



The treatment of detergent industry wastewaters by supercritical water oxidation

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This study presents the results of our research regarding the treatment of the detergent industry wastewaters by supercritical water oxidation. The experiments were carried out at a constant pressure of 25 MPa, in the temperature range of 400–600°C and in the reaction time range of 20–60 s. During the supercritical water oxidation of the wastewaters, hydrogen peroxide was used as the oxygen source. The effects of temperature, reaction time and oxidant use on the total organic carbon contents of the liquid effluents were examined. As a result, it was seen that supercritical water oxidation was a very effective method for the treatment of detergent industry wastewaters. Treatment efficiencies up to 97.8% in terms of total organic carbon conversion were achieved in very short reaction times.

Keywords: Detergent industry wastewater, supercritical water, oxidation, treatment.

Introduction

Synthetic household detergents, whose production and consumption have increased dramatically nowadays, are one of the most hazardous environmental pollution sources. When the wastewaters of this industry are discharged to the environment without being subjected to adequate treatment, they cause undesired conditions such as the decrease of oxygen in aquatic media, eutrophication and contamination of drinking water¹. If the concentration of active compounds in detergents is greater than 0.5 mg/L in the receiving waters, foam formation may be encountered. The overspread foam on the water surface, in turn may block the aeration of water. The dissolved oxygen present in water is also consumed through the decomposition of the aforementioned active compounds by biochemical reactions. The rapid oxygen decrease in the aquatic media is a vital threat to the aquatic life¹.

Moreover, the phosphate present in detergents cause eutrophication. Oxygen decrease, discoloration, turbidity, decay, putrefaction and a major decrease in the number of living species are the possible effects of this phenomenon². Considering the effects on soil properties, Siggins *et al.*³ have reported that the long term disposal of these wastewaters may result in an increase of soil chemical parameters, such

as pH, phosphate, sodium adsorption ratio and pathogen indicators (such as *E. coli*), which if allowed to accumulate, can have detrimental effects on soil and human health. The decline in soil structure in progress of time may also intensify the risk of groundwater contamination⁴.

Considering its threat to the environment, various methods are being employed for the treatment of detergent industry wastewaters, some of which are biological remediation, adsorption, chemical precipitation, membrane processes, chemical and electrochemical oxidation. Today, "Activated Sludge Biological Treatment Method" is the most widely used method for industrial scale detergent wastewater treatment⁵. However, foam formation and low degradation rates are the main problems encountered during the employment of these methods⁶. At the same time, bacteria poisoning can occur when attempting to treat detergent-containing wastewaters at high concentrations⁷. Moreover, these methods are not very effective for biocompatible surface active substances that are difficult to degrade biologically; and there is a possibility that the products formed as parting agents are toxic.

In the recent years, environmental regulations have begun to be stricter due to the increased sensitivity towards ecological risks and health regarding environmental pollu-

tion. Therefore, advanced treatment technologies have been developed to meet these rules, for the treatment of wastewaters containing difficult-to-decompose and/or toxic contaminants⁸. One of these promising technologies is supercritical water oxidation (SCWO). During the process, organic matter reacts with oxygen at conditions exceeding the critical point of water (374 °C and 22.1 MPa). Under these circumstances, water behaves as solvent with a low polarity, in which molecular oxygen and organic compounds are completely miscible. Its diffusivity increases and viscosity decreases, causing increased thermal reaction rates. At temperatures of near-critical and supercritical region, H_3O^+ and OH^- ions are formed due to the self-dissociation of water^{9–11}. Therefore, water can behave as a catalytic precursor for acidic or basic reactions. What is more, since organic compounds have complete miscibility and a very high solubility in supercritical water, chemical reactions with high efficiencies and without interfacial transport limitations can be obtained. Therefore, supercritical water oxidation can rapidly and efficiently decompose organic substances into carbon dioxide and water, in very short reaction times^{12,13}.

