



Supercritical Water Oxidation of Phenolic Wastewater with Glycol

GUANG-QIANG MA* and MIN ZOU

Panzhuhua University Institute of Chemical Technology, Panzhuhua 617000, P.R. China

*Corresponding author: Tel/Fax: +86 812 3371021; E-mail: magq3218@163.com

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Phenolic wastewater is a typical kind of industrial effluents containing high toxicity and poor biodegradability. Huge quantities of polluted phenolic waters are formed through several chemical operations which includes coking, coal gasification, oil refineries, plastics, pesticides, steel and phenolic resin production. This paper deals with treatment of high concentrated phenolic wastewater by supercritical water oxidation method. The effects of H₂O₂ dosage, reaction time, temperature and concentration of glycol on removal efficiency of phenol were studied with laboratory bench-scale experiments. The results indicated that the removal process was more effective under the experimental conditions. The best removal efficiency of phenol reached 99.8 %. This investigation will provide fundamental method for developing a pretreatment method of industrial phenolic wastewater with flexibility, simplicity and high activity.

Keywords: Supercritical water oxidation, Phenolic wastewater, Glycol, Removal.

INTRODUCTION

Phenolic wastewater is a typical kind of industrial effluents with high toxicity and poor biodegradability. Huge quantities of phenol-polluted waters are formed from many chemical operations including coking, coal gasification, oil refineries, plastics, pesticides, steel and phenolic resin production^{1,2}. Phenolic compounds and their derivatives are considered preferred controlled pollutants in water since they can pose a severe health hazard as mutagens and carcinogens and cause serious damage to aquatic animals and microorganisms even at low concentrations³⁻⁶. Various species of phenolic pollutants at high concentrations from hundreds to thousands mg/L are identified in the industrial wastewaters especially from heavy chemical or petrochemical industries. Once released into the environment, they may have adverse effects on ecological health and represent a serious environmental problem⁷. Therefore, removal of phenolic compounds from wastewater becomes urgent in the field of practical industrial wastewater treatment.

Traditionally, efficient treatment of phenolic wastewater can be conducted by either conventional physical-chemical^{8,9} or biological techniques¹⁰. However, these treatments are very complex and expensive. This situation is triggering the development of new treatment technologies for phenolic wastewater, especially technologies claiming a small production of additional waste sludge¹¹.

Supercritical water oxidation (SCWO) shows a substantial promise for clean and efficient decontamination of many aqueous

organic wastes¹²⁻¹⁵. supercritical water oxidation can rapidly and efficiently destroy organic substances into H₂O and CO₂ in significantly short residence times.

The ability of an oxygenate additive to enhance the oxidation rate of a targeted organic compound and mixtures is well known in combustion¹⁶, but only recently have several studies showed similar effects in supercritical water oxidation reactions¹⁷⁻¹⁹. In supercritical water oxidation, the oxidation mechanism is assumed to be similar with that involved in combustion and the former process can take advantage of the vast scientific database of the latter.

In this work, the treatment of the phenolic wastewater is performed using hydrogen peroxide as an oxidant in a flow reactor at sub- and supercritical conditions of water. We report experimental oxidation results of the phenolic wastewater *via* supercritical water oxidation and to examine the feasibility of the technology as a pre-treatment for biological remediation to reduce toxic organic compounds. The effects of H₂O₂ dosage, reaction time, temperature and concentration of glycol on removal efficiency of phenol were studied.

EXPERIMENTAL

Characteristics of phenolic wastewater: The phenolic wastewater sample is taken from a gasification plant. The main characteristics are intensive violet-dark brown colour, strong specific offensive smell, a large number of bubbles and high degree of organic pollution. Some relevant indices of water quality are shown in Table-1.

