydrogen peroxide which was pumped with the other small high pressure metering pump to the inlet of the reactor. Then the mixture entered the sand bath reactor, which had been set at a desired temperature. The effluent from the reactor was cooled rapidly in the heat exchanger. Then the cooled products passed into the separator where gaseous and liquid effluents were removed for analysis. The gaseous effluent was exhausted to the atmosphere and the liquid effluent was collected in an external vessel for analysis. The residence time was controlled by adjusting the flow rate with a high pressure metering pump, which was calibrated frequently with water at the test pressure. Two thermocouples were inserted into the center of the preheater and the reactor to provide feedback for the temperature controller. The system pressure was controlled by the back pressure regulator at the end of the system. After running for 20 min to allow the system temperature and pressure to stabilize, a liquid sample was collected at the bottom of the gas–liquid separator and an influent sample drawn from the feed tank. Then, the TOC in the samples was determined using a Shimadzu model 15B TOC analyzer. The TOC removal efficiency (D) was calculated utilizing the following equation:

$$D\,(\%) = \left(\frac{1 - [TOC]_e}{[TOC]_i} \right) \times 100 \tag{1}$$

where the terms $[TOC]_e$ and $[TOC]_i$ are the TOC values of effluent and influent samples, respectively.

3. Results and discussion

3.1. Supercritical water oxidation of aniline

3.1.1. Effect of oxidant dose

Most researchers note that under SCW reaction conditions, organic carbon can be converted to CO_2, hydrogen to H_2O, chlorine to HCl, and nitrogen to N_2 or N_2O [10,22,23]. Based on these finding, the oxidation formulas of aniline in SCW by hydrogen peroxide can be written as:

$$2C_6H_7N + 31H_2O_2 = 12CO_2 + 38H_2O + N_2$$
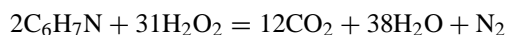
For a given system, the mass or molar concentration of aniline is known. The amount of hydrogen peroxide needed to convert C, H, N into final products can be calculated utilizing the above equation. Calculated are stoichiometric amounts of hydrogen peroxide. In the tests, the dose ratio of actually added to stoichiometric amounts of hydrogen peroxide was defined as K, which represented the level of oxidant added.

As shown in Fig. 2, where the experimental conditions were a temperature $T = 450\,°C$, a pressure $P = 30\,MPa$ and a residence time $t = 100\,s$, the destruction efficiency (D) increased with increasing K values during aniline oxidation in SCW. Especially, for K values less than about 1.1, the D values increased rapidly with increasing K values. Over the range, slightly increased D values with K values were observed. The turning point of the curve in the figure would shift a little with changing experimental conditions.
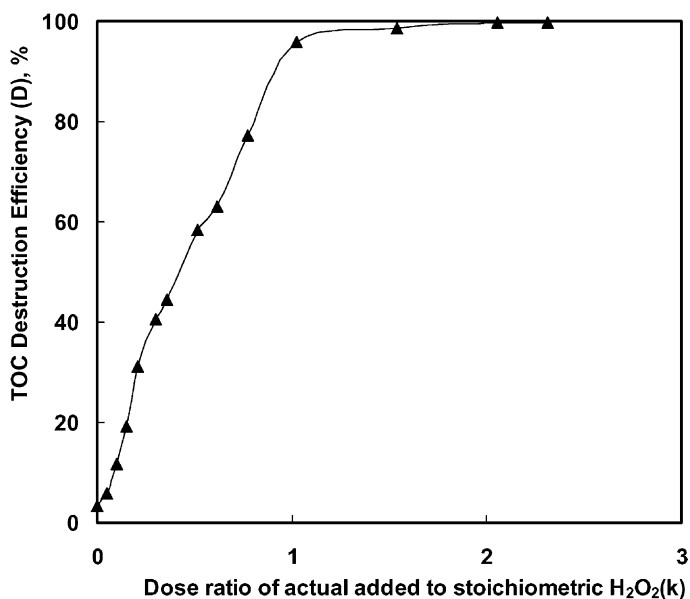

