

초임계수 산화 기술을 이용한 산업 폐수들의 처리와 유용성분 회수

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Treatment of Industrial Wastewaters by Supercritical Water Oxidation

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Introduction

Supercritical water oxidation (SCWO) is a remarkably effective process for wastewater treatment. In supercritical water condition ($>374^{\circ}\text{C}$, $>22.13\text{MPa}$), the organic compound and oxygen are all present in a single, dense fluid phase, minimizing mass-transfer resistance and providing rapid reaction rates. Such advantages make SCWO as one of the most promising technologies for treating of hazardous industrial chemicals [1-2].

In this work, the decompositions of wastewaters from terephthalic acid (TPA) process, liquid crystal display (LCD) process and acrylonitrile process have been accomplished in supercritical water. During experiments, we found that there are possibilities of recycling valuable materials for each wastewater.

Experiment

A schematic diagram of laboratory scale continuous-flow reactor system for SCWO experiment apparatus is shown in Figure 1. The oxidant and wastewater streams were pressurized in two different lines by two high pressure pumps and then separately pre-heated. In order to assure that all H_2O_2 is decomposed to give H_2O and O_2 , the oxidant was pre-heated by flowing through 6m coiled 1/8-in. o.d. SS 316 tubing. After pre-heating, two streams were mixed at the reactor inlet using a SS 316 mixing tee. After exiting the reactor, the effluent was cooled rapidly by passing through a shell and tube heat exchanger and afterwards the particles was filtered out by a $0.5\mu\text{m}$ inline filter before it was depressurized by a back-pressure regulator. The product stream was then separated into liquid and vapor phases. The liquid products were collected in a graduated cylinder, and their volumetric flow rate was determined by measuring the time interval.

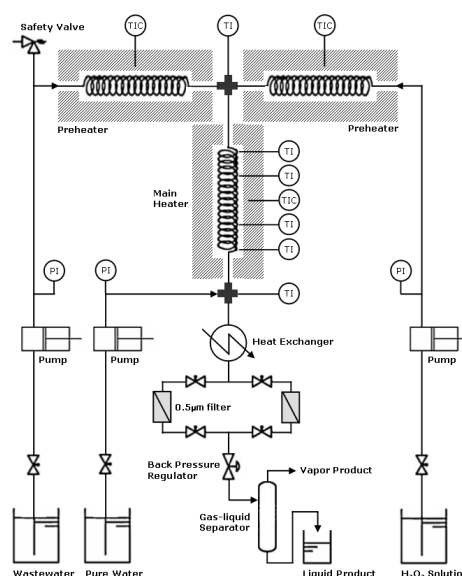


Figure 1. Schematic diagram of the continuous-flow reactor system for SCWO experiment.

Results and Discussion*Wastewater from TPA process*

The catalytic liquid-phase oxidation of p-xylene is one of the most important chemical processes to terephthalic acid for uses in poly (ethylene terephthalate) and polyester. Major by-products of the TPA manufacturing process in which the air oxidation of p-xylene in acetic acid solution in the presence of Co-Mn-Br catalytic system become major components of wastewater which are composed of benzoic acid, 4-formylbenzoic acid, p-tolualdehyde, p-toluic acid, cobalt acetate, manganese acetate and so on.

Ninety-five oxidation experiments were performed for wastewater in an isothermal, isobaric packed-bed flow reactor with or without catalyst of commercial bulk $\gamma\text{-Al}_2\text{O}_3$. The reaction conditions ranged over pressures of 220-300bar, temperatures of $418\text{-}513^{\circ}\text{C}$. The initial COD concentration of

wastewater at reaction conditions ranged from 3.99×10^{-3} to 2.81×10^{-2} M. The COD concentrations of wastewater in feed tank were between 2400 and 14917 ppm. The oxygen concentrations at reaction conditions were between 1.4×10^{-3} and 7.4×10^{-3} M.

Figure 2 shows the effect of feed COD concentration on the COD conversion at given $W/F_{\text{COD}0}$ during catalytic SCWO and reaction rate and conversion of the COD at a given $W/F_{\text{COD}0}$ increase with increasing the COD concentration in the reactor feed when the oxygen concentrations were set at 4 mmol/l. Figure 3 shows that COD disappearance rate or conversions at a given $W/F_{\text{COD}0}$ also are enhanced by increasing oxygen concentrations in the feed. We used a non-linear regression analysis to fit the rate of reaction, and made estimates of the parameter values in order to predict the rate of reaction. The kinetics of wastewater decomposition by catalytic SCWO were best fit by the global rate law as $\text{rate} = -2.67 \times 10^2 \exp(-55.4567/RT) [\text{COD}]^{0.81} [\text{O}_2]^{0.49}$. Where the reaction rate has units of mmol/(kg cats), COD are in mmol/l, and the activation energy is in kJ/mol.