TABLE-1
SOME WATER QUALITY INDICES OF PHENOLIC
WASTEWATER FROM COAL GASIFICATION

Water quality index	Original wastewater
Total phenols (mg/L)	1000
COD _{Cr} (mg/L)	6000
BOD ₅ (mg/L)	120
BOD ₅ /COD _{Cr}	0.02
pH	7.45

Experimental procedure: General set up of the system including the supercritical water oxidation reactor is shown in Fig. 1.

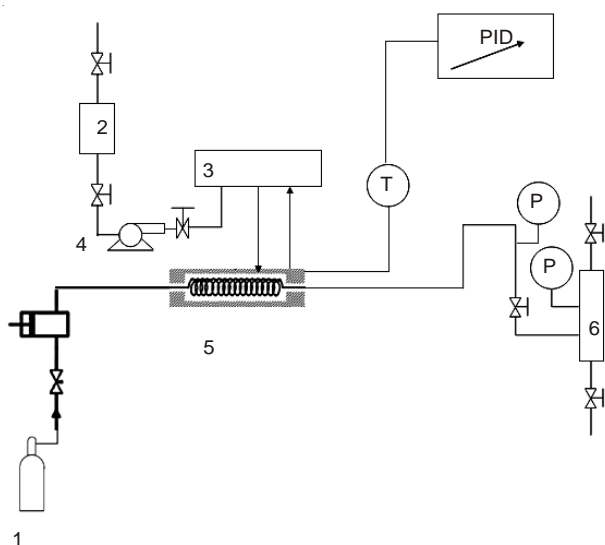


Fig. 1. Schematic diagram of the experimental setup, (1) Nitrogen tank; (2) Oxidant tank; (3) Heater; (4) High pressure pump; (5) Reactor; (6) Gas-liquid separator

Supercritical water oxidation experiments were performed in a continuous-flow reactor system. The oxidant feed stream was prepared by dissolving hydrogen peroxide with deionized water in a feed tank. Another feed tank was loaded with the phenolic wastewater. The two feed streams were pressurized in two different lines using two high-pressure pumps and then they were separately pre-heated, until the reactor temperature had reached the desired value (± 0.1 °C). After pre-heating, two lines were mixed at the reactor inlet using a mixing tee. Upon exiting the reactor, the effluent was cooled rapidly by passing through a heat exchanger. Afterwards the particles, which would be formed presumably, were filtered out by a 0.5 min line filter, before the effluent was depressurized by a back-pressure regulator. The flow rates of the oxidant and wastewater were ranged from 1 to 7 mL/min at pump conditions. The system pressure was maintained at desired pressures (± 0.1 MPa) by the back-pressure regulator. The product stream was then separated into liquid and vapor phases. The liquid products were collected in a graduated cylinder.

RESULTS AND DISCUSSION

Effect of temperature and reaction time on phenol removal: As expected, rising temperature increased the phenol removal (Fig. 2). Phenol removal reached about 82 and 93%

after 1 and 9 min at 445 °C, respectively. Therefore, temperature had a significant impact on the oxidation of phenolic wastewater. The reason is due to the fact that when the temperature increased, the reaction rate accelerated. Eventually, it led to increasing oxidation rates of organic matter degradation of phenolic wastewater.

Fig. 2 showed phenol removal for supercritical water oxidation of phenolic wastewater at different temperatures. The results appeared that reaction time had a significant effect on phenol removal of phenol wastewater. Within each set of isothermal experiments, the phenol removal increased rapidly during the first 1 min of reaction and slowed down afterwards.

