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Original Research

Effective Pharmaceutical Wastewater Degradation via SCWO with Ethylene Glycol

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Abstract

Pharmaceutical wastewaters are generated through complex manufacturing processes that contain a variety of organic and inorganic constituents, and are usually characterized by a high concentration of chemical oxygen demand (COD), suspended solids, dissolved solids (salts), toxicity, and refractory compounds. Therefore, it must be treated. The treatment of a pharmaceutical wastewater (PWW) using the supercritical water oxidation (SCWO) method was investigated to improve the degradation of the complex-mixture of organic compounds present in the wastewater. The effects of H_2O_2 dosage, reaction time, temperature, initial COD, and concentration of ethylene glycol on COD removal were studied with laboratory bench-scale experiments. The results indicated that the removal process was more effective under experimental conditions. Adding ethylene glycol accelerates the destruction of pharmaceutical wastewater. The best COD removal of pharmaceutical wastewater reached 97.8%. This investigation will provide a fundamental method for developing a pretreatment method of industrial pharmaceutical wastewater with flexibility, simplicity and high activity.

Keywords: supercritical water oxidation, pharmaceutical wastewater, ethylene glycol, removal

Introduction

Pharmaceuticals present in wastewaters are considered an emerging environmental problem due to their toxicity and chemical persistence in the environment [1]. They can remain in the environment for a long time and their presence is considered dangerous in both low and high concentrations [2-9]. It has been estimated that up to half of the pharmaceutical wastewater produced worldwide is released without any treatment [10]. These pollutants are non-biodegradable, so application of non-biological processes such as advanced oxidation processes (AOPs) for their destruction will be necessary [11].

Supercritical water oxidation (SCWO) shows a substantial promise for clean and efficient decontamination of many aqueous organic wastes [12-15]. SCWO can rapidly and efficiently destroy organic substances into H_2O and CO_2 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 combustion [16], but only recently have several studies showed similar effects in SCWO reactions [17-19]. In SCWO, 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 pharmaceutical wastewater is performed using hydrogen peroxide as an oxidant in a flow reactor at supercritical conditions of water. We report experimental oxidation results of the pharmaceutical wastewater via SCWO, and to examine the feasibility of the technology as a pre-treatment for biological remediation to reduce toxic organic compounds. The effects of H_2O_2 dosage, reaction time, temperature, and concentration of ethylene glycol on COD removal were studied.

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Table 1. Characteristics of the pharmaceutical wastewater.

Items	Value
COD_{Cr} (mg/L)	19,000
pH	7.7
Nitrites (mg/L)	1
Nitrates (mg/L)	38
Turbidity (NTU)	50
Sulphates (mg/L)	800
BOD_5 (mg/L)	4,000
Total nitrogen (mg/L)	300
TSS (mg/L)	280
TDS (mg/L)	25,000
Na^+ (mg/L)	8,000

Experimental

Characteristics of Pharmaceutical Wastewater

The wastewater for this study was collected from a pharmaceutical company located in China. It was generated mainly from the process of product (antibiotics from the penicillin family) manufacturing and equipment cleaning, and thus contained various organic and inorganic constituents, such as intermediates, spent solvents, reactants, and catalysts. The pharmaceutical wastewater was characterized for its average physicochemical parameters, as given in Table 1.

Experimental Procedure

The general set-up of the system including the SCWO reactor is shown in Fig. 1.

SCWO experiments were performed in a batch reactor with a volume capacity of 600 ml designed to a maximum temperature of 600ºC and maximum pressure of 40 MPa. The oxidant feed stream was prepared by dissolving hydrogen peroxide with deionized water in a feed tank. Another feed tank was loaded with the pharmaceutical wastewater. The two feed streams were pressurized using two high-pressure pumps, and reaction temperature was monitored directly using a thermocouple (inserted inside the reactor) and controlled within 0.1ºC by a temperature controller (Jiang Su Liantai Instrumentation Co., NF-6000-2 digital controller). The wastewater sample was well mixed in the feed tank before feeding to SCWO. Upon exiting the reactor, the effluent was cooled rapidly by passing through a heat exchanger. The system pressure was maintained at desired pressures (±0.1MPa) 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

Effects of Temperature and Reaction Time on COD Removal

The results are presented in Fig. 2. As expected, rising temperature increased COD removal. COD removal reached about 80.1 and 90% after 120 s and 420 s at 460ºC, respectively. Therefore, temperature had a significant impact on the oxidation of pharmaceutical wastewater.

