EXPERIMENTAL STUDY OF THE SUPERCRITICAL WATER OXIDATION OF TANNERY WASTEWATERS

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ABSTRACT

Leather industry wastewaters, also known as tannery wastewaters, are considered as a serious environmental threat to receiving surface waters, not only because of the high chemical oxygen demand (COD), but also for the presence of heavy metals such as chromium ions used in the scarcely industrialized manufacturing process. Conventional as well as emerging biological wastewater treatment processes have shown to be ineffective for handling this type of wastewaters, which are practically disposed of in municipal wastewaters systems without any treatment. Accordingly, this work reports on the experimental results of a batch supercritical water oxidation study of real tannery wastewaters in the temperature range 450 to 550 °C, reaction time of 10 to 20 minutes and percent oxidant excess over the stoichiometric amount required for complete oxidation from 100% to 300% at a constant pressure of 400 bar. Organic matter destruction, measured as COD disappearance, was higher than 70% in all the runs and a maximum of 95% was obtained at 550 °C, 20 minutes reaction time and an oxidant excess of 100% over the stoichiometric oxygen demand. The analysis of variance showed a positive effect of temperature and time factors, as well as an interaction between time and oxidant excess, which suggests to carry out further experiments with longer reaction times using lower oxidant excess. In addition to organic matter conversion, removal of toxic chromium ions, initially measured in the raw wastewater at an extremely high concentration of 844 mg/L by means of UV-VIS spectrometry, was higher than 99%.

Keywords: SCWO, tannery wastewaters treatment, COD

1. INTRODUCTION

Tanning industry is often associated to a high contamination potential due to scarcely industrialized process and consequently disposal of untreated effluents with not only a high chemical oxygen demand (COD) but also the presence of toxic heavy metals. Several waste treatment technologies have been proposed for dealing with these complex wastes. However, no single technology has proved to be effective. Table 1 summarizes some of the conventional and advanced oxidation technologies used for treating tannery wastewaters as well as the efficiency, measured as COD disappearance and main limitations which limit their full-scale application.

Table 1. Conventional and advanced oxidation process used for treating tannery wastewaters: efficiency and main limitations

Process	Efficiency (%)	Reaction time	Limitations	Reference
UASB reactors in series	82.4%	12 h	Long reaction times.and high sludge production.	El-Sheikh et al., 2011
SBBGR reactors with O_3	97.5%	8 h	Long reaction times.and high sludge production.	Di Laconi et al., 2009
Electrofenton	99.5%	15 min	High sludge production	Kurt et al., 2006
Ultraviolet oxidation and O_3	12%	12 h	Low efficiency	S.G. Schrank et ál., 2004

The supercritical water oxidation technology or *SCWO* has been suggested as a sound and efficient alternative for dealing with complex residues such as tannery wastewaters. Different research studies have shown efficiencies near 100% in the oxidation of a wide spectra of industrial wastewaters, with practically no byproducts or sludge formation and producing a non-toxic effluent. Conversions near 100% have been obtained in the experimental destruction of several chemical compounds such as polychlorinated biphenyls wastes (PCBs) (Marulanda and Bolaños, 2010) as well as industrial wastewaters (Park et al, 2003). Brunner (2009) reviews the applications of supercritical water with a focus on oxidation reactions. At supercritical conditions water has practically no hydrogen bonds and becomes completely miscible with organic compounds and oxygen, which makes it a perfect media to carry out oxidation reactions without mass transfer limitations and at a high temperature. Accordingly, this work reports on the experimental results of the SCWO of tannery wastewaters in a batch reactor. Temperature, oxidant excess and time were assessed through an experimental design to obtain the optimal reaction conditions, measured as COD disappearance and chromium recovery.

2. EXPERIMENTAL METHODOLOGY

A sample of tannery wastewater was directly taken from the effluent of a tanning industry in the city of Bogotá, Colombia. The initial COD of the taken sample was measured as 17000 mg/L. Experimental runs were carried out in a batch reactor made from high pressure tubing and fittings. A 10 wt % hydrogen peroxide solution, which was regularly titrated with $KMnO_4$ to verify the concentration, was used as the oxidant agent. The volume of wastewater and oxidant solution to inject in the reactor was determined by means of steam tables according to the temperature, pressure and oxidant excess for a specific run in the experimental design.

A 2^k experimental design with the factors temperature (450 and 550 °C), reaction time (10 and 20 min) and oxidant excess (100% and 300%) was conducted to assess the optimal reaction condition measured as the maximum COD disappareance. High and low levels of the factors in the experimental design (-1 and 1) were determined according to previous preliminary experimental. Pressure was kept constant at 400 bar. A full experimental design replicate was run, for a total of 16 runs. Table 2 indicates the resulting treatments according to the established nomenclature for high and low levels of each factor, the measured conversion as COD disappearance and the average mean for each treatment in the experimental design.

