

Treatment of desizing wastewater from the textile industry by wet air oxidation

LEI Le-cheng^{*}, SUN Yuan

(Department of Environmental Science and Engineering, College of Chemical Engineering, Zhejiang University, Hangzhou 310027, China. E-mail: lclei@mail.hz.zj.cn)

Abstract: This paper describes the application of wet air oxidation to the treatment of desizing wastewater from two textile companies. A two-liter high temperature, high pressure autoclave reactor was used in the study. The range of operating temperatures examined was between 150 and 290°C, and the partial pressure of oxygen ranged from 0.375 to 2.25 MPa. Variations in pH, COD_{Cr} and TOD content were monitored during each experiment and used to assess the extent of conversion of the process. The effects of temperature, pressure and reaction time were explored extensively. More than 90% COD_{Cr} reduction and 80% TOC removal have been obtained. The results have also been demonstrated that WAO is a suitable pre-treatment methods due to improvement of the BOD₅/COD_{Cr} ratio of desizing wastewater. The reaction kinetics of wet air oxidation of desizing wastewater has been proved to be two steps, a fast reaction followed by a slow reaction stage.

Key words: wet air oxidation; wastewater treatment; textile wastewater

Introduction

Wastewater discharged from textile desizing processes is characterized by its very high chemical oxygen demand(COD_{Cr}) and is one of the most difficult textile wastewater to treat. The desizing wastewater from natural fibre processing operations mainly contains starch, glucose, surfactant and auxiliary and has a COD_{Cr} value of 10000 to 20000 mg/L and biological oxygen demand(BOD₅) from 5000 to 10000 mg/L. Man-made fibre desizing wastewaters typically have polyvinyl alcohol(PVA) as the major content, at COD_{Cr} levels of between 10000 and 40000 mg/L as well as a relatively small amount of BOD₅ (500 to 1000 mg/L). The low BOD₅/COD_{Cr} ratio means that this kind of wastewater is very difficult to biodegrade.

In selecting an appropriate treatment method, four processes were considered. Chemical oxidation, i. e. adding strong oxidizers such as ozone and hydrogen peroxide to the wastewater at ambient temperature and pressure was examine first. Typical chemical oxidation processes are relatively simple to operate but only really cost-effective for pollutants at low concentrations, i. e. they would be expensive for high COD_{Cr} wastes such as those from desizing operations. Biological oxidation is an established treatment system for biodegradable pollutants such as starch and glucose, but it is often prohibitively expensive due to its high oxygen supply and large space requirement. Furthermore, the traditional biotreatment process is not suitable for high COD_{Cr} levels(above about 10000 mg/L) and the large quantities of sludge produced by biotreatment impose further problems. Incineration may convert the pollutants effectively to innocuous end products, however, it has been shown that such a process will not be economically attractive unless the COD_{Cr} of the waste is above 100000 mg/L. Wet air oxidation(WAO), which mineralizes pollutants at elevated temperatures and pressures, has the ability to convert most organic and inorganic compounds into carbon dioxide, water and mineral acids. A high pressure is required to maintain water in the liquid state and to provide enough dissolved oxygen. Since it can also achieve very high conversion rates, the wet oxidation process typically requires much less space and produces much lower quantities of secondary pollutants compared with more traditional technologies (Baillod, 1982; Vedprakash, 1995; Levec, 1990; Dietraich, 1985; Randall, 1980). Moreover, the biodegradability for

^{*} Corresponding author

refractory wastewater can be significantly improved during the WAO treatment process. Thus the wet air oxidation process might be an economically feasible alternative method for the treatment specially for the pretreatment of desizing wastewater.

1 Experimental

A schematic of the wet air oxidation(WAO) system used for the present investigation is shown in Fig. 1. There are three major elements in the WAO apparatus—the wastewater feed, the gas mixing system and the two liter high-temperature, high-pressure reactor. The reactor is equipped with a stirrer for mixing and with an electric heating jacket and an internal water cooling coil to control reaction temperature.