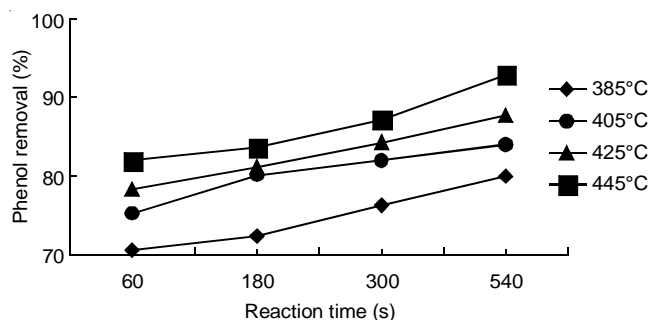


Fig. 2. Effect of temperature and reaction time on phenol removal

Effect of H₂O₂ dosage on phenol removal: Fig. 3 shows that phenol removal is affected by H₂O₂ dosage. The phenol removal increased with increasing H₂O₂ dosage, however, the COD removal increasing trend is gentle when H₂O₂ dosage is over 5000 mg/L, so the optimum H₂O₂ dosage is 5000 mg/L.

The reason is that when H₂O₂ dosage increased, it could be helpful for the formation of strong oxidation species (O₂⁻, HO₂[•], etc.). Therefore, high H₂O₂ dosage can accelerate the oxidation of the organic pollutant.

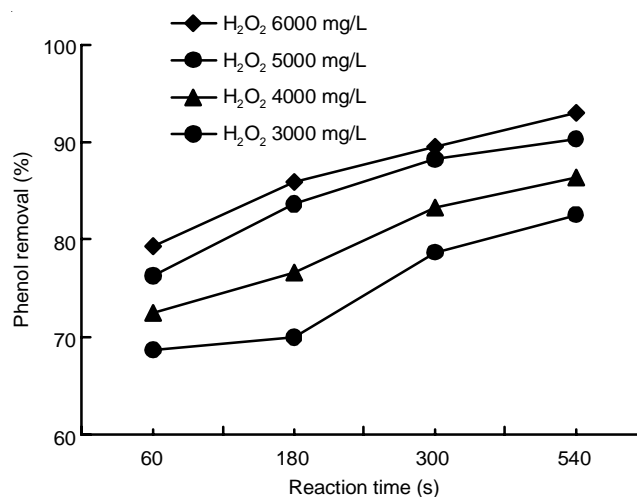


Fig. 3. Effect of H₂O₂ dosage on phenol removal

Effect of glycol on phenol removal: Table-2 shows the phenol removal of phenolic wastewater in supercritical water oxidation in relation to the effect of temperature from 385 to 445 °C without glycol, or with glycol. Experimental results show that the phenol removal increased with the increasing reaction temperature.

TABLE-2
EFFECT OF GLYCOL ON PHENOL REMOVAL

Temperature (°C)	H ₂ O ₂ dosage (mg/L)	Reaction time (s)	Phenol removal without glycol (%)	Phenol removal with 50 mg/L of glycol (%)
385	5000	60	70.66	70.97
		180	71.43	73.54
		300	75.23	79.55
		540	78.89	81.63
405	5000	60	75.24	76.41
		180	80.16	84.65
		300	82.56	85.96
		540	82.89	86.52
425	5000	60	80.57	83.88
		180	81.35	88.66
		300	84.64	91.63
		540	89.63	96.64
445	5000	60	81.77	88.65
		180	83.78	90.97
		300	87.46	93.97
		540	90.80	99.80

Experimental results show that the supercritical water oxidation of phenolic wastewater system by adding a small amount of glycol can raise the phenol removal. The high concentration of phenol causes an increase in the phenol removal when temperature is 445 °C, reaction time is 540 s and H₂O₂ dosage is 5000 mg/L from 90.8 % without glycol present to 99.8 % with 50 mg/L of glycol, the phenol removal increases 9 %.

Conclusion

To consider supercritical water oxidation as a treatment method to convert bioresistant organics to more readily biodegradable intermediates, knowledge of the impact of the operating conditions such as temperature, reaction time and H₂O₂ dosage is required. Experimental results indicated that in the supercritical water oxidation process, 90.8 % phenol removal was obtained after 540s at temperature of 445 °C, H₂O₂ dosage of 5000 mg/L. Adding the glycol accelerates the destruction of phenolic wastewater. The best removal efficiency of phenol occurred at 99.8 %.

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