

# Catalytic Oxidation of Olive Mill Wastewater

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**Abstract**—Catalyst based on Cu supported on 13X zeolite has been prepared and tested for catalytic wet peroxide oxidation of olive oil mill wastewater. The influence of catalyst postsynthesis treatment as well as operating temperature in oxidation process has been studied. The efficiency of the process was evaluated to determine organic compound and total organic carbon reduction. Catalysts' activity decreases when thermally treated catalysts are used in the respect of total phenols oxidation and H<sub>2</sub>O<sub>2</sub> decomposition. The TOC abatement in the CWPO reactions remains unaffected by postsynthesis treatment. The calcined catalyst exhibits significantly higher stability of both active metal component and catalyst's support showing greater resistance to leaching and adsorption of intermediate products.

**Keywords**—Catalytic wet peroxide oxidation, catalytic activity and stability, olive oil mill wastewater, zeolite

## I. INTRODUCTION

**P**RODUCTION of olive oil is traditionally of primary economical importance to the countries of the Mediterranean region. During the extraction process excessive amount of phytotoxic wastewater that contains a number of harmful organic contaminants such as lignin, tannins and especially dangerous phenolic compounds is produced. The presence of these toxic molecules makes olive oil mill wastewater (OOMW) a serious threat to the ecosystems into which it's released, often without prior treatment. Usually, the biological treatment is used for the treatment of wastewater with high content of organic matter. However, these processes are not applicable for the treatment of olive oil mill wastewater due to the presence of phenols and polyphenols and their proven toxicity towards the microorganisms used in the aerobic biological processes. Therefore, in the current research studies that address this issue, the focus of investigation is on developing viable treatment processes that will reduce or eliminate toxic content of the olive oil mill wastewater and improve the biodegradability of such effluents [1-3].

Catalytic wet peroxide oxidation, known as CWPO process

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is one of the methods that can be used for the minimization of phenolic pollution in practice. With the use of catalyst the process can be successfully operated under mild conditions with low energy consumption (atmospheric pressure and temperatures below 353 K). Zeolites modified with copper and other transition metals possess good catalytic properties when compared to the other types of heterogeneous catalysts tested in CWPO reaction. Promising results were obtained during oxidation of phenols, polyphenols, chlorinated phenols, styrene, low molecular carboxylic acids, as well as the significant decrease of COD and TOC when real effluents such as OOMW were used [4-6].

Based on the literature overview and actual trends in scientific research concerning development of new catalytic oxidation processes for treatment of wastewaters burdened with organic pollutants, FAU zeolite (type X) was selected as catalyst support for copper Cu<sup>2+</sup> cations. Activity and stability of such prepared catalysts was tested in catalytic wet peroxide oxidation of olive oil mill wastewater. Influence of reaction parameters and postsynthesis treatment on their catalytic properties was investigated. Acquired experimental data was tested to a proposed kinetic model for total phenols oxidation and hydrogen peroxide decomposition.

## II. EXPERIMENTAL/METHODOLOGY

The catalysts were prepared by ion exchange from commercial 13X zeolite (13X-APG Molsiv™ UOP Italy, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 3.2, w<sub>N<sub>2</sub>O</sub> = 20 wt. %) by conventional method [7]. Postsynthesis thermal treatment consisted in calcination of prepared Cu/13X samples at 1273 K for 5h (ramp 2 K min<sup>-1</sup>) and was conducted in order to obtain zeolite based materials that exhibit higher stability to the loss of active metal component during the reaction.

Textural characterization of the catalyst samples was performed by means of nitrogen adsorption/desorption isotherms at 77 K. Crystalline structures of all prepared catalysts were checked by X-ray diffraction analysis (5° < 2θ < 60° range, step size of 0.02). Stability of used catalysts was monitored through the extent of copper leaching as well as the stability of zeolite support. Copper content on catalyst and in the reaction mixture was determined by EDTA titrimetric method and by atomic absorption spectrometry, while the stability of catalysts' support was checked using XRD analysis.

