# Sub- and super-critical water oxidation of wastewater containing organic and heavy metallic pollutants and recovery of superfine metallic particles

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A B S T R A C T

The wastewater containing organic and heavy metallic pollutants is studied with sub- and super-critical water oxidation. First the in situ change was obtained with the simulated wastewater containing ethanol as organic pollutant and zinc acetate as heavy metal by an optical fused silica capillary and Raman spectroscopy and it is observed that there is deposition of superfine particles up to the temperature of 523 K during oxidation degradation. In the temperature range of 573–633 K, the degradation kinetics based on the chemical oxygen demand (COD) by a global power-law rate expression was determined to give the apparent reaction activation energy (Ea) of 45.51 KJ/mol. According to the simulated wastewater, the industrial leather wastewater containing heavy metal Cr and organic pollutants was treated. The Cr was fast converted to superfine $Cr_2O_3$ particles and the COD was easier removed with lower Ea of 36.96 KJ/mol.

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## 1. Introduction

The wastewater containing organic and heavy metallic pollutants is widely discharged from industrial fields such as leather, electroplate and wet metallurgy. Owing to the coexistence of organic and heavy metallic pollutants, it is a typical environmental pollution and the total detoxication is complicated. The traditional treatment is a greatly burden to discharge factory and it is usually secretly discharged especially in China because the advantage usually relies on the low production cost. Therefore, from both economical and environmental point of view, it is very important to develop an effective and simple process for co-detoxification of the wastewater.

The sub- and super-critical water oxidation is a new effective way to degrade organic pollutants of difficult disposal because most organic pollutants and oxidants can dissolve to form a homogenous phase [1–7]. The process is superior to incineration for no hazardous by-products such as POPs. Furthermore, owing to the very fast oxidative reaction, as for some metals in wastewater, they are usually converted to superfine particles [8–11]. The fast preparation of metal oxide nanoparticles in sub- and super-critical water now becomes an eco-friendly and high efficient method with organic assistance for its very fast decomposing, oxidation or reduction [12–17]. Therefore, as for the wastewater containing organic and heavy metallic pollutants, with the sub- and super-critical water oxidation, the organic pollutants can be fast degraded and the heavy metal can be recovered to obtain superfine particles. The process has both environmental and economical benefits. Moreover, as for the forming of some heavy metallic superfine particles, it can probably accelerate the degradation of organic pollutant because most of the type of ingredient has the catalytic effect [18].

Two types of wastewater of simulation and industrial leather were studied. The simulated wastewater adopted the ethanol and zinc acetate as organic and heavy metallic pollutants, respectively. It is known that alcohol and acid are usually important and typical intermediate products of oxidative degradation of organic pollutants such as the degradation of 4,4′-DBB [19]. In addition, the alcohol in sub- and super-critical water oxidation can be used as auxiliary fuel and co-fuel to improve the oxidative process [20].

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Based on the simulated wastewater, the industrial leather wastewater containing complicated organic and heavy chromic pollutants which usually needs complex process and high cost was treated to total harmlessness and recovery of superfine chromic particles.

## 2. Materials and methods

### 2.1. Materials

Ethanol ($C_2H_5OH$), zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$) and 30% (wt.%) hydrogen peroxide ($H_2O_2$) aqueous solution adopted as oxidant were used as purchased without further purification from Sinopharm Chemical Reagent Co. LTD. (Shanghai, China). The simulated wastewater containing organic and heavy metallic pollutants was ethanol and zinc acetate with the each initial COD of 500 mg/L. The industrial leather wastewater was provided by Shanghai Xinhua Leather Co., Ltd. (Shanghai, China).

The fused-silica capillary tubing (360 O.D. and 100 μm I.D.) was purchased from Polymicro Technologies LLC (Phoenix, AZ, USA).

