

COD REMOVAL EFFICIENCY OF AROMATIC COMPOUNDS IN SUPERCRITICAL WATER

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ABSTRACT

Phenol, aniline and nitrobenzene were oxidized in supercritical water. It was found that the chemical oxygen demand (COD) removal efficiency of the organic compounds could be achieved 90% in short resident time at high enough temperature. Increasing temperature, pressure and residence time, the COD removal efficiency of the organic compounds increases. It was found that temperature and resident time offer greater influence than pressure. The difficulty of oxidizing three compounds was in the order: nitrobenzene > aniline > phenol. Aniline and nitrobenzene were difficult to be oxidized to CO₂ and H₂O when the temperature was less than 873.15K and 923.15K respectively. Only at the temperature of more than 873.15K and 923.15K, did the COD removal efficiency of aniline and nitrobenzene can be achieved 90%.

Keywords: Phenol, Aniline, Nitrobenzene, Supercritical Water, Oxidation, COD, Organic Compounds

1. INTRODUCTION

Oxidation in supercritical water (SCWO) is a technology being developed as an economically viable and ecologically safe ultimate destruction technology to treat aqueous waste streams containing 1 to 20 % organic compounds by weight. The SCWO process involves the reaction of organic compounds and oxygen in an aqueous phase at conditions that exceed the critical temperature and pressure of water ($T_c=374.2$ °C, $P_c=218$ atm). Operating at supercritical conditions leads to a homogeneous reaction mixture in which organic compounds, water, and oxygen can exist in a single phase^{1,2}). Under these reaction conditions, organic carbon can be converted to CO₂, hydrogen to H₂O, chlorine to HCl, and nitrogen to N₂ or N₂O. As such, supercritical water can sustain a highly efficient oxidizing environment.

The concept of applying SCWO for wastewater treatment appears to have been first disclosed in the late 1970s³). SCWO research and development activities accelerated in the mid.1980s. Although the early SCWO work demonstrated that high destruction efficiency could be achieved for a wide range of organic pollutants⁴), limited kinetic as well as mechanistic data have become available. Furthermore, most kinetic or mechanistic studies have dealt with simple hydrocarbon or oxygenated hydrocarbons^{5, 6}).

Since many organic pollutants contain heteroatoms- such as nitrogen, halogens, sulfur, and phosphorous the presence of heteroatoms can influence the physical characteristics of SCWO processes. Understanding the role of heteroatoms in the reaction mechanisms can prevent the formation of unwanted by-products and maximize process efficiencies. Therefore, the knowledge of SCWO reaction pathways as well as kinetics for heteroatom-containing organic compounds is of critical design importance. However, little has been reported about reactions of nitrogen-containing organic compounds in supercritical water.

The major concerns of this study are the COD removal efficiency of nitrogen-containing organic compounds which are often found in dye and medicine industry. Because of the difficulty of removing heterocyclic nitrogen, experiments were conducted by examining the reactivities of phenol, aniline and nitrobenzene.

2. EXPERIMENTAL

The test apparatus used in this study was a laboratory-scale, continuous-flow SCWO reactor system, as shown in **Figure 1**. The major components of the system comprised two feed tank 3 and 4, double suction feed pump 5, preheater 6 (influent heat exchanger), coiled-

tube reactor 7, mixer 8, condenser 9 (effluent heat exchanger), gas-liquid separator 10 and sample collector 11.

