

TEXTILE WASTEWATER TREATMENT BY SUPERCRITICAL WATER OXIDATION AND ITS KINETICS: A CASE STUDY

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ABSTRACT

Degradation of a mixture of several organic contaminants in wastewater supplied from a textile plant using supercritical water oxidation (SCWO) is investigated in this work. The wastewater contains textile dyes C.I. Basic Red 46, C.I. Basic Blue 3, C.I. Basic Blue 159, C.I. Basic Yellow 13 and conditioning chemicals imidazolyne, dimethyl cocobenzyl ammonium chloride and acetic acid. The proportions of these contaminants are unknown, however, the total organic carbon (TOC) concentration of the wastewater was measured as 744 mg/L. Aqueous hydrogen peroxide, which was prepared by dissolving hydrogen peroxide with deionized water, was used as the oxidant. The reaction conditions ranged from temperatures of 400–600°C, and residence times of 8–16 s. Treatment yields in terms of TOC conversion were obtained between 92.0% and 100.0% under various reaction conditions. The TOC content of the liquid phase product decreased with increasing temperature, reaction time and oxidant concentration. A global rate expression was regressed from the complete set of data using STATISTICA with a reliability of $R=96.25\%$. As a result of regression analysis, the reaction rate expression based on TOC was determined with the activation energy of $18.694 \text{ kJmol}^{-1}$ and the pre-exponential factor of $0.081 \text{ mmol}^{-0.244} \text{ L}^{0.244} \text{ s}^{-1}$; and the reaction orders for the wastewater (based on TOC) and the oxidant were 1.169 and 0.075 in a 95% confidence level.

INTRODUCTION

Textile wastewaters contain many organic pollutants, which are dissolved in water, depending on the kind of dyeing solution used. Since the dyes used in textile industry have very complex chemical structures and are synthetic, the treatment of textile wastewaters is difficult and expensive. Organic pollution and color are the main pollutants that make the treatment process difficult as the dyes present in textile wastewater, especially organic materials, are resistant to biological dissolution.

For the elimination or reduction of textile wastewater's pollution effects, numerous technologies e.g. physicochemical separation processes, biological and chemical oxidative processes, have been widely employed, but these techniques usually produce pollutant conversions of only between 50-70% and require several hours to weeks depending to the method for reaching those conversion ratios [1-9].

Some other advanced oxidation methods for dyeing wastewater treatment are wet air oxidation (WAO) and catalytic wet air oxidation (CWAO), which are performed at subcritical temperatures and pressures of water. These processes are considered as a pretreatment step to the conventional biological oxidation for purifying dyehouse wastewaters. In literature, the treatment efficiencies for various dyes by using WAO [10] and CWAO [11] vary between 50% and 90% at the residence times of 30 - 240 min, in batch or continuous flow reactors. Supercritical water oxidation (SCWO) which is performed in supercritical conditions of water (374.8°C and 22.13 MPa) is a promising alternative method for the treatment of textile wastewater. SCWO can rapidly and efficiently destroy organic substances into H_2O and CO_2 with conversion rates at 500 to 650°C in significantly short residence

times [12-16]. In this work, treatment of the wastewater which was obtained from an industrial textile dyeing plant is performed by SWCO in a tube reactor.

MATERIALS AND METHODS

Materials

Hydrogen peroxide solution was prepared by diluting a 30 wt.% solution of H₂O₂ (J.T. Baker) with deionized water to the desired concentration. The wastewater was obtained from an industrial textile dyeing plant, and used without diluting in the experiments after it was roughly filtered. The wastewater contains a variety of textile dyes and other chemicals including C.I. Basic Blue 3 (C₂₀H₂₆ClN₃O), C.I. Basic Blue 159 (C₂₂H₃₃O₇ClN₅S), C.I. Basic Red 46 (C₁₈H₂₁BrN₆), C.I. Basic Yellow 13 (C₂₀H₂₃ClN₂O), dimethyl cocobenzyl ammonium chloride and imidazolyne based softener.