The catalytic tests were carried out in a glass reactor in batch operation mode equipped with pH meter at atmospheric pressure, constant hydrogen peroxide concentration (0.2 mol

$\text{dm}^{-3}$  catalyst loading ( $25 \text{ g dm}^{-3}$  and stirrer speed (600 rpm). Influence of temperatures (323-343 K) on catalytic activity and stability of prepared catalysts in the catalytic wet peroxide oxidation of olive oil mill wastewater were investigated. The OOMW was supplied by private oily *Olearia Sud S.R.L., Policastro, Crotona, Italy* with following properties at 25 °C: pH 4.1, total phenols concentration of  $4.5 \text{ g dm}^{-3}$  (gallic acid equivalent) and TOC level of  $27.5 \text{ g dm}^{-3}$ . The decreases in total phenols concentration, as well as the decomposition of hydrogen peroxide were analytically monitored by UV-VIS absorbance by standard Folin-Ciocalteu method at 765 nm and ammonium metavanadate method at 450 nm, respectively. Total organic carbon (TOC) was determined with TOC-V CSN Shimadzu analyser from diluted reaction solutions.

### III. RESULTS

In Table 1 physical and chemical properties of prepared catalysts are shown. The incorporation of copper on 13X zeolite did not have a significant effect on the measured surface area and pore volume since the values obtained for 13X and Cu/13X are in good accordance. On the other hand, as shown in Table 1, the thermal treatment caused the decrease of both BET surface area and pore volume.

TABLE 1  
PHYSICAL AND CHEMICAL PROPERTIES OF PREPARED CATALYST

Sample	BET surface area ( $\text{m}^2 \text{g}^{-1}$ )	pore volume, $\text{cm}^3 \text{g}^{-1}$	Cu content, wt %
13X	453,4	0.33	-
Cu/13X	439,2	0.31	8.0
Cu/13Xcalc.1273 K	0.7	<0.01	8.0

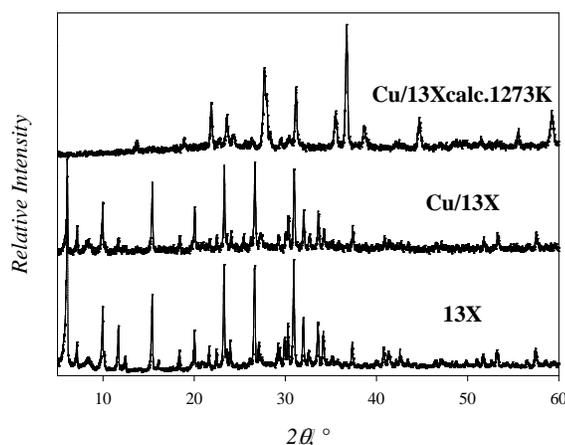


Fig. 1. X-ray diffraction patterns of 13X and Cu/13X samples before and after thermal treatment

The change of physical properties was pronounced in catalyst calcined at 1273 K, which can be attributed to ceramization process that occurs during thermal treatment in the course of which a change in crystalline structure occurs. Copper content of all samples was 8 wt % and was not affected by thermal treatment.

To confirm structure and crystallinity, the samples were studied by X-ray diffraction (Figure 1).

In the XRD patterns of 13X and Cu/13X samples presented in Figure 1, all peak positions matched those reported for the FAU structure and no-impurity phase was observed. No shift in the peak positions and no significant diffraction lines assigned to any new phase are observed. The high intensities of peaks and low background lines suggest high crystallinity of copper bearing 13X zeolite denoting that incorporation of copper into the zeolite framework via ion exchange method does not have an influence on the crystal structure of the zeolite. These results indicate that  $\text{Cu}^{2+}$  ions seem to be well dispersed in the zeolite framework. Copper bearing zeolite calcined at 1273 K exhibit a change in number, intensity, and position of peaks indicating that Cu/13X catalyst undergoes phase transformations: recrystallization of new phase that was identified as nepheline - anhydrous analogue of zeolite. The fact that there is no peak attributable to copper cations implies that the copper is very dispersed into the zeolite framework and that no Cu-containing phase was formed during postsynthesis thermal treatment.