In literature, up to our current knowledge, there is no study regarding the treatment of detergent industry wastewaters by supercritical water oxidation. Therefore, aiming to contribute to the deficient knowledge regarding this area, this study presents the results of our research regarding the treatment of detergent industry wastewaters by supercritical water oxidation. The studies were carried out by using hydrogen peroxide as the oxygen source. The experiments were carried out in the temperature range of 400–600 °C and for the reaction time range of 60–150 s, at a constant pressure of 25 MPa. The effects of temperature, reaction time and oxidant use on the total organic carbon contents of the liquid effluents, therefore on the treatment efficiencies were examined.

Materials and methods:

Materials: The detergent wastewater was supplied from a detergent factory located in Çerkezköy (Turkey) and used without further processing. During the experiments, it was used without diluting after being roughly filtered. The some characteristic properties of the detergent wastewater are given in Table 1. Hydrogen peroxide was used as the oxygen source during the SCWO experiments. The feed solu-

Table 1. The characteristics of the detergent wastewater

Parameter	Value
Chemical Oxygen Demand (mg O_2 /L)	8600
Total Organic Carbon (mg/L)	3112
Inorganic Carbon (mg/L)	30.11
Total Carbon (mg/L)	3142
Total Nitrogen (mg/L)	22
Total Phosphorus (mg/L)	1.04
Anionic Surfactants (mg/L)	67
Total Suspended Solids	375
pH	8.45

tions were prepared by diluting a 30 weight % hydrogen peroxide solution (J. T. Baker) with deionized water to the desired concentrations.

Apparatus and procedure: The SCWO experiments were performed in a coiled tubular reactor system as shown in Fig. 1. The experimental apparatus consist of a coiled tubular reactor (137 cm length×3.05 mm i.d.), the wastewater pre-heating line (50 cm×3.05 mm i.d.) and the oxidant pre-heating line (100 cm×3.05 mm i.d.), which are placed into a PID controlled split furnace (Protherm, model SPT 11/70/750). From the feeding pumps to the gas-liquid separator, all wetted parts of the system were made of 316 SS. The wastewater and oxidant are pumped into the furnace through 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, H_2O_2 decomposes to oxygen and water completely as verified in previous works¹⁴. After exiting the furnace, the effluent is cooled rapidly by passing through a heat exchanger, and the reaction stops immediately. The possible solid particles in the effluent, which would be formed, are removed with a 0.5 μm inline filter before the stream is depressurized by a back-pressure regulator (BPR) (GO Regulator Inc.). The system pressure is maintained at 25 ± 0.1 MPa by the BPR. Then the product stream is separated into liquid and vapor phases under ambient conditions and liquid products are collected in a graduated cylinder.

The concentrations of the wastewater and liquid phase reactor effluents were characterized in terms of total organic carbon concentration (TOC). TOC analyses were performed using a total organic carbon-total nitrogen analyser (HACH-

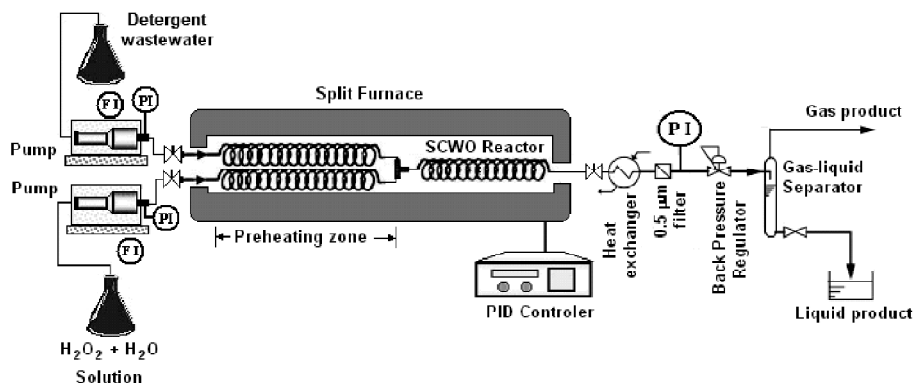


Fig. 1. The experimental setup for the SCWO experiments.