The operating procedures were as follows: First the reactor was preheated to 60–70°C. The wastewater was then charged into the reactor using the water pump. Pure nitrogen was used of purge the air inside the reactor at a total pressure of 1 MPa for two minutes after which the system was isolated. The reactor was heated to the desired reaction temperature (between 150 and 290°C) which took between one and two hours. Once the selected reaction

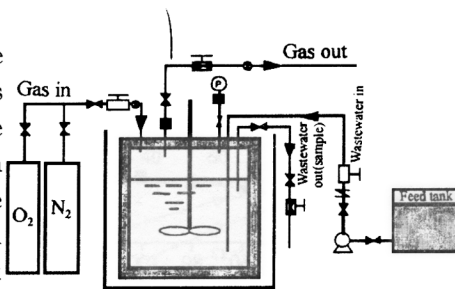


Fig. 1 Schematic of the wet air oxidation system

temperature was reached, pure oxygen was introduced into the reactor and the reaction was assumed to start (time $t = 0$). At designated time intervals thereafter, liquid samples were taken from the reactor and analyzed for COD_{Cr} , BOD_5 , total organic carbon (TOC) content and pH. At the end of the reaction time, the heating jacket was turned off and the reactor was cooled for half an hour. Tap water was then passed through the cooling coil to further cool the reactor to 60–70°C. Pure nitrogen was passed through the reactor to discharge the treated wastewater. The reactor was filled with deionized water and the stirrer was operated at 1000 r/min for 5 minutes. This final step was repeated three or four times until the discharge water was visually clean.

The operating temperature employed for these studies varied between 150°C and 300°C, and the partial oxygen pressure ranged from 0.375 MPa to 2.25 MPa. In each experimental run 1400 ml of the desizing wastewater, was pumped into the reactor. The desizing wastewaters investigated in this study were provided by two textile companies. The first was from a cotton desizing process and the second was from a man-made fibre desizing process. Chemical oxygen demand (COD_{Cr}) is assayed with HACH-DR 2000 COD direct reacted spectrophotometer. The analytical agent, which consists of 0.05g HgSO_4 , 2.5 ml 98% H_2SO_4 , 0.5 ml 1mol/L $\text{K}_2\text{Cr}_2\text{O}_7$, is mixed with 2 ml wastewater sample and incubated at 150°C for 2h. COD_{Cr} is then assayed after cooling down with the COD analyzer. TOC was determined by a SHIMADU TOC-5000 analyzer and the method for

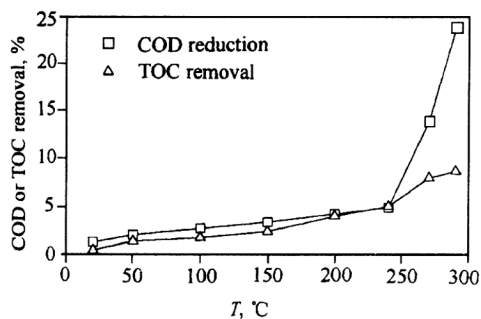


Fig. 2 COD_{Cr} and TOC reduction during the reactor heating time for cotton desizing wastewater

quantification of BOD_5 was adopted from the standard using traditional 5 days culture.

2 Results and discussion

Since heating the reactor to the desired reaction temperature took from one to two hours, the COD_{Cr} and TOC variations during the heating period in the absence of oxygen were examined first. Fig. 2 shows the COD_{Cr} and TOC reductions of the cotton desizing wastewater when it was heated from ambient temperature to 290°C. The initial COD_{Cr} , BOD_5 and TOC values for the cotton desizing wastewater were 10280 mg/L, 3754 mg/L and 3558 mg/L, respectively. The reduction or removal is