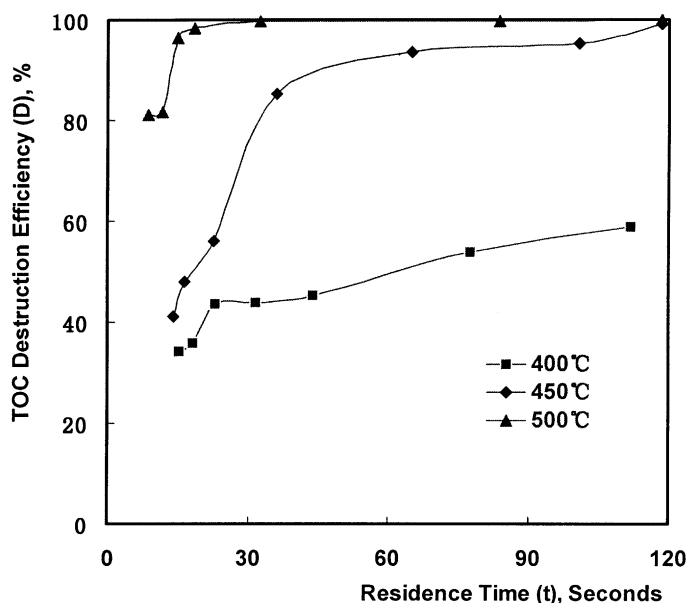Fig. 2. K–D plot for destruction efficiency of aniline ($T = 450\,°C$, $P = 30\,MPa$, $t = 100\,s$).

Fig. 3. The t–D plots for aniline destruction efficiency at different temperatures ($P = 28$ MPa, $K = 1.1$).

3.1.2. Effect of temperature, pressure and residence time

As shown in Fig. 3, where the experimental condition were $P = 28$ MPa and $T = 400$, 450 and 500 °C, respectively. It is obvious that the D values of aniline were increased with increasing T or t, they were increased slightly with increasing t at $T = 400$ °C; and were increased rapidly when $t < 45$ s and then increased slowly with t at $T = 450$ °C; when T increased to 500 °C, the D values also increased rapidly but when $t < 15$ s there was little change.

The variation of D in SCW experimental conditions of $T = 400$ °C, $K = 1.1$ and $T = 450$ °C, $K = 1.1$ at different pressures was plotted against the residence time in Figs. 4 and 5, respectively. It can be seen in Fig. 4 that the t–D plot for both $P = 25$ and 28 MPa overlap, while the t–D plot for $P = 32$ MPa shows higher D values, which illustrates that the variation of pressure has little effect on D under the conditions of $T = 400$ °C, $P < 28$ MPa. But, when P reaches 32 MPa, D values improve remarkably. But in Fig. 5, the t–D plots for $P = 25$, 28 and 32 MPa almost overlap. That is to say, the variation of pressure had little effect on D under the conditions of $T = 450$ °C and even $P = 32$ MPa. The possible reason is as follows.