LANGE IL550 TOC-TN). Physicochemical properties of the wastewater such as chemical oxygen demand (COD) and total suspended solids (TSS) were determined according to the standard methods¹⁵.

Results and discussion

The effect of temperature and reaction time: In order to see the temperature effect without using any oxygen source, hydrothermal treatment of the detergent wastewater was performed at supercritical conditions, before the oxidative treatment. The experiments were carried out in temperature values between 400°C and 600°C, at a constant pressure of 25 MPa, and for a reaction time of 20 s. The treatment efficiency was measured in terms of TOC removal. As seen from Fig. 2, temperature is an important factor on the degradation of organic molecules in the wastewater. The treatment efficiency based on TOC removal is increasing with increasing temperature, even though an oxidant was not used. While 61% of the organic carbon was removed at the temperature

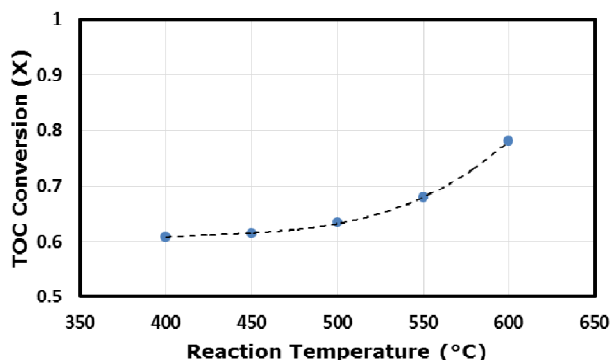


Fig. 2. The change of TOC conversion with reaction temperature during the hydrothermal treatment.

of 400°C, it was 79% at 600°C.

The SCWO treatment employed to the detergent wastewater was performed at five different temperatures (400, 450, 500, 550 and 600°C) and five different reaction times (from 20 s to 60 s), by using 0.5:1 O₂ oxidant per required O₂ ratio (O₂/COD), at a constant pressure of 25 MPa. A low oxidant concentration was chosen, since it was seen in the preliminary studies that the treatment efficiency was greatly enhanced by the use of oxidants at elevated concentrations. This enhancement was so great that neither temperature, nor reaction time effects could be clearly investigated. Fig. 3 shows the change of TOC conversions of the liquid effluents obtained during SCWO experiments, with respect to reaction temperature and time. As it can be seen from the figure, temperature had a much higher impact on the treatment efficiency of the detergent wastewater than that of reaction

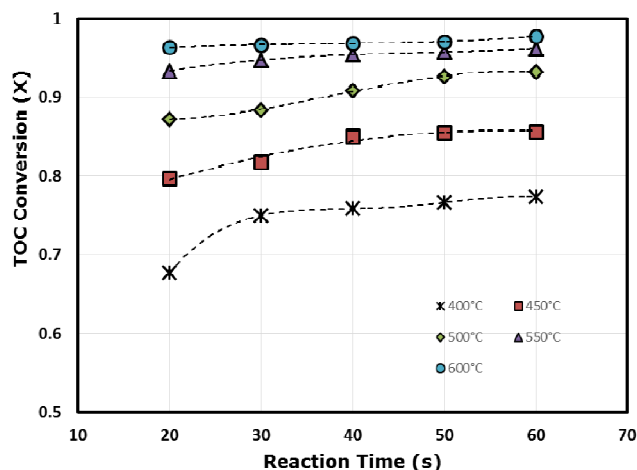


Fig. 3. The change of TOC conversion of the liquid effluents with reaction temperature and time.

time. At 400°C and 20 s of reaction time, the treatment efficiency was found to be 67.7%. This value increased to 77.4% as the reaction time increased to 60 s. Considering elevated temperatures on the other hand, TOC conversions increased from 96.4% to 97.8%, as the reaction time increased from 20 s to 60 s, at 600°C.