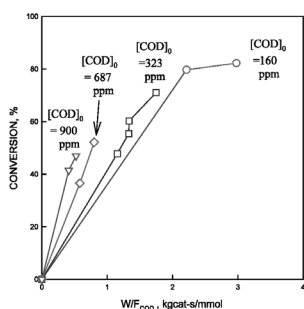


Figure 2. Effect of wastewater feed concentration on COD conversion during catalytic SCWO. 470°C, 240bar, $[\text{O}_2]_0 = 4 \text{ mmol/l}$.

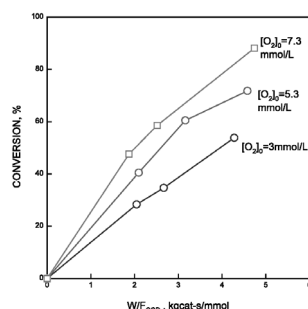


Figure 3. Effect of oxygen feed concentration on wastewater conversion during catalytic SCWO. 420°C, 240bar, $[\text{COD}]_0 = 6 \text{ mmol/l}$.

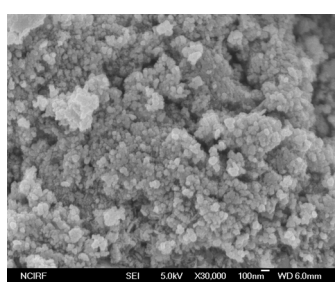


Figure 4. Scanning electron micrograph of precipitated Co-Mn oxide generated during SCWO.



Figure 5. SCWO commercial plant for wastewater from TPA manufacturing plant

Based on this kinetics, we have studied the optimal operation condition of SCWO commercial plant (Figure 5) to decompose wastewater from TPA process. Most of all, valuable Co-Mn catalyst used in TPA process is recycled as cobalt oxide and manganese oxide after accelerating decomposition of wastewater in SCWO commercial plant. Figure 4 shows the SEM of Co-Mn oxide generated during SCWO. The size of Co-Mn oxide particles is 1-10 μm and they are recycled to TPA manufacturing process after precipitation and filtration.

Wastewater from LCD process

Wastewater from LCD manufacturing plants contains a wide variety of organic pollutants and heavy metal chromium. The COD of LCD wastewater is 37,191-41,323 mg/l and total Cr and N are 3,495-3,622 mg/l and 10,987-54,306 mg/l, respectively.

Fifty-nine supercritical water oxidation experiments were performed in an isothermal, isobaric packed bed flow reactor under oxygen excess. The reaction condition ranged over pressure of 25–29 MPa, temperature of 396–615°C, and residence time of 9–23 s. The initial COD concentration at reaction condition ranged from 126 to 19,428 mg/l and the concentration in feed tank ranged from 251 to 38,855 mg/l. The oxidant concentrations at reaction condition were between 4.66×10^{-3} and 1.34×10^{-1} mol/l. LCD wastewater was easily oxidized in the supercritical water oxidation; up to 99.99% of COD decomposition was obtained within 10 s at the reaction temperature 615°C.

Figure 6 shows that conversion of COD at a given oxidant concentration increases with increasing the COD concentration in the reactor feed. This is the indication of the fact that the global reaction order for COD greater is than zero. Figure 7 shows that increasing oxidant concentration also enhances the COD conversions. This implies that the global reaction order for oxidant also greater than zero.

A non-linear regression analysis is used to fit the rate of reaction and estimation of the parameter values was made in order to predict the rate of reaction. 59 data led to the kinetics of decomposition by the global rate law as $\text{rate} = -2.78(\pm 0.71) \times 10^2 \exp(47.79(\pm 1.52)/RT) [\text{COD}]^{1.01 \pm 0.01} [\text{O}_2]^{-0.065 \pm 0.01}$.

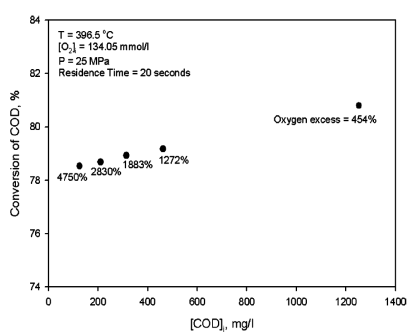


Figure 6. Effect of wastewater feed concentration $[COD]_i$ on COD conversion.