That is because when the temperature increased, the reaction rate accelerated. Eventually it led to increasing oxidation rates of organic matter degradation of pharmaceutical wastewater. Therefore, it is shown that COD removal increases when temperature increases.

Fig. 2 showed COD removal for SCWO of pharmaceutical wastewater at different temperatures. The results appeared that reaction time had a significant effect on COD removal of pharmaceutical wastewater. Within each set of

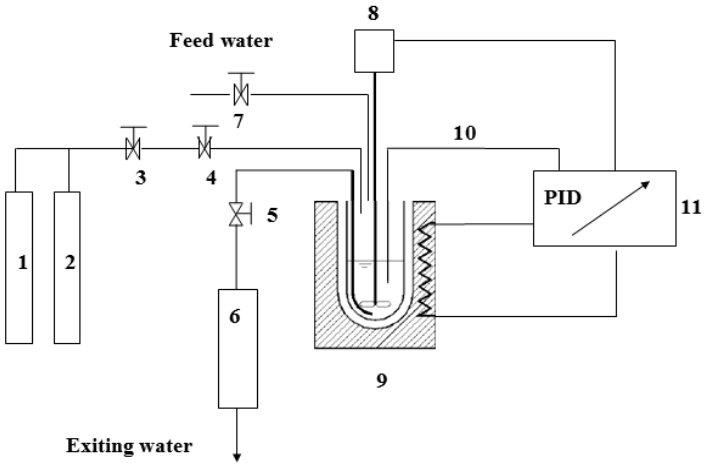

Fig. 1. Schematic diagram of the experimental setup for SCWO.
1. Nitrogen Cylinders, 2. Oxygen Cylinder, 3. Pressure-Reducing Valve, 4. Intake Valve, 5. Exiting Water Valve, 6. Condenser, 7. Feed Water Valve, 8. Mixing Device, 9. High-pressure Autoclave, 10. Thermocouple, 11. PID – proportional-integral-derivative.

isothermal experiments, the COD removal increased rapidly during the 120s of reaction and slowed down afterward.

Effect of Initial COD on COD Removal

Fig. 3 showed that COD removal is affected by initial COD. As expected, rising initial COD increased COD removal. COD removal reached about 78 and 90% after 120s and 420s at 460ºC, respectively. Therefore, initial COD had a significant impact on the oxidation of pharmaceutical wastewater.

Effect of H_2O_2 Dosage on COD Removal

Fig. 4 showed that COD removal is affected by H_2O_2 dosage. The COD removal increased with increasing H_2O_2 dosage. The increasing trend of COD removal is gentle when H_2O_2 dosage is over 6,000 mg/L, so the appreciate H_2O_2 dosage is 6,000 mg/L.

When H_2O_2 dosage increased, it could be helpful for accelerating strong oxidation species ($O_2\bullet^-$, $HO_2\bullet$, etc.). Therefore, high H_2O_2 dosage can accelerate the oxidation of organic pollutants.

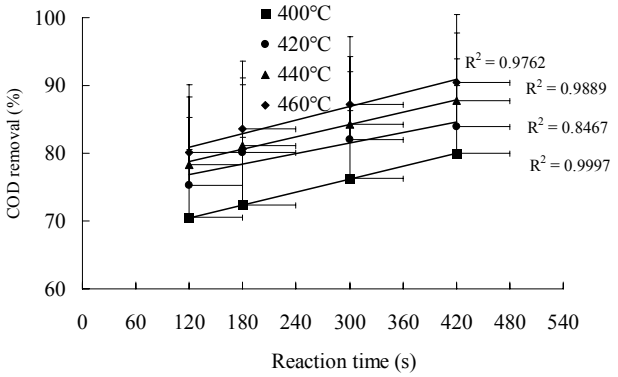

Fig. 2. Effect of temperature on SCWO of pharmaceutical wastewater. Conditions: reaction pressure 30 MPa, initial COD 10,000 mg/L, H_2O_2 dosage 4,000 mg/L.

