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Supercritical Water Oxidation of Wastewater from LCD Manufacturing Plant

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Abstract

The range of LCD products is larger every year and these products make a valuable contribution to different manufacturing industries and, in the end, to our current standard living. However, LCD production also leads to millions of tons of wastewater, and the elimination of these waste is now a key factor for the development of the "green" industry. One remarkably effective process for the treatment and disposal wastewater is supercritical water oxidation (SCWO). In this study, SCWO of the wastewater from a LCD manufacturing plant was carried out in an isothermal, isobaric tubular flow reactor with a H_2O_2 oxidant. All experiments were performed at pressure 250 bar and at temperature from 395 to 615 ^{o}C. At the reactor entrance, the initial chemical oxygen demand (COD) concentrations of wastewater were between 6.88×10^{-4} and 1.08×10^{-1} M; the oxidant concentrations were between 1.53×10^{-2} and 2.69×10^{-1} M. As the result of experiment, the power-law rate expression that best correlation of the experimental results for the conversion of COD was determined to be:

$$rate = -2.88 \times 10^2 \exp(-47.96/RT)[COD]^{1.01}[H_2O_2]^{0.064}.$$

Introduction

LCD manufacturing plants generate several million tons of wastewater annually. The wastewater generated by these industries contains a wide variety of organic pollutants. Conventional treatment methods as coagulation or membrane separation have major disadvantages since they generate a concentrated stream that is more harmful than the original waste [1]. Generally, it is a waste too dilute to be incinerated, and due to its toxicity, it is difficult to treat biologically.

SCWO is a promising emerging technology useful to eliminate a wide range of problematic wastes from a broad variety of industries [2, 3]. Several researchers have proved its effectiveness and have studied the reaction kinetics involved [4]. However, there are no references in the literature about SCWO of LCD wastes, even though these industrial wastes are quite important due to their large volume and high toxicity. Thus, in this paper we describe experiments designed to identify kinetic reaction rate in the SCWO of LCD wastes.

Experiments

Fig 1. shows a schematic diagram laboratory scale SCWO experiment apparatus. All wetted parts, from the high pressure pumps to the back-pressure regulator, were made of stainless steel 316. The
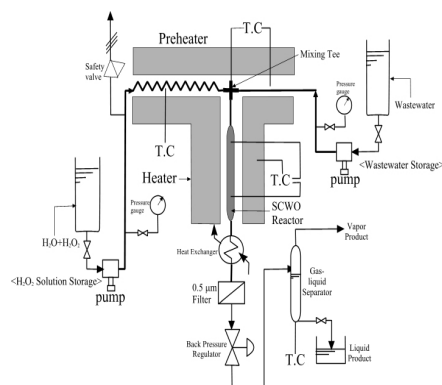
Figure 1. Schematic diagram of the
continuous-flow reactor system for SCWO

reactor was constructed from a 28 cm length of 9.5 mm i.d. tubing. The oxidant feed stream were prepared by dissolved hydrogen peroxide with deionized water in a feed tank. Another feed tank was loaded with LCD wastewater. The two feed streams were pressurized in two different line by two high-pressure pumps and then separately preheated. In order to assure that all H_2O_2 is decomposed to give H_2O and O_2, the oxidant was preheated by flowing through 6 m coiled 1/8 in. o.d. tubing. The wastewater feed stream was preheated by flowing through 0.5 m 1/8 in. o.d. tubing. After preheating, two lines were mixed at the mixing tee.

Upon exiting the reactor, the effluent was cooled rapidly by passing through a shell and tube heat exchanger and afterwards, 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. The concentration of wastewater and liquid-phase reactor effluents were analyzed by COD_{cr} (Chemical Oxygen Demand by $K_2Cr_2O_7$) using closed reflux calorimetric method (5220D). COD decomposition, X, defined as follows, was used to evaluate the extent of oxidative decomposition, where $[COD]_i$ is the initial COD and $[COD]_f$ is the residual COD after reaction.

$$X = \left(1 - \frac{[COD]_f}{[COD]_i}\right) \tag{1}$$

Results and discussion

In order to investigate the effect of the concentrations of COD, oxidant and water one by one on the decomposition rate of COD, we carried out a series of experiments in which one concentration was changed while the other two remained constant during the experiment. The derivative at any point on curves (figures 2-4) is equal to the COD disappearance rate because the mole balance equation for an isothermal, isobaric plug flow reactor is as follow

$$\text{rate} = -\frac{d[COD]}{dt} \tag{2}$$

Fig. 2 shows that conversion of COD at given oxidant concentration increase with increasing the COD concentration in the reactor feed. This indication of the fact that the global reaction order for COD is greater than zero. Fig. 3 shows that effect of oxidant concentration on the COD conversion at given COD concentration. The COD conversions are also enhanced by increasing oxidant concentration. This implies that the global reaction order for oxidant also greater than zero. Fig. 4 shows that when the pressure is increased from 230 to 290 bar with constant temperature, COD and oxidant concentrations, the COD conversion does not appreciably change. Since the pressure is related

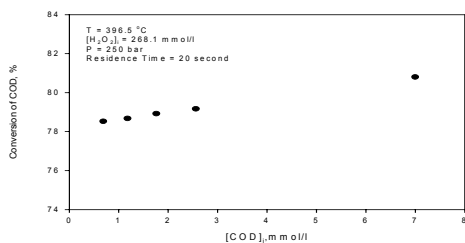to the water density, so we did not consider the effect of water concentration change.