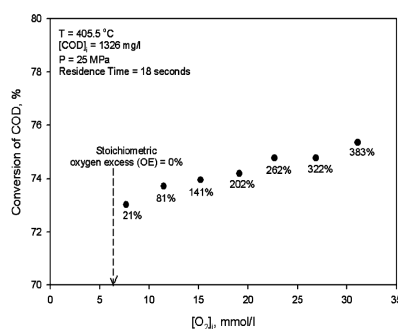


Figure 7. Effect of oxidant feed concentration $[O_2]_i$ on COD conversion.

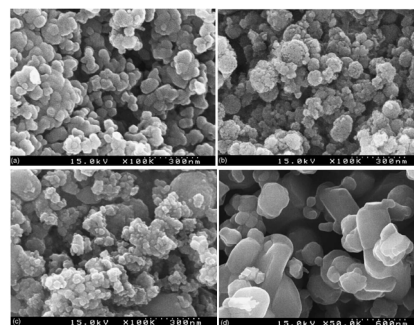


Figure 8. Scanning electron micrograph of particle obtained from experiment at temperatures (a) 396°C, (b) 552°C, (c) 603°C and (d) after 4 hour calcinations at 1000°C.

During SCWO process, in situ formation of chromium oxide nanoparticles (α -HCrO₂ and Cr₂O₃) was found by decomposition of ammonium chromate, which is contained in wastewater. Also more than 97% chromium in the wastewater can be recovered as chromium oxide particles. Based on SEM and ELS analyses, the size of particles ranges from 200nm to 400nm and the temperature affects their size. From the SEM observed, as can be seen in Figure 8, the morphology of particles obtained at temperature 396, 552, and 603°C were non-faceted crystalline and at temperature 1000°C were smooth faceted crystalline Cr₂O₃ particles. It also shows the particles growth as temperature increased in agreement with the result of average size of particle analyzed using ELS technique.

Wastewater from acrylonitrile process

Wastewater from the manufacture of acrylonitrile is difficult to biodegrade. They contain eight major organic components such as acrylonitrile, acrylamide, acrylic acid, acrolein, cyanopyridine, fumaronitrile, succinonitrile and maleimide. The TOC and T-N concentrations of acrylonitrile wastewater are 27,240mg/l and 11,995mg/l.

Eighty-two supercritical water oxidation experiments were performed in an isothermal, isobaric tubular reactor. The reaction condition ranged over pressure of 25–26MPa, temperature of 300–600°C, and residence time of 2–30s. The initial TOC concentration at reaction condition ranged from 3,160 to 19,260mg/l and the concentration in feed tank ranged from 3,405 to 27,240mg/l. The oxidant concentrations at reaction condition were between 0.5–2.5 stoichiometric ratio of O₂ based on initial TOC. Acrylonitrile wastewater was easily oxidized in the supercritical water oxidation; up to 97.02% of TOC decomposition was obtained within 15s at 552°C.

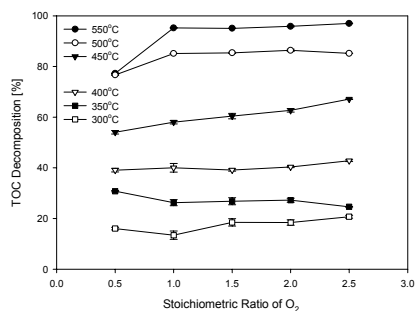


Figure 9. Effect of stoichiometric ratio of O₂ for TOC decomposition. Feed TOC=6,810ppm, RT=15sec.

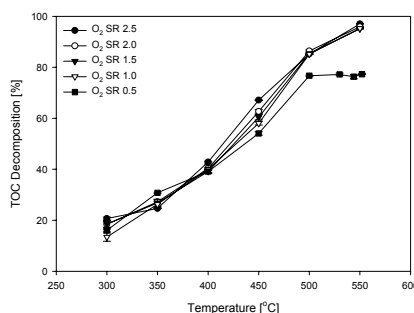


Figure 10. Effect of temperature for TOC decomposition. Feed TOC=6,810ppm, RT=15sec.

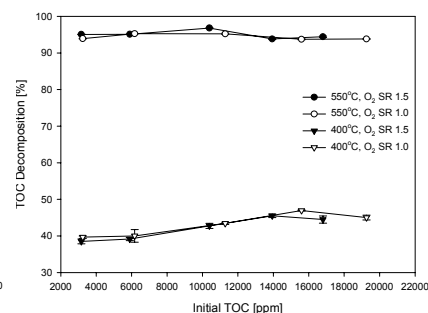


Figure 11. Effect of initial TOC for TOC decomposition. RT=15sec.