### 2.2. Preparation of fused silica capillary micro hydrothermal vessel and in situ measurement

In order to know the in situ change under the extremely high temperature and pressure of sub- and super-critical water oxidation, the optical fused silica capillary technique was adopted which is fit for the in situ observation and Raman spectroscopic measurement up to the temperature of 723 K [21,22].
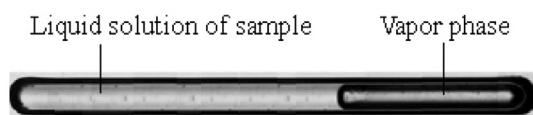


**Fig. 1.** Photomicrograph of capillary micro hydrothermal vessel.

The preparation of capillary micro hydrothermal vessel is according to the method described by Chou et al. [21]. To prepare a sample, a section of silica capillary of about 20 mm length was cut, and one end of the tube was sealed with oxyhydrogen flame. The simulated wastewater with excess hydrogen peroxide was injected into the capillary with micro syringe and centrifuged to the closed end. Then the closed end of the capillary was immersed in liquid nitrogen and the open end was quickly sealed with oxyhydrogen flame to form a micro hydrothermal vessel (Fig. 1) of about 8–12 mm. The sealing procedure was fast enough (within 5 s) to avoid increasing the temperature of the liquid inside the vessel and preventing sample loss.

A capillary micro hydrothermal vessel was loaded in the chamber of the stage on the microscope platform and the temperature (accurate to ±0.1 K) was adjusted via a controller (Instec., STC200, USA) with a heating rate of 20 K/min. At the set temperature, the stage with the vessel was moved to the Raman spectroscopy for measurement.

Raman measurement was by a Raman micro-spectrometer (RENISHAW System RM-2000, English made) with a long-working-distance objective (×20, Olympus), allowed acquisition of spectrum to 673 K without damaging to the objective. The measurements used an ionized $Ar^+$ laser, $\lambda_0 = 514.5$ nm, 50 mW, entrance slit 50 nm, collection time 60 s, and range 100–4000 $cm^{-1}$.

### 2.3. Oxidation degradation with traditional hydrothermal vessel

The traditional hydrothermal vessel is a stainless batch type autoclave which has an inner volume of 20 ml and the total volume of the sample put into the vessel is about 12 ml to maintain appropriate pressure and keep relatively smooth reaction. Owing to that the critical temperature of water is about 647 K, the temperatures ranged from 573 to 663 K were studied to know the sub- and super-critical oxidation.

After the degradation reaction, the autoclave was taken out from the furnace and quenched in ice water bath in order to stop the reaction immediately. The solid particles and liquid were separated by filtering.
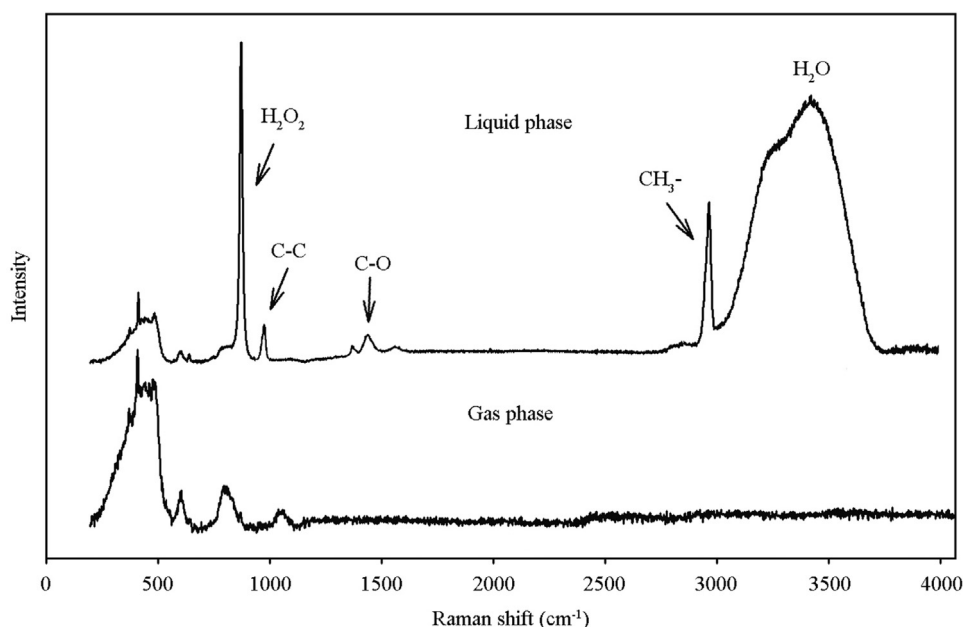


**Fig. 2.** Raman spectra of simulated wastewater at ambient temperature.