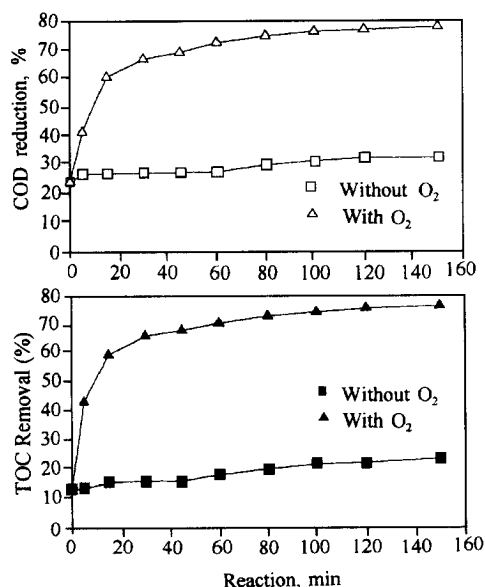


Fig. 3 Effect of oxygen on the WAO of cotton desizing wastewater at 290°C

defined as the difference between the initial COD_{Cr} or TOC value and its value at a given time divided by its initial amount. It was seen that there was very little change in COD_{Cr} or TOC when the temperature was below 240°C. When the wastewater was further heated to 290°C, there was a significant COD_{Cr} reaction. A COD_{Cr} reduction of 24% and a TOC removal of 8% can be achieved by simple thermal decomposition at 290°C (Skaates, 1981). This is the reason why the COD_{Cr} or TOC reduction at zero reaction time has a finite number instead of zero in the following figures.

However, by keeping the reactor at 290°C for a longer time-up to 150 minutes-little further reduction in COD_{Cr} or TOC was observed in the absence of oxygen, as shown in Fig. 3. Fig. 3 also shows that a significant increase in both COD_{Cr} and TOC removal (over 75%) was observed in the presence of oxygen at a partial pressure of 1.5 MPa-which is twice the required stoichiometric amount to mineralize the organic carbon

in the cotton desizing wastewater. This implies that the organic compounds in the cotton desizing wastewater are relatively stable to heating but can be oxidized by oxygen at high temperatures.

The effect of reaction temperature on the performance of the WAO system was studied by carrying out further experiments at temperatures of 150, 200, 240, 270 and 290°C, while keeping the oxygen partial pressure fixed at 1.5 MPa. The COD_{Cr} and TOC reduction percentages versus the reaction time are plotted in Fig. 4 for different reaction temperatures. As anticipated, both the COD_{Cr} and TOC reduction rates were seen to increase with increasing reaction temperature.

The effect of the partial pressure of oxygen in the reactor is shown in Fig. 5. Five oxygen partial pressure levels, 0.375, 0.75, 1.125, 1.5 and 2.25 MPa, were studied. The reaction temperature was kept constant at 240°C. Once again, as intuitively expected, faster COD_{Cr} and TOC removal rates were obtained at a higher oxygen partial pressure probably due to the high dissolved oxygen concentration in the reaction solution.

Having shown WAO to be a useful tool in the treatment of cotton desizing wastewater, its applicability to the treatment of desizing wastewater from a man-made fibre processing operation was examined. The initial COD_{Cr} , BOD_5 and TOC values of this wastewater were 12600 mg/L, 620 mg/L and 3824 mg/L, respectively. The extremely low $\text{BOD}_5/\text{COD}_{\text{Cr}}$ ratio (0.05) implies that this wastewater is very difficult to be treated by biological methods. Fig. 6 shows the effect of temperature on the WAO treatment of this wastewater at an oxygen partial pressure of 2 MPa and four different reaction temperatures. A higher oxygen pressure (2 MPa) was used here because the chemical fibre desizing