Figure 9 shows the effect of O₂ concentration at given feed concentration and reaction time. This implies that O₂ concentration wasn't so important at short residence time over 300–550°C in case O₂ concentration was above 1.0 stoichiometric ratio. Figure 10 is the indication of the fact that there was

no more decomposition of TOC above 500°C if stoichiometric ratio of O₂ was kept as 0.5. This also means that hydrolysis of wastewater occurred about 20%. Figure 11 shows that initial TOC made no effect for TOC decomposition when the other operation variables were kept the same. In this graph, small increase of TOC decomposition at 400°C might be due to the hot spot caused by relatively high initial TOC to reaction temperature.

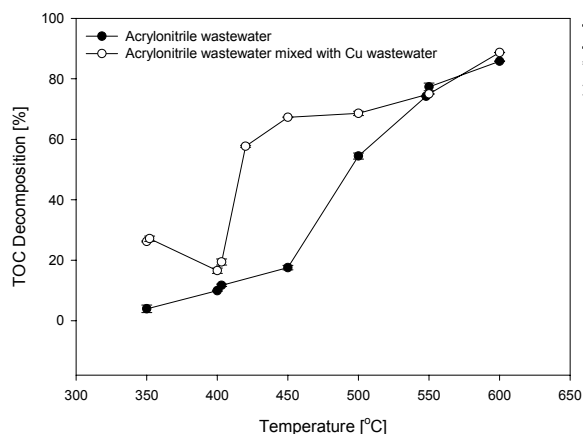


Figure 12. Effect of Cu wastewater added in acrylonitrile wastewater. Feed TOC=6,810ppm, RT=2sec. O₂ SR=1.5.

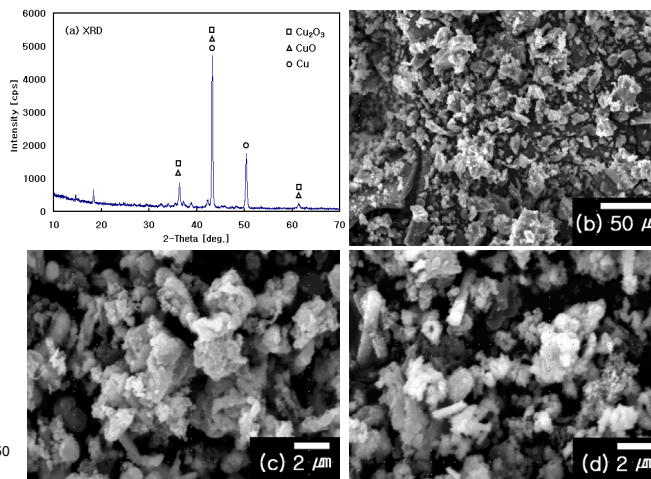


Figure 13. (a) X-ray diffraction spectra of particles at 500°C and Scanning electron micrograph of particle obtained at (b) 350°C, (c) 500°C, (d) 600°C.

In the vicinity of acrylonitrile manufacturing process, another wastewater containing 1,142 mg/l Cu ions is emerged. TOC and Cu ions should be removed from this Cu containing wastewater. We happened to adapt new idea that acrylonitrile wastewater mixed with Cu wastewater may be decomposed more easily because of Cu oxides generated during SCWO. Figure 12 shows TOC decomposition of acrylonitrile wastewater with or without Cu wastewater at the same operation condition. There is a huge difference of TOC decomposition at 420–500°C. Added to that, Cu ions in wastewater are precipitated as Cu oxides after supercritical oxidation and can be reused. Figure 13 shows the XRD result that Cu₂O₃, CuO, Cu particles were generated at 500°C. This also shows that the size of Cu oxide particles was decreased as reaction temperature increased.

Conclusion

SCWO had been demonstrated as an effective means of oxidizing wastewater from PTA, LCD and acrylonitrile manufacturing plant. One can get almost 100% conversion of each wastewater at longer contact time, higher temperature or higher concentration of oxygen. A series of experiments was carried out to examine the effect of the wastewater and oxidant concentration, residence time, reaction temperature and catalysts. Experimental data were used to fit the rate of reaction in a non-linear regression analysis, assuming a zero-order dependence on water concentration.

The most important aspect of this study is that valuable materials from wastewaters were recycled as fine particles during SCWO process. Co-Mn catalyst in TPA wastewater is recycled as cobalt oxide and manganese oxide after accelerating decomposition of organics in SCWO commercial plant. Chromium oxide nanoparticles are formed during SCWO of LCD wastewater and recovered above 97%. Cu containing wastewater accelerates the decomposition of acrylonitrile wastewater and Cu ions are precipitated as reusable Cu oxides after SCWO process.

References

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- [2] J.R. Portela, E. Nebot, E. Martinez de la Ossa, "Generalized kinetic models for supercritical water oxidation of cutting oil wastes", *J. Supercrit. Fluids* 21, 135-145(2001).