In general vapor and supercritical state chemical reactions, temperature and pressure are two important factors affecting the reaction rate. In our experiments, increasing temperature could improve reaction rate, so could pressure. But their effects on reaction rate were different. When the temperature is 400 °C and pressure is relatively low (for example, 25–28 MPa), the effect of pressure increasing is minor compared to that of temperature. At 400 °C the pressure was an important factor affecting reaction rate. But pressure increase had little effect on TOC removal of aniline when $T = 450$ °C even at a pressure of 32 MPa
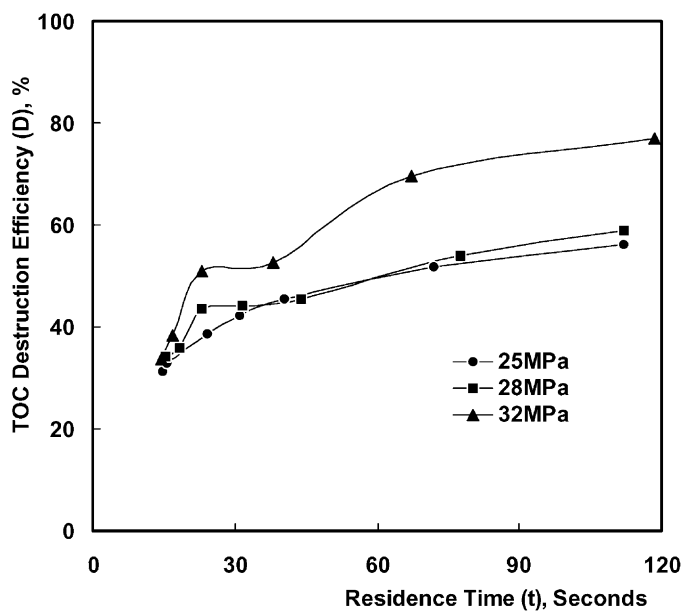
Fig. 4. The *t*–*D* plots for aniline destruction at different pressures ($T = 400\,^\circ$C, $K = 1.1$).
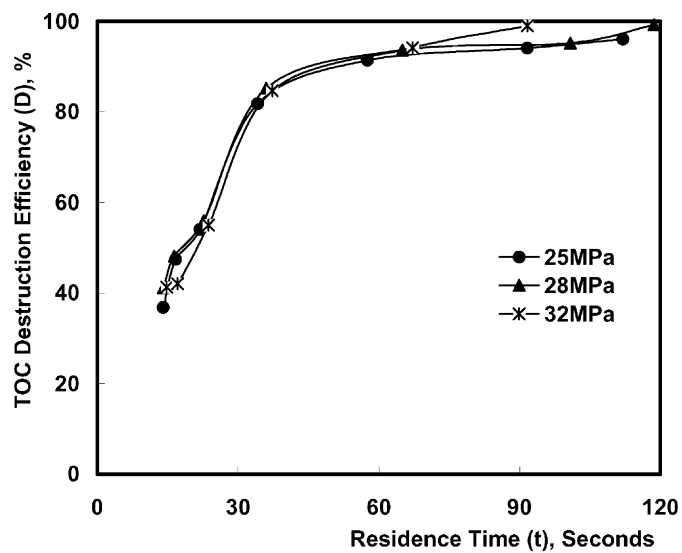

Fig. 5. The *t*–*D* plots for aniline destruction at different pressures ($T = 450\,^\circ$C, $K = 1.1$).

because at this time the effect of pressure increased from 28 to 32 MPa on reaction rate is minor than that of temperature being 450 °C, so when $T = 450$ °C, the t–D plots for $P = 25$, 28 and 32 MPa are almost overlapping. Extending t can also increase D.

By examining Figs. 3 and 4, a marked difference in the D values of aniline as a result of varying system pressure and temperature can be observed. The effect of increasing temperature on the destruction of aniline was more evident than that of a pressure increase. D values of aniline approached 100% when $T = 500$ °C, $t = 30$ s, even if the system pressure was 25 MPa.

3.1.3. Effect of initial TOC concentration

Fig. 6 shows that the effect of initial TOC concentration of aniline wastewater on the destruction efficiencies. It can be seen that D increased with an increasing initial TOC. D was 89.3% when initial TOC was 427.2 mg/l and D was 98.2% when initial TOC reached 4900 mg/l. One could conclude that there is a wide TOC range for the oxidation of aniline by using SCWO process and the higher the initial TOC, the higher the D value.

3.2. Homogeneous catalytic supercritical water oxidation of aniline

3.2.1. Alternative catalysts

Catalysts have been widely used in wet air oxidation. Photodegradation oxidation and electrolytic oxidation have been effective.

Some metallic salts such as manganous sulfate, ferrous sulfate and cuprous nitrate were chosen as catalysts. The concentration of catalyst was 5 mg/l based on metallic ion concentration. The effect of catalysts on aniline removal efficiencies is shown in Figs. 7 and 8.
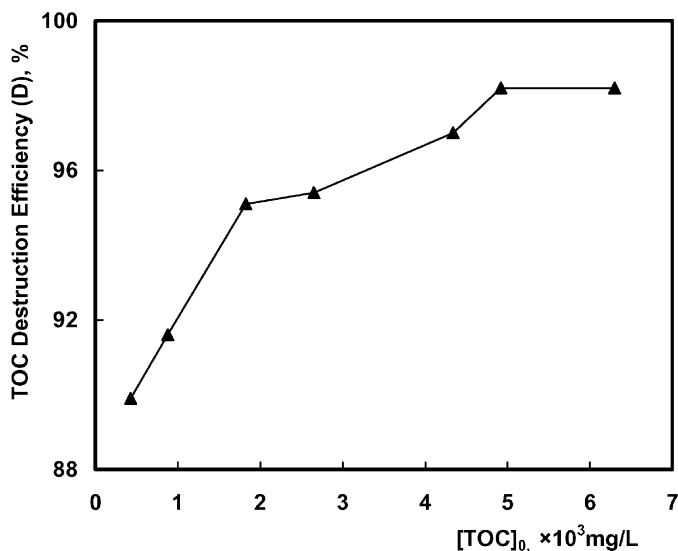