The effect of oxidant use: Another series of experiments were performed to see the effect of oxidant concentration on the treatment efficiency, the results of which are presented in Fig. 4. The experiments were conducted at 500°C, for a reaction time of 20 s. 500°C was preferred as the reaction temperature for this set of experiments, as the TOC conversions were close to each other at elevated temperatures and relatively small at lower temperatures. The oxidant concentrations investigated were 0.5:1, 1:1, 1.5:1, 2:1 and 2.5:1 O₂/COD. Fig. 4 clearly presents the effect of oxidant use, as TOC conversions increased from 87.2% to 97.2%, as the oxidant concentration was 2.5 times increased.

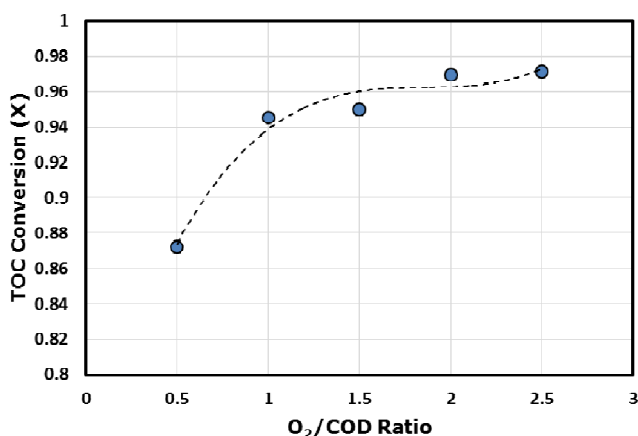


Fig. 4. The effect of O₂ on TOC conversions of the liquid effluents.

Kinetic evaluation of the SCWO of detergent industry wastewater: The change of TOC conversion of the liquid effluents with temperature and time had been presented in Fig. 3. Accordingly, the carbon conversion can be calculated as below:

Carbon conversion (%) =

$$\left\{ 1 - \frac{\text{TOC in liquid phase} \left[\frac{\text{mg}}{\text{L}} \right]}{\text{TOC in feedstock} \left[\frac{\text{mg}}{\text{L}} \right]} \right\} \times 100 \quad (1)$$

The catalytic decomposition taking place in supercritical water can be described as follows:

$$-\frac{d[C_n]}{dt} = k_0 \exp(-E_a/RT)[C_n]^\alpha [O_2]^\beta [H_2O]^\gamma \quad (2)$$

where [C_n], [O₂] and [H₂O] are the concentrations of the reactant, oxygen and water in mmol/L, respectively. α, β and γ represent the reaction orders, E_a is the activation energy and k₀ is the pre-exponential factor that are received from Arrhenius equation.

The experimental data show that water had a role either as a reactant or a reaction media in supercritical conditions. However, since the water amount in the reaction medium was generally greater than 98%, the reaction order term γ in eq. (2) becomes 0 and the effect of H₂O concentration changes is neglected. In terms of TOC, the expression for the reaction rate becomes as follows:

$$-\frac{d[\text{TOC}]}{dt} = k_0 \exp(-E_a/RT)[\text{TOC}]^\alpha [O_2]^\beta \quad (3)$$

After eq. (3) is rearranged with respect to TOC conversion term expressed in eq. (1), the reaction rate can be expressed as:

$$\frac{dX}{dt} = k_0 \exp(-E_a/RT)[\text{TOC}]_0^{\alpha-1} [1-X]^\alpha [O_2]_0^\beta [1-X]^\beta \quad (4)$$