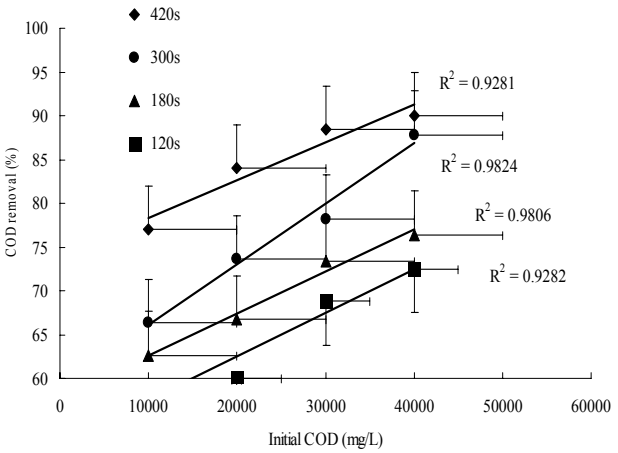

Fig. 3. Effect of initial COD on SCWO of pharmaceutical wastewater. Conditions: reaction temperature 460ºC, reaction pressure 30 MPa, H_2O_2 dosage 4,000 mg/L.

Table 2. Effect of ethylene glycol on COD removal.

Temperature (ºC)	H_2O_2 dosage (mg/L)	Reaction time (s)	COD removal without glycol (%)	COD removal with 25 mg/L of glycol (%)
400	6000	120	68.67	70.83
400	6000	180	72.15	74.09
400	6000	300	74.99	77.03
400	6000	420	78.33	81.22
420	6000	120	77.93	82.25
420	6000	180	80.08	83.64
420	6000	300	82.44	85.11
420	6000	420	84.77	87.99
440	6000	120	83.51	85.83
440	6000	180	85.33	89.61
440	6000	300	87.41	92.02
440	6000	420	89.61	95.53
460	6000	120	81.72	89.61
460	6000	180	84.44	91.55
460	6000	300	88.41	94.51
460	6000	420	90	97.8

Effect of Ethylene Glycol on COD Removal

Table 2 shows the COD removal of pharmaceutical wastewater in supercritical water oxidation in relation to the effect of temperature from 400ºC to 460ºC without ethylene glycol, or with ethylene glycol. Experimental results show that COD removal increased with the increasing reaction temperature.

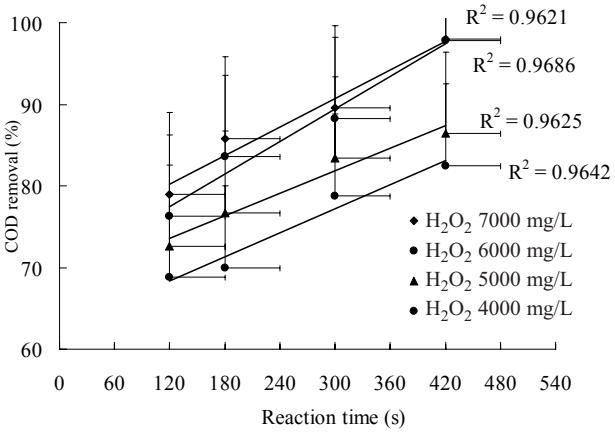

Fig. 4. Effect of H_2O_2 dosage on SCWO of pharmaceutical wastewater. Conditions: reaction temperature 460ºC, reaction pressure 30 MPa, initial COD 10,000 mg/L.

Experimental results show that the supercritical water oxidation of the pharmaceutical wastewater system by adding a small amount of ethylene glycol can raise COD removal. When temperature is 460ºC, reaction time is 420s, and H_2O_2 dosage is 6,000 mg/L, COD removal reached 90% without ethylene glycol present to 97.8% with 25 mg/L of ethylene glycol, and COD removal increases 7.8%.

Conclusions

The treatment of pharmaceutical wastewater (PWW) using the supercritical water oxidation (SCWO) method was investigated to improve the degradation of the complex mixture of organic compounds present in the wastewater. Experimental results indicated that in the SCWO process, 90% COD removal was obtained after 420s at 460ºC, H_2O_2 dosage of 6,000 mg/L. Adding the ethylene glycol accelerates the destruction of pharmaceutical wastewater. The best removal efficiency of COD reached 97.8%.

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