Postsynthesis thermal treatment of Cu/13X catalyst had a profound effect on its physical, chemical and catalytic properties. The activity decreased after calcination showing that structural changes that were expressed through the reduction of pore volume and surface are directly affects the catalytic properties [7] as presented on Fig. 2.

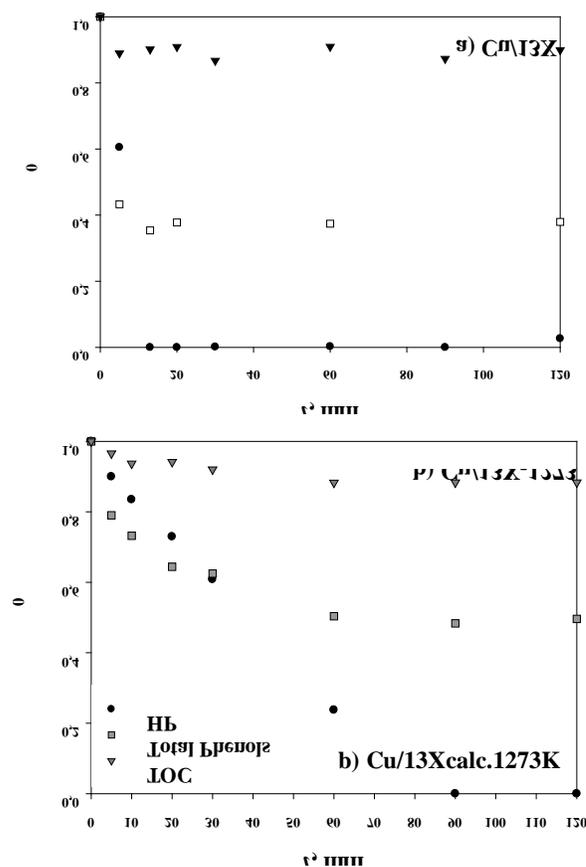


Fig. 2. Activity of prepared catalysts at 343 K: a) Cu/13X before thermal treatment and b) Cu/13X-K1273 after thermal treatment ( $C_{\text{HP},0} = 0.2 \text{ mol dm}^{-3}$ ,  $m_{\text{CAT}} = 25 \text{ g dm}^{-3}$ ,  $N = 600 \text{ rpm}$ )

Even though the hydrogen peroxide decomposition was significantly slowed when Cu/13X-K1273 catalyst was used, the rate of total phenols oxidation and TOC reduction were similar in both cases.

The stability measurements showed that thermal treatment stabilizes the catalyst since the leaching of copper is significantly lower for the calcined catalyst (Fig. 3) in all reactions and at all temperatures.

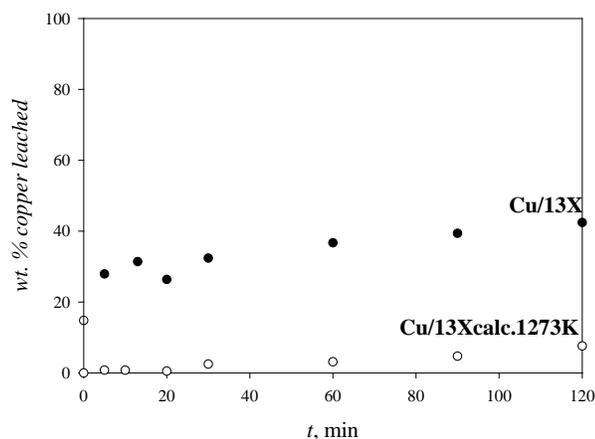


Fig. 3. Stability of calcined and non-calcined catalysts ( $T=343\text{ K}$ ,  $c_{\text{HP},0} = 0.2\text{ mol dm}^{-3}$ ,  $m_{\text{CAT}} = 25\text{ g dm}^{-3}$ ,  $N = 600\text{ rpm}$ )

These results were confirmed by XRD analysis of catalysts' support showing that Cu/13X-K1273 catalyst retains its crystal structure in the CWPO reaction yielding all the major peaks of dominant crystal phase comparable to the catalyst before reaction.