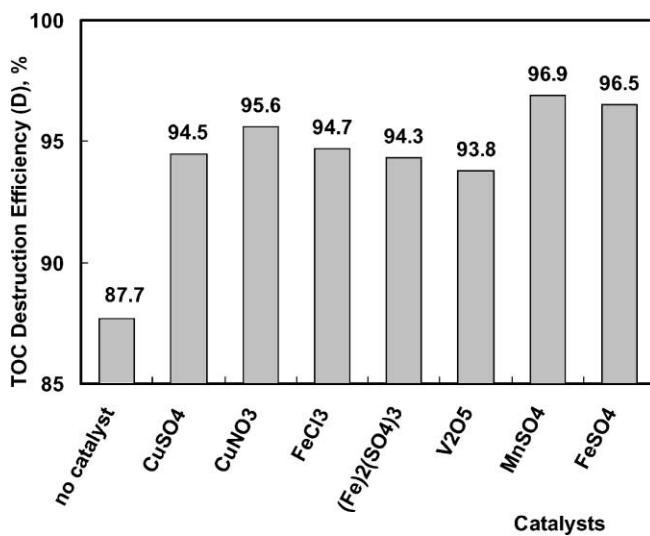Fig. 6. Effect of initial aniline concentration on the D values ($T = 400$ °C, $P = 30$ MPa, $t = 67.2$ s).

Fig. 7. Effect of different catalysts on the oxidation of aniline ($T = 450\,^{\circ}$C, $P = 28\,$MPa, $t = 26.9\,$s, pH 4.0).

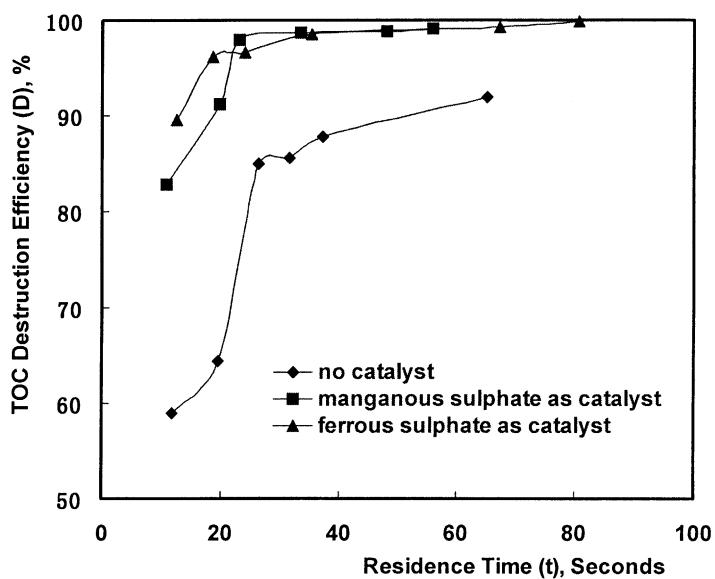
Fig. 8. Comparison between catalyzed and non-catalyzed SCWO process ($T = 450\,^{\circ}$C, $P = 28\,$MPa, $K = 1.1$).
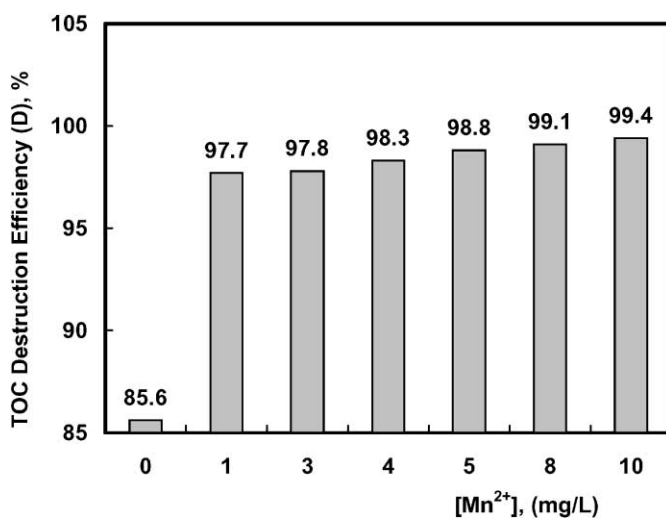
Fig. 9. Effect of concentration of Mn^{2+} on the oxidation of aniline.