Table 2. Treatments and COD disappearance in the experimental runs

Temperature	Time	Oxidant	Run 1	Run 2	Average
-1	-1	-1	75.37	73.83	74.6
1	-1	-1	86.67	89.13	87.9
-1	1	-1	91.72	88.04	89.88
1	1	-1	88.13	93.41	90.77
-1	-1	1	92.1	65.12	78.61
1	-1	1	93.44	86.29	89.865
-1	1	1	79.58	90.86	85.22
1	1	1	94.73	89.9	92.315

3. RESULTS AND DISCUSSION

As shown in Table 2, each treatment in the experimental study resulted in organic matter conversions higher than 75%. In addition, conversion increases with the high level for each factor. An analysis of individual effects, which consists on a graphical assessment of the average effect of each factor in the response of all the runs when this is in the low and high levels was carried out, and the results are shown in Figs. 1, 2, 3, being A the temperature, B the time and C the oxygen excess.

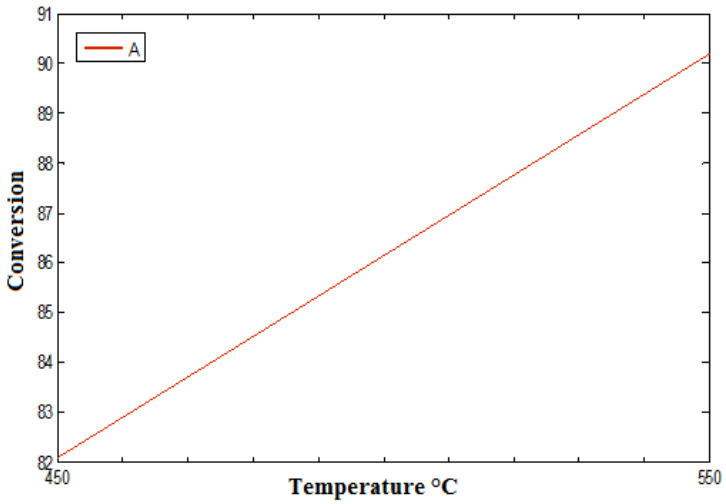

Fig. 1. Effect of Temperature in Conversion

As can be observed in Figs. 1, 2 and 3, the average response increases when each factor moves from the low to the high level. Of the three main effects, the least variation is observed in the oxidant excess, which increases from 85.8 to 86.5 from the low to the high level. It is also observed that even though in the low levels, conversion is higher than 80%. This is due to the proper election of the factors variation, which was based on preliminary runs that were carried out to define the conditions that allow an advanced oxidation of the organic matter.

A similar methodology was implemented to analyze the possible interactions between the factors, by calculating the average of the conversion depending on the level of the assessed factor. The results are shown in Figs. 4, 5 and 6.