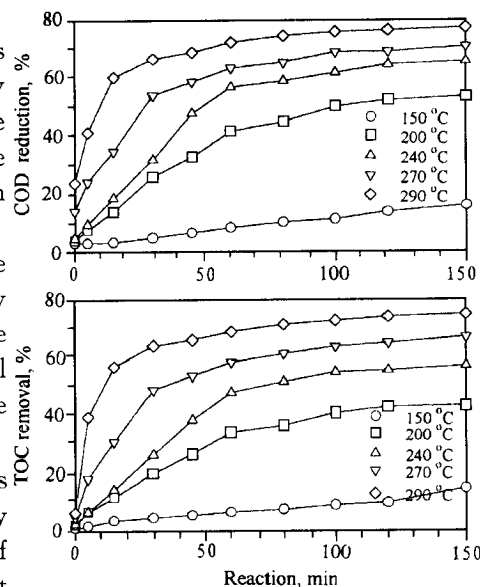


Fig. 4 Effect of reaction temperature on the WAO of cotton desizing wastewater at 1.5 MPa partial oxygen pressure

wastewater had a large COD_{Cr} value so more oxygen was required to completely oxidize the waste content. The choice of 2 MPa was again based on providing the system with twice the required stoichiometric amount to mineralize the organic carbon in the wastewater. Similar to cotton desizing wastewater, the COD_{Cr} and TOC removals were improved by increasing reaction temperature. At 270°C, 90 % COD_{Cr} reduction and 80 % TOC removal were achieved after two hours.

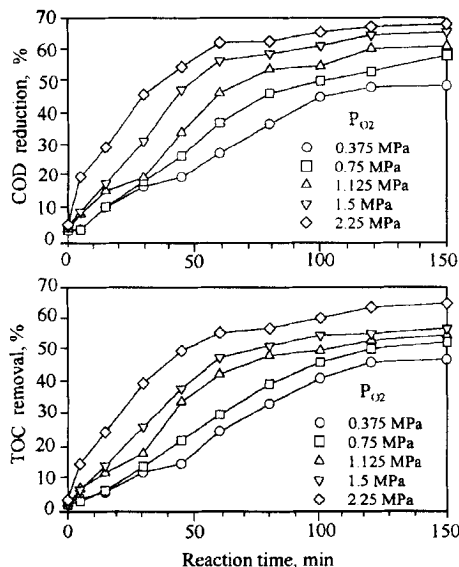


Fig. 5 Effect of reaction pressure on the WAO of cotton desizing wastewater at 240°C

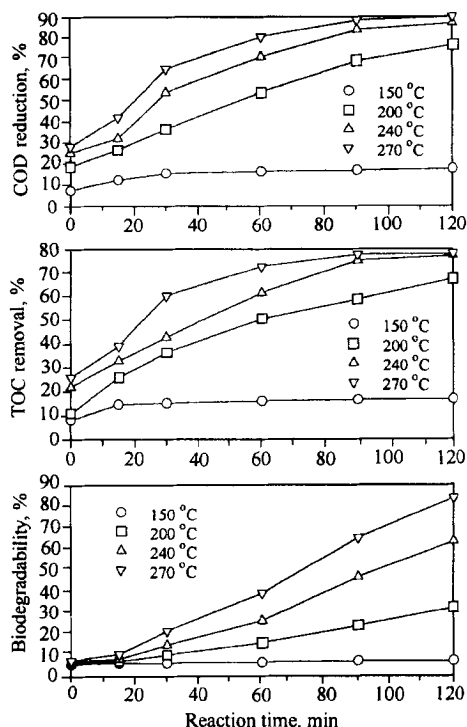


Fig. 6 Effect of reaction temperature on the WAO of chemical fibre desizing wastewater at 2 MPa partial oxygen pressure

Fig. 6 also shows the biodegradability change for the man-made fibre desizing wastewater. The biodegradability is defined as the BOD_5 to COD_{Cr} ratio. After the WAO treatment, the biodegradability was significantly enhanced—more than 80 % was obtained at a reaction temperature of 270°C for two hours. An increase in the reaction temperature helps to enhance the biodegradability of wastewater. The increase in BOD_5 to COD_{Cr} ratio is due to the decomposition of the large relatively biologically stable molecule (PVA) into smaller more biodegradable molecules. This suggests that WAO should be a suitable pre-treatment step before biological degradation.