Apparatus and Procedure

The SCWO experiments were performed in a coiled tubular reactor system, which is placed into a PID controlled split furnace, as described in the previous work [17]. The wastewater and oxidant are pumped into the furnace (Protherm, model SPT 11/70/750) in separate pipelines using two high pressure pumps (Autoclave Engineers, Series III pump). After passing the preheating zones both streams mix in a mixing tee and continue into the reactor. Before reaching the mixing tee, H₂O₂ decomposes to oxygen and water completely as verified in previous works [18]. After exiting the furnace, the effluent was cooled rapidly by passing through a heat exchanger, and reaction stops immediately. The solid particles in the effluent, which would be formed presumably, were removed with a 0.5 μm inline filter before the stream was depressurized by a back-pressure regulator (BPR) (GO Regulator Inc.). From the feeding pumps to the gas-liquid separator, all wetted parts of the system, such as tubing, fittings etc., were made of 316 SS. The system pressure was maintained at 25 ± 0.1 MPa by the BPR. Then the product stream was separated into liquid and vapor phases under ambient conditions and liquid products were collected in a graduated cylinder.

Analytical Methods

The concentrations of wastewater and liquid phase reactor effluents were characterized by analyzing the TOC. TOC analyses were performed using a total organic carbon - total nitrogen analyzer (HACH-LANGE IL550 TOC-TN). The gas samples were analyzed according to ISO 6974-6 method with GS-Gaspro, Molsieve and Plot Q capillary columns by using an Agilent 7890N chromatograph coupled one FID and two ECD detectors. According to analysis results, the sample consists of 1.82% methane, 10.59% carbon dioxide, 49.2% oxygen and 16.33% nitrogen.

Calculations

The reactor residence time is calculated by using the following equation:

$$\tau = (V_{\text{Reactor}} / F_T) \times (\rho_{SC}(P, T) / \rho_L) \quad (1)$$

where V_{Reactor} is the reactor volume, $\rho_{SC}(P, T)$ is the density of fluid at reaction pressure and temperature in g/mL, ρ_L is the density of fluid at feed pump conditions in g/mL, and F_T is the total volumetric flow rate including both the wastewater and the oxidant that fed into the system in mL/s. Since the experiments were performed with dilute solutions of pollutants and oxygen in the water, the fluid mixture density in feed is assumed to be that of water. The density of the mixture at reaction conditions was calculated for pure water by the Peng-Robinson-EoS as described below [19]:

$$P = [RT/(V - b)] - [a(T)/(V(V + b) + b(V - b))] \quad (2)$$

where $a(T)$ and b are generalized functions of the critical temperature T_c , critical pressure P_c , and acentric factor ω of pure water. TOC and TN conversions are being used to evaluate the extent of oxidative decomposition, X , which is defined as follows:

$$X = (X_0 - X_f) / X_0 \quad (3)$$

where X_0 represents the initial TOC concentration, and X_f represents the residual TOC concentration in the liquid product effluent after the reaction. Initial total organic carbon and oxidant concentrations at the reaction conditions were calculated using following equations:

$$N_{TOC} = (C_{TOC}/12) \times (F_{wastewater}/F_T) \times (\rho_{SC}(P,T)/\rho_L) \quad (4)$$

$$N_{O_2} = ([H_2O_2]/2) \times (F_{H_2O_2}/F_T) \times (\rho_{SC}(P,T)/\rho_L) \quad (5)$$

where N_{TOC} and N_{O_2} are the initial concentrations of TOC and O_2 in mmol/L, C_{TOC} is the TOC concentration in the feed stock in mg/L, $[H_2O_2]$ is H_2O_2 concentration in the feed stock in mmol/L, $F_{wastewater}$ and $F_{H_2O_2}$ are wastewater and H_2O_2 feed flow rates into reactor in mL/s, F_T is the total feed flow rate including both the wastewater mixture and the oxidant fed into the system in mL/s, and $\rho_{SC}(P,T)$ is the density of water at reaction pressure and temperature. In the calculation of initial concentration of the oxidant, H_2O_2 concentration is divided by two in Eq. (5), because 1 mol of H_2O_2 is decomposed into 0.5 mol of O_2 and 1 mol of H_2O .

RESULTS

24 individual experiments under 25 MPa system pressure were performed under various parameter values in order to determine the effects of the parameters on the reaction rates. Initial TOC and initial O_2 concentrations at reaction conditions ranged from 0.79 to 5.79 mmol/L, and from 4.10 to 36.20 mmol/L, respectively. The reaction condition ranged from temperatures of 400–600°C, and residence times of 8–16 s. Thermal hydrolysis data in liquid effluent are not available for this wastewater sample, because of high amounts of solid particles produced under non-oxidative conditions. All experiments were performed with excess of O_2 . The best TOC removal efficiency (100%) was obtained using oxygen concentration of 5.79 mmolL⁻¹ for the residence time of 30 s at 600°C and 25 MPa. At this reaction condition, gas phase product composition was detected as 1.82% methane, 10.59% carbon dioxide, 49.2% oxygen and 16.33% nitrogen by GC analysis. As shown in Figures 1-3, treatment efficiency based on TOC increases with increasing reaction temperatures, reaction time and oxygen concentration. However, the most effective parameter on the treatment in supercritical water conditions is reaction temperature (Fig. 1-2).