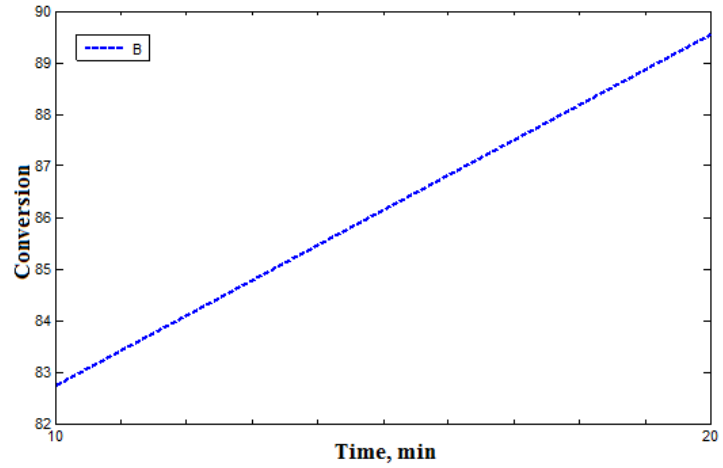

Fig. 2. Effect of Time in Conversion

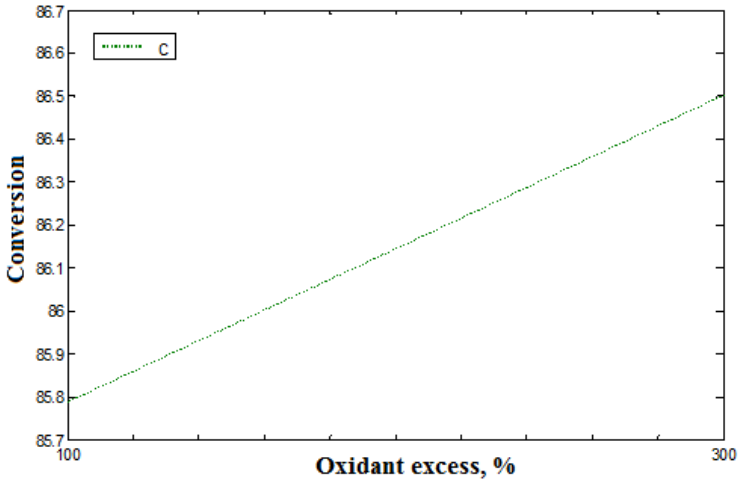

Fig. 3. Effect of Oxidant excess in Conversion

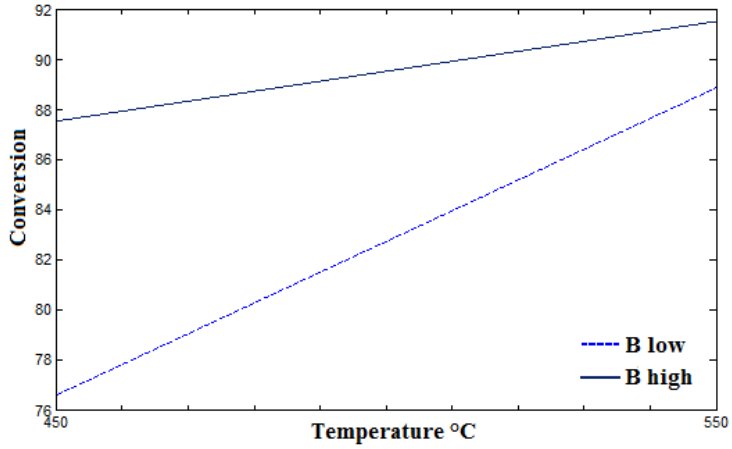

Fig. 4. Effect of Temperature and Time variation in Conversion

The analysis of interactions show similar results to those obtained for individual effects, which means the response is higher in the high levels, except for the interaction of time and oxidant excess in Fig. 6, which suggest that the process could be effectively conducted working at longer reaction times while decreasing the oxidant excess.

Chromium oxide was collected as an insoluble solid residue in the samples, which according to literature (Veriansyah et al., 2007), can be attributed to a change in oxidation state of initially present toxic chromium ions.

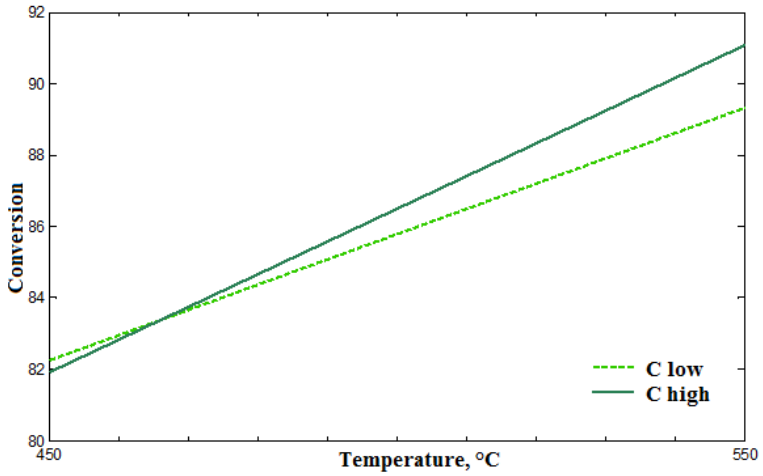

Fig. 5. Effect of Temperature and Oxidant excess in Conversion

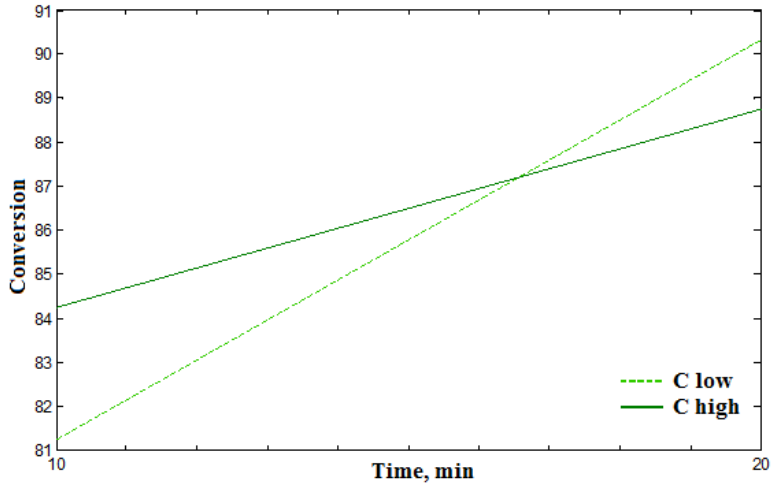

Fig. 6. Effect of Time and Oxidant excess in Conversion

4. CONCLUSIONS

Supercritical water oxidation is a promising technology for implementing and industrial waste treatement operation for handling tannery wastewaters. This technology has not been applied to this type of wastewaters. Further research should be conducted on a continuous reactor in order to assess the feasibility of the process.

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