It can be concluded that the promising catalyst in the reaction of olive mill wastewater oxidation with hydrogen peroxide is Cu/13X calcined at 1273 K, because at mild reaction conditions ( $T = 343\text{ K}$ , atmospheric pressure, initial  $\text{H}_2\text{O}_2$  concentration of  $0.2\text{ mol dm}^{-3}$ , and the reaction time of 3 h this catalyst allows complete elimination of phenol and other aromatic compounds with acceptable TOC conversion and without significant leaching of copper ions from the zeolite matrix.

The obtained experimental data was tested to a proposed kinetic model for phenol oxidation, hydrogen peroxide decomposition and TOC reduction.

$$-\frac{dc_{\text{UPh}}}{dt} = k_{\text{UPh}}c_{\text{UPh}}c_{\text{HP}}$$

$$-\frac{dc_{\text{HP}}}{dt} = k_{\text{HP}}$$

$$-\frac{dc_{\text{TC}}}{dt} = k_{\text{TC}}c_{\text{TC}}c_{\text{HP}}$$

The parameters of kinetic model were estimated using the Nelder-Mead method of nonlinear regression in Micromath Scientist program package. The residual sum of squares calculated from the difference between the experimental and predicted concentrations was minimized in the regression.

The rate of phenol oxidation and TOC reduction is first order toward the concentration of phenol and first order toward the concentration of  $\text{H}_2\text{O}_2$ , and the rate of  $\text{H}_2\text{O}_2$  decomposition is zero order. The results of mathematic modelling are presented as lines in Figs. 4 and 5.

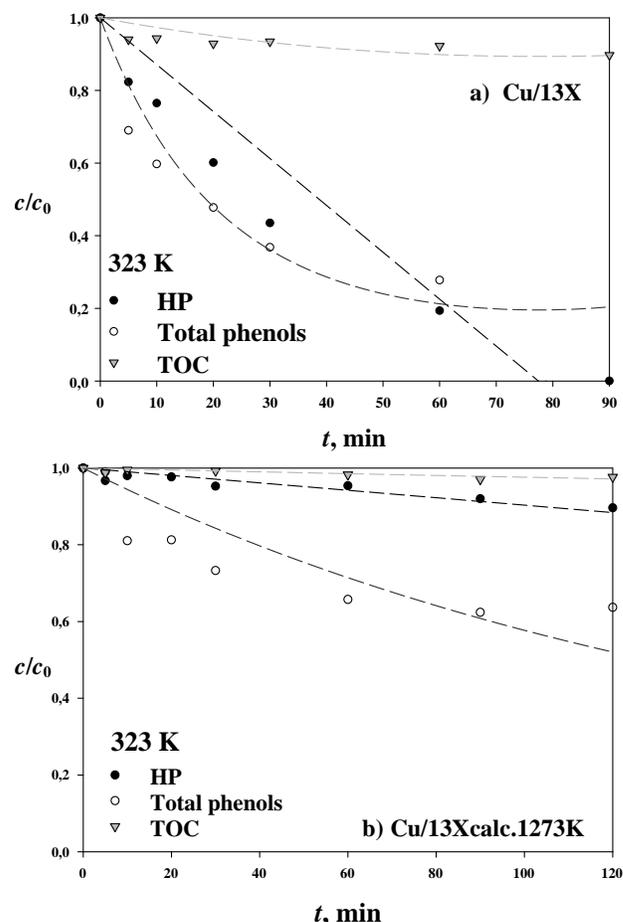


Fig. 4. Activity of prepared catalysts at 323 K: a) Cu/13X before thermal treatment and b) Cu/13X-K1273 after thermal treatment ( $c_{\text{HP},0} = 0.2\text{ mol dm}^{-3}$ ,  $m_{\text{CAT}} = 25\text{ g dm}^{-3}$ ,  $N = 600\text{ rpm}$ )

As can be seen, from Figs. 4 and 5 the proposed model adequately fits the experimental data when the oxidation of olive mill wastewater is performed at different temperatures over fresh and calcined Cu/13X catalysts. As expected, the increase of the reaction temperature considerably increases the reaction rate and the extent of phenols oxidation TOC reduction and hydrogen peroxide decomposition for all catalysts.