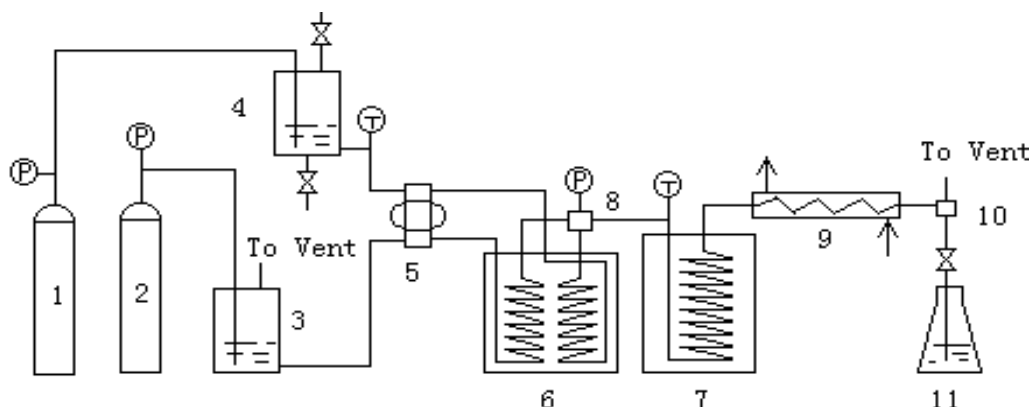


Figure 1 Schematic diagram of SCWO reactor system.

Oxygen was used as the oxidant and was supplied from oxygen cylinder 1. The oxidant solution (feed solution) was prepared by dissolving oxygen into deionized water in feed tank 4. Pressure of oxygen in feed tank 4 was controlled at 9 ~ 13 MPa. The dissolved oxygen concentration in the feed solution was determined by Henry Law. The derivation of oxygen concentration is within 10 %.

A aqueous solution of organic compounds was prepared from distilled/ deionized water and was added into the feed tank 3. Organics aqueous solution was purged with nitrogen gas from N₂ cylinder 2 prior to each experiment to reduce the amount of dissolved oxygen. Double piston high-pressure metering pump 5 was used to pressurize the feed streams (organics solution and oxidant solution). The pressured feed streams were preheated by flowing through coiled tube immersed in a temperature-controlled, isothermal electric heater 6. The preheated feed streams then flowed into a cross at the inlet of reactor 7 and were mixed there. The isothermal, plug flow reactor was made of a length of 3.7 m, 8-mm.-o.d. × 1.5 stainless steel (1Cr18Ni9Ti) tubing and submerged in a temperature-controlled, isothermal electric heater. After passing through the reactor, the reactor effluent was cooled and depressurized in condenser, which was cooled by drain water.

The cooled and low pressure effluent then flowed into a gas-liquid separator. The gaseous effluent was removed from the top of the separator and directed to vent. The liquid effluent flowed from the separator into a container for disposal. Liquid effluent samples were collected in sample collector.

We oxidized phenol or aniline or nitrobenzene at temperatures of 525 to 700 °C and pressures of 20 and 28 MPa in the plug flow reactor. Residence time in the reactor ranged from 6 to 40 s. The COD of effluent and influent was analysed by potassium dichromate method. The concentration of organic compounds is 2.351×10^{-3} mol/L.

3. RESULTS AND DISCUSSION

3.1 Influence of residence time on the COD removal efficiency

Figures 2 ~ 4 exhibit the influence of residence time in reactor on the COD removal efficiency of phenol, aniline and nitrobenzene at different temperatures. The COD removal efficiency of phenol, aniline and nitrobenzene increases and tends a constant value with increasing residence time in reactor. The higher temperature, the higher the constant values. At high temperature, the COD removal efficiency reaches the constant value quickly because high temperature is advantageous to the reaction rate. It can be supposed that aniline and nitrobenzene could not be decomposed completely in supercritical water at temperature of lower than 873.15 and 923.15 K respectively. The COD removal efficiency of more than 90% could be achieved in phenol, aniline and nitrobenzene oxidation within half minute at temperature of 873.15, 948.14 and 973.15 K respectively. This indicates that high COD removal efficiency can be obtained by SCWO at high enough temperature.