As previously shown in Fig. 1 for the natural fibre desizing wastewater, some degree of thermal decomposition was also observed for this system. Once again, different initial COD_{Cr} and TOC reductions were observed at different reaction temperatures (Fig. 4 and 6). However, the biodegradability could not be improved by simply heating the wastewater. This is evident from Fig. 6 where the BOD_5 to COD_{Cr} ratios have the same initial value for different reaction temperatures.

3 Reaction kinetics

The reactions during WAO are very complex in terms of many intermediate and ultimate products (Hao, 1993). No attempt is made to provide a detailed reaction analysis on individual compounds. Instead a brief discussion on the kinetics study of COD_{Cr} reduction will be given. Since

the reactor was well stirred and the oxygen supply was maintained twice in excess of the stoichiometric requirement, the mass transfer controlled regime is eliminated and the dissolved oxygen concentration is assumed constant for a given partial oxygen pressure. The rate data were modeled by first order kinetics as in the following equation, with the "reactant" concentration given as $\text{COD}_{\text{Cr}}(C)$:

$$-\frac{dC}{dt} = kC, \quad (1)$$

where t is reaction time, and k is the specific reaction rate constant which has the following temperature dependency:

$$k = k^0 \exp(-E/RT), \quad (2)$$

where k^0 is a pre-exponential factor, E is the activation energy, R is the universal gas constant and T is the temperature in Kelvin. Integrating Eq. (1) gives:

$$\ln\left(\frac{C_0}{C}\right) = kt, \quad (3)$$

where C_0 is the initial COD_{Cr} value. By plotting $\ln(C_0/C)$ versus time, the slope is the specific reaction rate constant k . A typical plot of the WAO treatment of cotton desizing wastewater at a fixed partial oxygen pressure of 1.5 MPa and four different reaction temperature (Fig. 4) is shown in Fig. 7. The data fit is well into two straight lines of a given temperature, indicating that oxidation proceed in two distinct steps: a fast initial reaction of large molecules decomposed into intermediate products, followed by a slow reaction of further oxidizing the intermediate products into end products of low molecular weight organic acids, carbon dioxide, and water.

To calculate the activated energies, Eq. (2) was transformed into a logarithmic form, which is plotted in Fig. 8. As expected, the rate constant increases with increasing temperature, but this temperature effect is more significant for the fast reaction step. As the slow reaction, the reaction rate is not very sensitive to the change of temperature. This indicates that the fast reaction has a high activation energy, while the slow reaction has a small activated energy. The calculated activated energies are $E_{\text{fast}} = 30 \text{ kJ/mol}$, $E_{\text{slow}} = 9.2 \text{ kJ/mol}$.

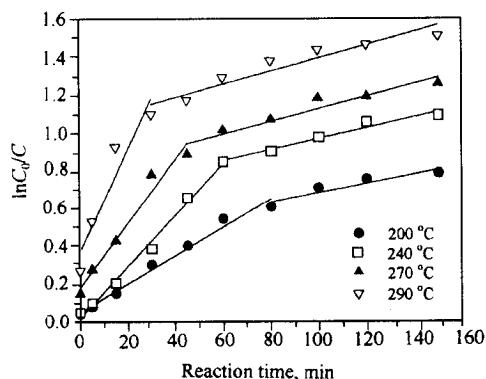


Fig. 7 WAO of cotton desizing wastewater at 1.5 MPa partial oxygen pressure

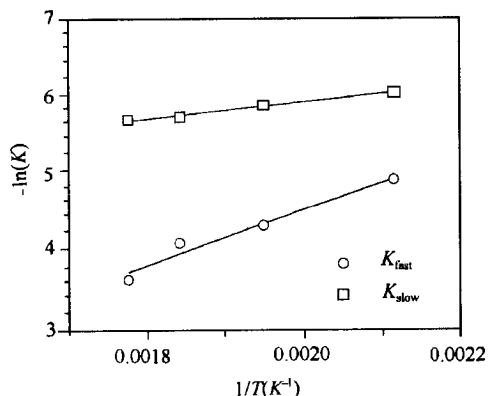


Fig. 8 Effect of temperature on rate constants of cotton desizing wastewater at 1.5 MPa partial oxygen pressure