Of the catalysts used in prior experiments for aniline oxidations, manganous sulfate and ferrous sulfate were best. Consequently we used both in our work.
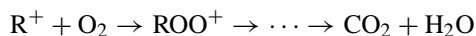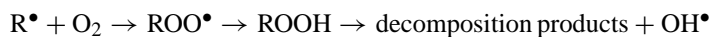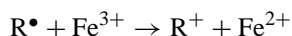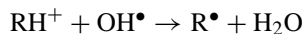
3.2.2. Effect of catalyst dose

The experimental conditions were $T = 450\,°C$, $P = 28\,MPa$, $K = 1.1$, $t = 30\,s$; only the catalyst dose was changed. Experimental results are shown in Figs. 9 and 10. TOC destruction efficiencies of aniline increased slightly with increasing catalyst dose when the catalyst concentrations were greater than 1 mg/l.

The catalysis oxidation mechanism can be interpreted as below (using ferrous sulfate as an example) [24]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \tag{2}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+ \tag{3}$$

The reaction speed of reaction (2) is very fast while reaction (3) is very slow. Fe^{2+} ion formed during reaction (3) reacts with hydrogen peroxide and forms hydroxyl radical ($OH^\bullet$) immediately. The $OH^\bullet$ radical has much stronger oxidation effect than the $HO_2^\bullet$ radical has, and it can oxidize most organic chemicals to carbon dioxide and water and then reduce TOC.

$$RH^+ + OH^\bullet \rightarrow R^\bullet + H_2O$$

$$R^\bullet + Fe^{3+} \rightarrow R^+ + Fe^{2+}$$

$$R^\bullet + O_2 \rightarrow ROO^\bullet \rightarrow ROOH \rightarrow \text{decomposition products} + OH^\bullet$$

$$R^+ + O_2 \rightarrow ROO^+ \rightarrow \cdots \rightarrow CO_2 + H_2O$$
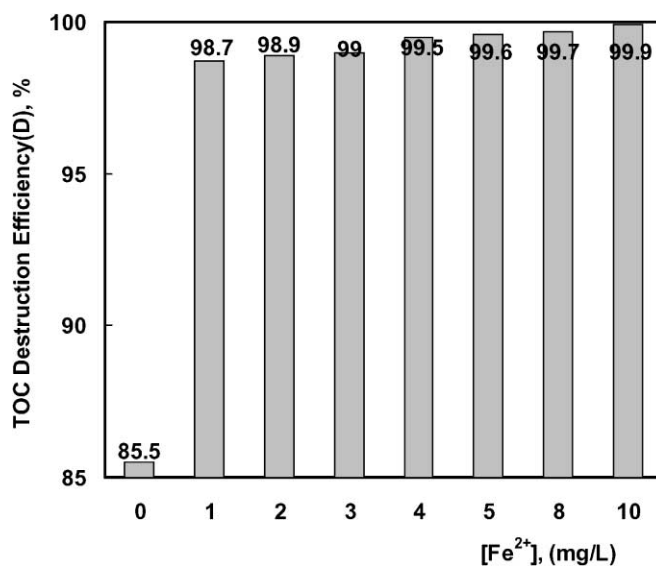
Fig. 10. Effect of concentration of Fe^{2+} on the oxidation of aniline.