For the experiments carried out at different temperatures,  $k$  values are correlated by an Arrhenius-type expression.

TABLE II  
ENERGY OF ACTIVATION FOR PHENOLS OXIDATION, HYDROGEN PEROXIDE DECOMPOSITION AND TOC REDUCTION OVER FRESH AND CALCINED CATALYST

Catalyst	$E_A$ , $\text{kJ mol}^{-1}$		
	$\text{H}_2\text{O}_2$ decomposition	Phenols oxidation	TOC reduction
Cu/13X	83.6	58.4	89.2
Cu/13Xcalc.1273 K	118.8	37.5	92.5

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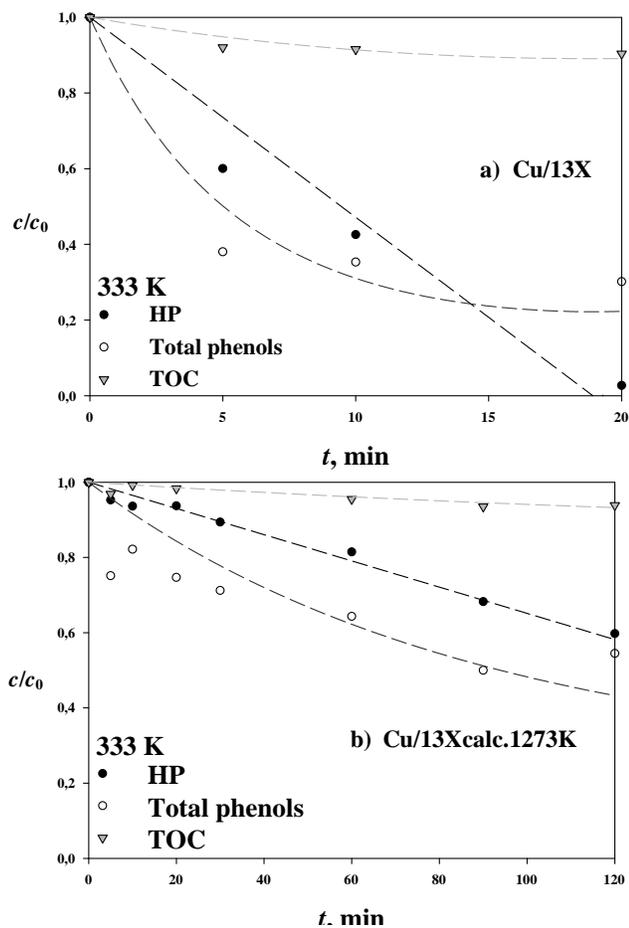


Fig. 5. Activity of prepared catalysts at 333 K: a) Cu/13X before thermal treatment and b) Cu/13X-K1273 after thermal treatment ( $c_{HP,0} = 0.2 \text{ mol dm}^{-3}$ ,  $m_{CAT} = 25 \text{ g dm}^{-3}$ ,  $N = 600 \text{ rpm}$ )

## IV. CONCLUSIONS

Catalysts' activity decreases when thermally treated catalysts are used in the respect of reaction rates of phenol oxidation and  $\text{H}_2\text{O}_2$  decomposition. The TOC abatement in the CWPO reactions for both catalysts remains unaffected by postsynthesis treatment. The calcined catalyst exhibits significantly higher stability of both active metal component and catalyst's support showing greater resistance to leaching and adsorption of intermediate products of reaction. The rate of phenol oxidation, hydrogen peroxide decomposition and TOC reduction increases with the increase of reaction temperature for all catalysts (calcined and non-calcined). The rate of phenol oxidation and TOC reduction is first order toward phenol and  $\text{H}_2\text{O}_2$  concentration. The rate of  $\text{H}_2\text{O}_2$  decomposition is zero order.