It should be remembered that the rate constant in Eq. (1) is the product of the true specific rate constant and the dissolved oxygen concentration in water which is a function of the partial oxygen pressure, i. e.

$$k = k' [P_{\text{O}_2}]^n. \quad (4)$$

The rate constant k can be reasonably assumed as constant for a given oxygen partial pressure only when oxygen is in a large excess. Otherwise as the partial oxygen pressure changes the rate

constant k may vary. This is shown in Fig. 9 for the WAO of cotton desizing wastewater at 240°C (Fig. 5). The partial oxygen pressure varies from 0.375 to 2.25 MPa. The extracted rate constants versus partial oxygen pressure are shown in Fig. 10.

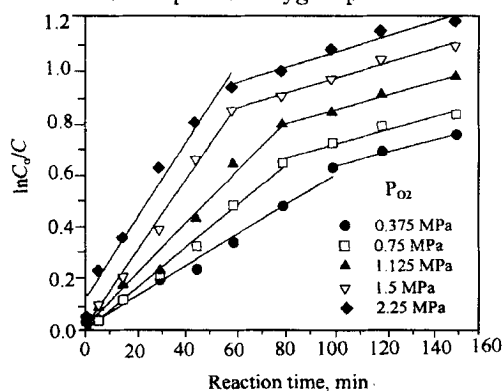


Fig. 9 WAO of cotton desizing wastewater at 240°C

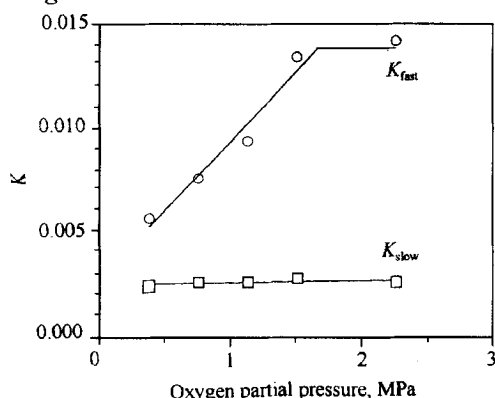


Fig. 10 Effect of oxygen concentration on rate constants of cotton desizing wastewater at 240°C

Since the stoichiometric oxygen requirement from complete oxidation of the cotton desizing wastewater is 0.75 MPa at 25°C, it has a significant effect on the rate constant of the fast reaction if the oxygen partial pressure is less than 1.5 MPa (twice the requirement). However, when oxygen is in a large excess (higher than twice the oxygen demand) the rate constant becomes independent of the partial pressure of oxygen because the dissolved oxygen concentration can be considered as constant in this case. The slow reaction stage has a weaker dependency on the oxygen partial pressure of for the whole pressure region considered indicating that the oxygen requirement of the slow reaction step is much less than that of the fast reaction.

4 Conclusions

Wet air oxidation is an effective process for the treatment of desizing wastewater from the textile industry. More than 90% COD_{Cr} reduction and 80% TOC removal can be obtained by properly choosing the reaction conditions. Increasing the reaction temperature and pressure helps to enhance the WAO efficiency. WAO was also demonstrated to be a suitable pre-treatment method before biodegradation because the BOD₅/COD_{Cr} ratio of desizing wastewater was significantly increased by WAO treatment. A preliminary investigation of reaction kinetics showed that wet air oxidation of desizing wastewater follows two steps, a fast reaction followed by a slow reaction stage.

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