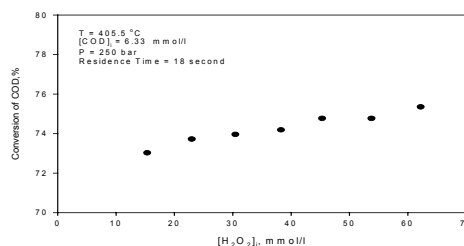Fig. 2. Effect of $[COD]_i$ on COD conversion
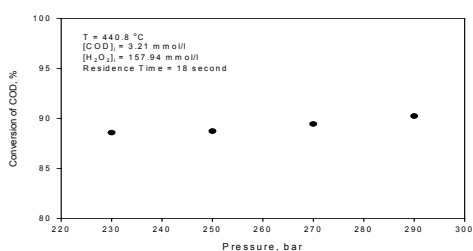

Fig.3. Effect of $[H_2O_2]_i$ on COD conversion

Fig.4. Effect of pressure on COD converstion

In order to determine the kinetic parameters, 53 data were taken under various conditions. Figs. 2-4 show that the COD conversion is function of the COD and oxidant concentrations but not the water concentration. The global power-law reaction rate can be described as follow:

$$\text{Rate} = -k\,[COD]^a[H_2O_2]^b \tag{3}$$

where a and b are the reaction orders of COD and H_2O_2, respectively. k is the rate constant, which can be expressed in Arrhenius form in equation $k = A \exp(-E_a/RT)$; where A and E_a are the pre-exponential factor and activation energy, respectively. Combining Eq. (2) and Eq. (3) leads to equation as follow :

$$\text{rate} = -\frac{d[COD]}{dt} = -k[COD]^a[H_2O_2]^b \tag{4}$$

In this research we assumed the oxidant concentration remained relatively variant from initial concentration, rate equation could be dependent upon COD, H_2O_2 concentration impartially. Thus, we might use the initial rate method and least square methods at the same time . If we use the method of initial rate then Eq. (4) can be solved analytically with the initial condition X=0 at at τ=0 to provide equation (5) as the relationship between the   COD removal efficiency and the experiment variables.

$$X = 1-[1-(1-a)k(T)\tau[COD]_o^{a-1}[H_2O_2]_o^{b}]^{1/(1-a)} \quad \text{if } a \neq 1 \tag{5}$$

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. We can search for those values that will minimize the sum of the squared differences of the experimental initial rates, and the predicted initial

rates. We want to find the sum of

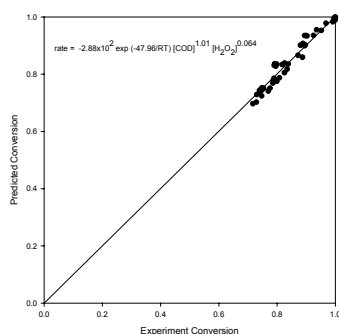$$S = \sum_{i}^{N_{\exp}} \left(X_{\exp} - X_{pred} \right)$$ for all data points to be minimum.

Figure 5. Parity plot for power-law

rate equation for COD conversion

These 53 data sets led to reaction orders of a=1.01 ($\pm$0.01) for COD, and b=0.064 ($\pm$0.01) for oxidant, respectively. The values of the Arrhenius parameters, A and E_a are 2.88 ($\pm$0.84)$\times 10^2$ $l^{1.074}$/(mmol$^{0.074}$ s) and 47.96 ($\pm$1.71) kJ/mol, respectively. The uncertainties reported here are the 95% confidence intervals.

Figure 5 shows a parity plot of the rate predicted from the global rate law using the parameters from experiments data in equation (5) against the rate obtained experimentally. A perfect fit of the model to the data would result in all the points lying on the 45° line. Our model fits reasonably well experimental data

Conclusion

SCWO had been demonstrated as an effective means of oxidizing wastewater from LCD manufacturing. Conversion greater than 99.99% can be obtained within 9 second at temperature 615°C. The kinetics of wastewater decomposition were best fit by the global rate law :

$$\text{rate} = -2.88 \times 10^2 \exp(-47.96/RT)[\text{COD}]^{1.01}[\text{H}_2\text{O}_2]^{0.064}$$

where the reaction rate has unit of mmol/s, COD and H_2O_2 are in mmol/l and the activation energy is in kJ/mol. Wastewater from LCD manufacturing plant could be completely destructed at supercritical temperature and pressure with sufficient amount of oxidant

References

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