3.2.3. Effect of initial pH

In a typical wet air oxidation process, the pH value of wastewater has a significant impact on the stability of oxidant hydrogen peroxide. OH^- ions in alkaline solutions can capture $OH^{\bullet}$ radicals produced by the destruction of hydrogen peroxide and reduce the
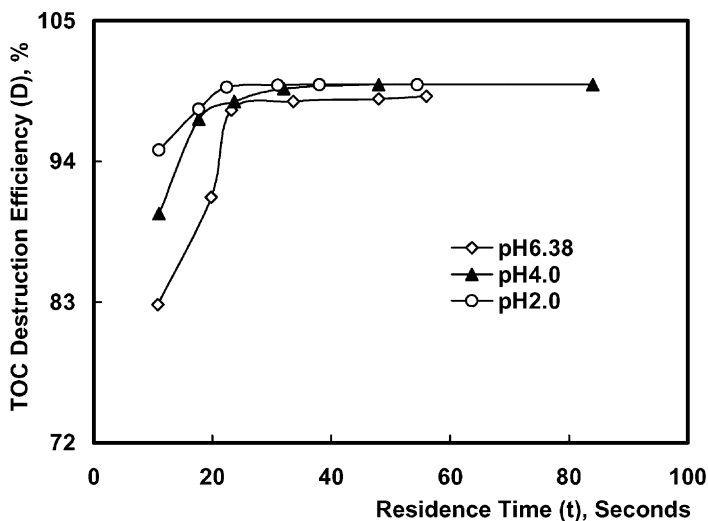

Fig. 11. Mn^{2+} as catalyst; effect of solution pH on the decomposition of aniline in ($T = 450\,^{\circ}C$, $P = 28\,MPa$, $K = 1.1$).

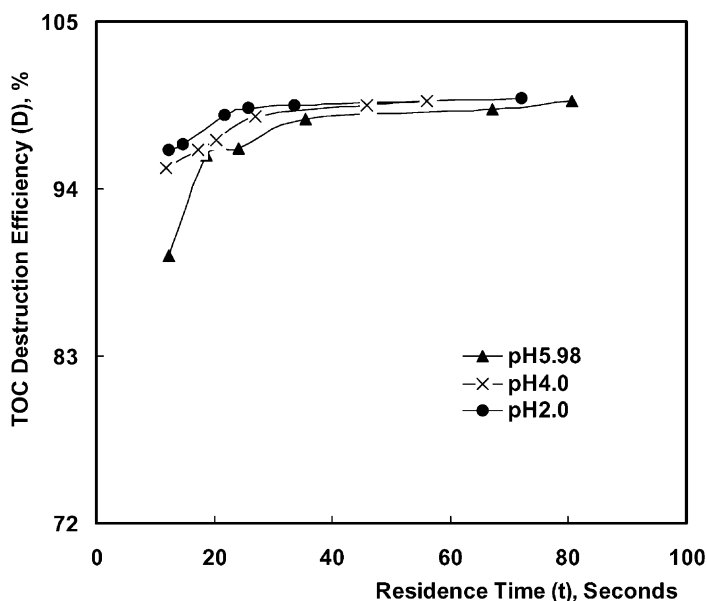Fig. 12. Fe^{2+} as catalyst; effect of solution pH on the decomposition of aniline in ($T = 450\,°C$, $P = 28\,MPa$, $K = 1.1$).

oxidation reaction rate [25]. Therefore, the experiments were conducted in an acid medium; other experimental conditions were $T = 450\,°C$, $P = 28\,MPa$, $K = 1.1$ and catalysts concentration 5 mg/l. As shown in Figs. 11 and 12, D values are a function of pH when t was short, but when t was greater than 22 s, the effect of pH on D was not significant.

4. Conclusions

The SCWO process has been shown to be efficient for achieving a high degree of aniline decomposition. The destruction efficiencies of TOC of aniline wastewater increased with increasing temperature, residence time and initial aniline concentration; consequently, we conclude the SCWO process is suitable for treating high concentration aniline wastewater. Increasing pressure could also increase TOC destruction efficiencies to some degree. The dosage of the oxidant H_2O_2 had an optimum value $K = 1.1$. Homogeneous catalysts ferrous sulfate and manganous sulfate increased the destruction efficiencies of aniline although increasing their concentrations have little effect on the destruction efficiencies. Changing pH value also has little effect on the destruction efficiencies at the range of pH values studied.

Acknowledgements

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