Although the COD removal efficiency increases with increasing

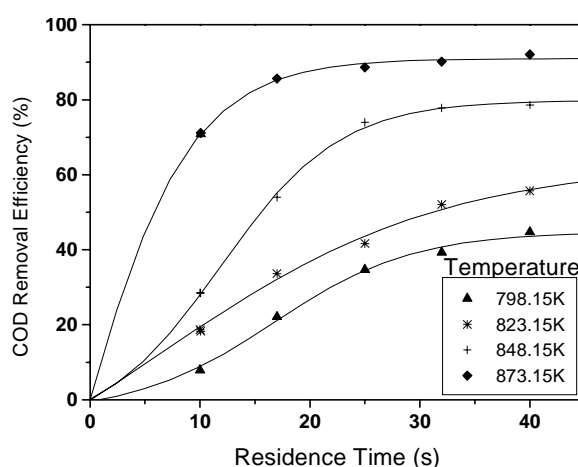


Figure 2 Influence of residence time on COD removal efficiency of phenol oxidation

($P=25\text{MPa}$, $E_{O_2}=300\%$, $C_A=2.351 \times 10^{-4}\text{mol/L}$).

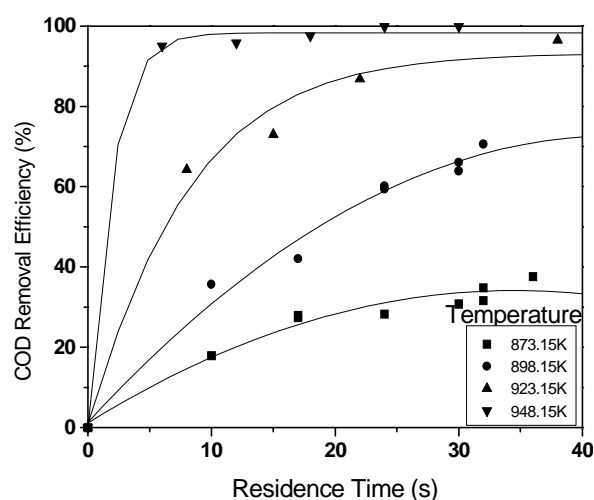


Figure 3 Influence of residence time on COD removal efficiency of aniline oxidation

($P=25\text{MPa}$, $E_{O_2}=300\%$, $C_A=2.351 \times 10^{-4}\text{mol/L}$).

temperature, phenol, aniline and nitrobenzene have different reactivities, and different COD removal efficiency can be obtained at the same temperatures in phenol, aniline and nitrobenzene oxidation. For example, the COD removal efficiency of more than 90 % could be achieved in phenol oxidation in residence time of half minute at temperature of 873.15 K, but the COD removal efficiency of only 30 and 15 %

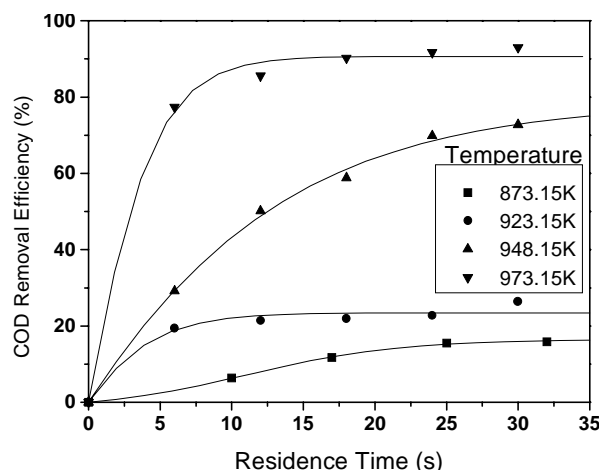


Figure 4 Influence of residence time on COD removal efficiency of nitrobenzene oxidation (P=25MPa, E_{o2}=300%, C_A=2.351 × 10⁻⁴mol/L).