The suggested rate expression in terms of TOC conversion is as follows:

$$-[TOC]_0 \frac{d(1-X)}{d\tau} = k_0 \text{Exp}(-E_a/RT) [TOC]_0^a (1-X)^a [O_2]_0^b \quad (6)$$

where $[TOC]_0$ is the initial TOC concentration under reaction conditions, τ is residence time in s, k_0 is the pre-exponential factor of Arrhenius equation, E_a is the activation energy in kJ/mol, R is the ideal gas constant in kJ/molK and a and b are the reaction orders for TOC conversions and oxygen.

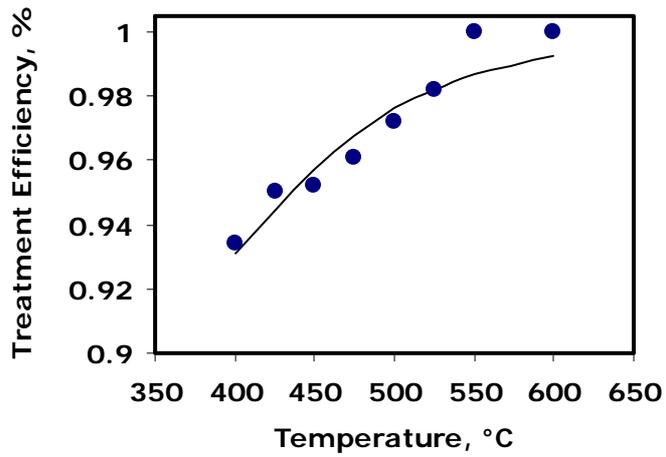


Figure 1. Effect of temperature on the treatment efficiency

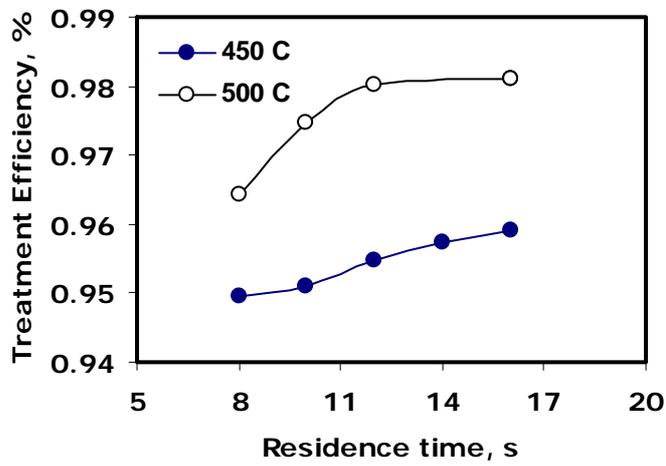


Figure 2. Effect of reaction time on the treatment efficiency

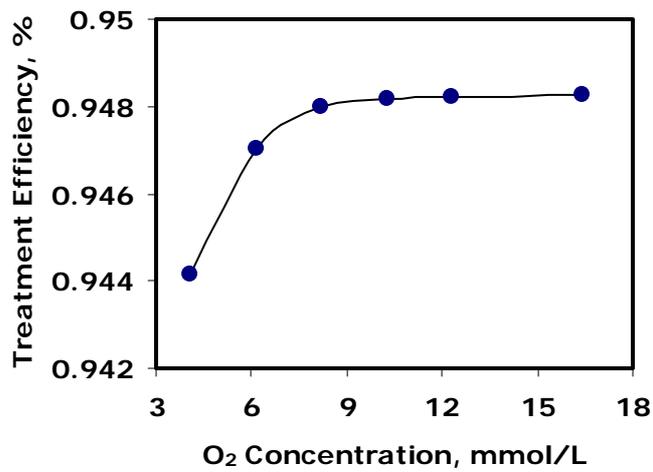


Figure 3. Effect of oxygen concentration on the treatment efficiency

if Eq. (6) is rearranged with respect to the TOC decomposition X , using the initial condition $X = 0$ at reaction time $\tau = 0$, it can be solved analytically to provide Eq. (7);

$$X = 1 - \left[1 + (a-1) I 10^{k_0} \text{Exp}(-E_a / RT) [\text{TOC}]_0^{a-1} [\text{O}_2]_0^b \tau \right]^{1/(1-a)} \quad \text{for } a \neq 1 \quad (7)$$