Under supercritical conditions, the initial TOC and O₂ concentrations at the entrance of the reactor were calculated from measured feedstock concentrations:

$$[\text{TOC}]_0 = \frac{C_{\text{TOC}}}{12} \cdot \frac{F_{\text{land}/1u}}{F_T} \cdot \frac{P_{\text{SC}(P/T)}}{\rho_L} \quad (5)$$

$$[O_2]_0 = \frac{H_2O_2}{2} \cdot \frac{F_{[H_2O_2]}}{F_T} \cdot \frac{P_{\text{SC}(P/T)}}{\rho_L} \quad (6)$$

In eq. (5), C_{TOC} and [TOC]₀ are the feedstock and initial reactant concentrations in mg/L and mmol/L, respectively. In the calculation of the initial concentration of the oxidant, H₂O₂ concentration is divided by two in eq. (6), because 1 mol of H₂O₂ is decomposed into 0.5 mol of O₂ and 1 mol of H₂O. If eq. (4) is rearranged with respect to the TOC conversion term X, using the initial condition X = 0 at reaction time t = 0, it can be solved analytically to provide eq. (7);

$$X = 1 - [1 + (\alpha + \beta - 1)k_0 \exp(-E_a/RT) [\text{TOC}]_0^{\alpha-1} [\text{O}_2]_0^\beta \tau]^{1/(1-\alpha-\beta)} \quad (7)$$

A multiple regression analysis (STATISTICA v6.0) was used to estimate the kinetic parameters k_0 , E_a , and the reaction orders α and β , in order to predict the reaction rate. The best-fit values were obtained by minimizing the sum of the squared differences of the experimental conversion and the predicted conversion for all data points. Using this procedure and taking all the data points into consideration, regarding the best-fit global rate expression for the SCWO of detergent industry wastewater, α was found as 0.97, β was found as 0.50, k_0 and E_a were calculated as 0.1 L/mol.s and 16513.39 J/mol, respectively. A comparison between the predicted and experimental TOC conversions is also shown in Fig. 5. As it can be seen from the figure, the dashed lines that indicate a deviation of $\pm 5\%$ conversion from the 45° line

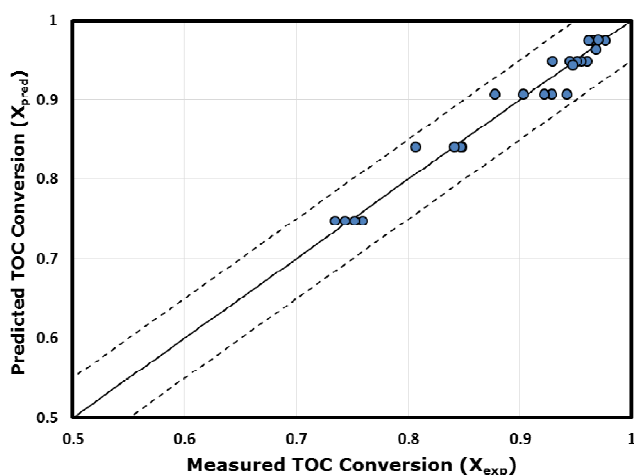


Fig. 5. Comparison between the predicted and experimental TOC conversions.

contain most of the data points. Hence, it can be said that the proposed model fits satisfactorily with our experimental data.

Conclusions

The present study aimed to investigate the supercritical water oxidation of detergent industry wastewaters. The experiments were made at five different temperatures (between 400 and 600°C) and at five different reaction times (between 20 and 60 s), at a constant pressure of 25 MPa. Moreover,

the effect of oxidant concentrations with 0.5:1, 1:1, 1.5:1, 2:1 and 2.5:1 O_2/COD ratios was examined. It was seen that temperature had a greater impact on treatment efficiency than that of reaction time. For an 0.5:1 O_2 oxidant per required O_2 ratio, a treatment efficiency up to 97.8% was obtained at a temperature of 600°C and reaction time of 60 s. Besides, the kinetic evaluation the SCWO of the wastewater was also accomplished. Hence, it can be concluded that SCWO is a very effective method for the treatment of detergent industry wastewaters, in very short reaction times.

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