could be obtained for aniline and nitrobenzene at the same temperature and residence time, respectively. Phenol was easy to be decomposed and nitrobenzene hard to be oxidized. Based on the analysis results of GC-MS, some transition products were identified in the oxidation reaction. The main intermediates formed in aniline oxidation are azobenzene and phenazine. Gopalan⁷⁾ reported that the main transition products in phenol oxidation in supercritical water were dimer, single-ring, ring-opening and gaseous products as well as a trace amount of dibenzofuran. Because of difficulty of oxidizing these transition products, the formation of transition products offers great influence on the COD removal efficiency. Low COD removal efficiency of aniline and nitrobenzene obtained at low temperature can be attributed to the formation of transition products which are difficult to be oxidized. **Table 1** displays the difference between the COD removal efficiency and conversion of phenol and aniline based on the initial concentration. Although most phenol and aniline were decomposed and conversion of more than 90% was obtained, the COD removal efficiency is low. This indicates that organic compounds such as phenol and aniline are firstly converted into some transition products, and then into CO₂ and H₂O. Therefore, the differences of reactivity reflect the difficulty of oxidizing transition products in SCWO of organic compounds.

Table 1 the COD removal efficiency and conversion of phenol and aniline in SCWO

Organics	Temperature T (K)	Pressure P (MPa)	Residence time RT (s)	Excess O ₂ E _{o2} (-)	Removal efficiency (RE) %	
					COD RE Conversion, X(%)	
phenol	773.15	25	10	300	COD RE Conversion, X(%)	<10 95.83
Aniline	723.15	25	24	300	COD RE Conversion, X(%)	<30 91.01

3.2 Effect of temperature on the COD removal efficiency

The effect of reaction temperature on the COD removal efficiency of phenol, aniline and nitrobenzene in supercritical water is shown in **Figure 5 - 7**. The COD removal efficiency of phenol, aniline and nitrobenzene in supercritical water increases with increasing the temperature under fixed other conditions. The COD removal efficiency of phenol, aniline and nitrobenzene increases fast when residence time is shorter than 18 seconds. This is due to increasing the temperature is advantageous to the reaction of great activation energy. However, when residence time exceeds 18 s, the COD removal efficiency of aniline and nitrobenzene increases slowly with increasing the temperature because of the formation of some transition products, which is difficult to be oxidized. Therefore it is difficult to obtain high COD removal efficiency at low temperature. If the oxidation of organic compounds were conducted at higher temperature, the COD removal efficiency is high.