The conversion rate data with parameter values for each individual experiment were analyzed using STATISTICA V6.0 program package for suggested kinetic model. The best fit values were obtained by minimizing the sum of the squared differences of the experimental and the predicted conversion for all data points using non-linear regression analysis. As a result of regression analysis, the reaction rate expression based on TOC was determined as follows:

$$-\frac{d[\text{TOC}]}{d\tau} = 0.081 (\text{mmol}^{-0.244} \text{L}^{0.244} \text{s}) \cdot \text{Exp}\left(\frac{-18.694 \text{ kJ/mol}}{RT}\right) \cdot [\text{TOC}]^{1.169} \cdot [\text{O}_2]^{0.075} \quad (8)$$

Figure 4 shows model versus experimental results graphically. This model fits satisfactorily with our experimental data (R=96.25%).

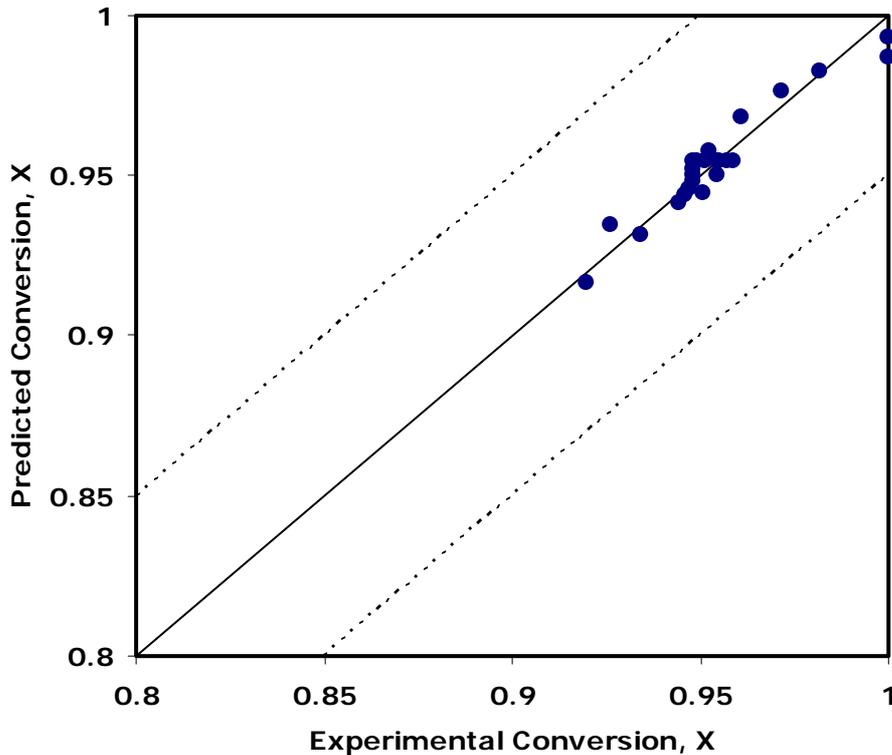


Figure 4. A comparison of predicted and experimental conversions

CONCLUSION

Oxidation of an aqueous waste directly from an industrial dyehouse was studied using a continuous flow reactor in supercritical water. The results demonstrated that the SCWO process decreased the TOC content up to 100% in residence times between 8-16 s at various reaction conditions. Main gas phase products consist of CO_2 , CH_4 , O_2 and N_2 . The total carbon of the liquid phase product was decreased with increasing temperature and oxidant concentration or excess O_2 . The liquid phase

products were clear and colorless. The activation energy of the reaction was 18.694 kJ/mol, the pre-exponential factor was $0.081 \text{ mmol}^{-0.244} \text{ L}^{0.244} \text{ s}$ and the reaction orders for pollutants (based on TOC) and oxygen were 1.169 and 0.075, respectively. The results show a confidence level of 95%, with $R=0.9625$. This wastewater sample was not suitable for taking healthy thermal hydrolysis data, because of the excessive amounts of solid particles formed under non-oxidative reaction conditions.

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