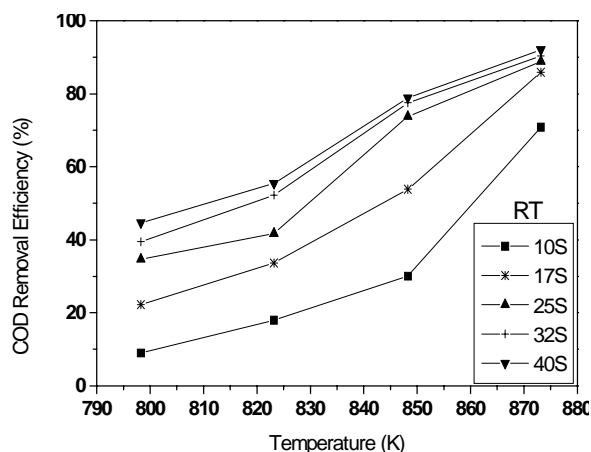


Figure 5 Relationship between temperature and COD removal efficiency

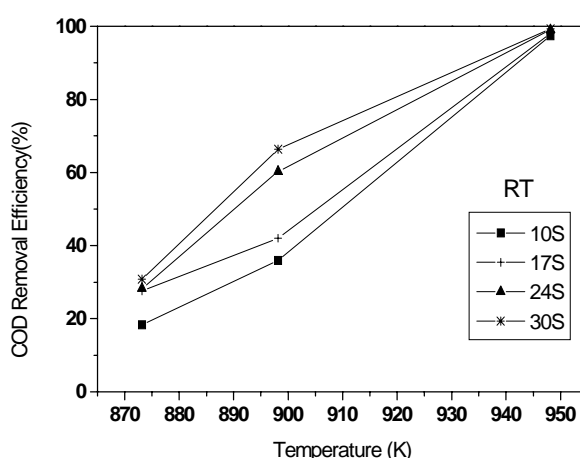


Figure 6 Relationship between temperature and COD removal efficiency

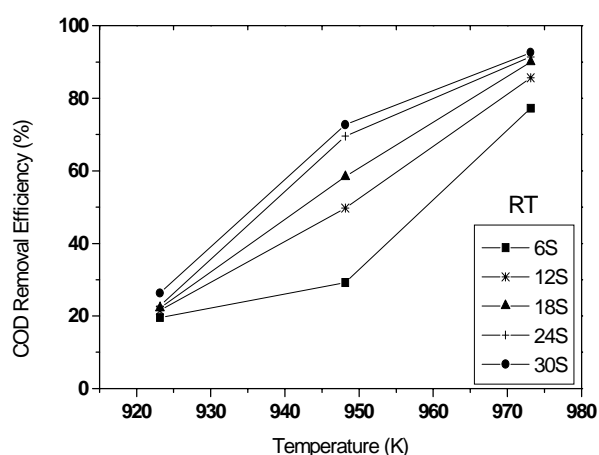


Figure 7 Relationship between temperature and COD removal efficiency

3.3 Effect of pressure on the COD removal efficiency

The effect of pressure on the COD removal efficiency of phenol, aniline and nitrobenzene in supercritical water is illustrated in **Figure 8**. Increasing pressure will increase

the COD removal efficiency because increasing pressure increases the density of water and increases the concentration. The COD removal efficiency increases slowly with increasing pressure at pressure of 20 – 22 MPa, which is lower than the critical pressure. The aqueous organic solutions were under gas-liquid Equilibrium State and the water density changes little with increasing pressure. This

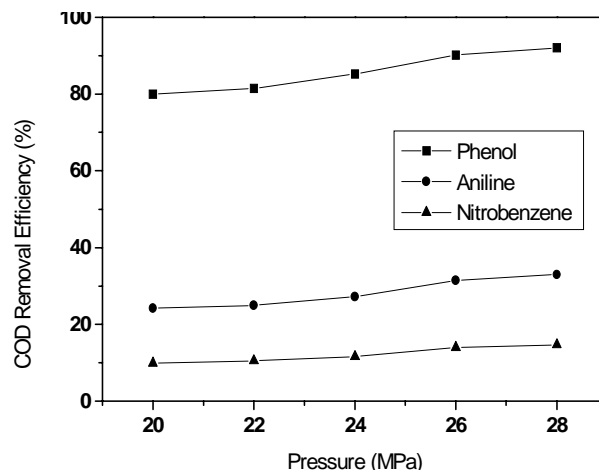


Figure 8 Effect of pressure on the COD removal efficiency ($E_{O_2}=300\%$, $t=20$ s, $T=873.15$ K, $C_A=2.351 \times 10^{-4}$ mol/L).

is why the COD removal efficiency increases slowly with increasing pressure. When experiment condition exceeds the critical condition, the COD removal efficiency increases fast with increasing pressure. The COD removal efficiency of phenol reached 90 % when the pressure is 24 MPa. However, the COD removal efficiency increases slowly again when the pressure is over 26 MPa. This is because aniline and nitrobenzene were converted into some transition products, which were difficult to be oxidized at temperature of 873.15 K. Although the COD removal efficiency increases with increasing pressure, it has weak dependence on pressure comparing the other factors.

4. CONCLUSION

Aromatic compounds such as phenol, aniline and nitrobenzene were oxidized in supercritical water. It can be found that the COD removal efficiency in supercritical water oxidation is over 90 % in half minute. Among phenol, aniline and nitrobenzene, nitrobenzene is most difficult to be decomposed under given conditions, and phenol the easiest. Aniline and nitrobenzene can not be oxidized completely when temperature is below 873.15 and 923.15 K respectively, because of the formation of reaction intermediate products. The COD removal efficiency increases with increasing the reaction temperature, pressure and residence time, but has weak dependence on pressure.

NOMENCLATURE

E_{O_2} = excess oxygen (-)

P = pressure, (Mpa)

T = temperature, (K) or (°C)

X = conversion, (-)

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