Catalytic Wet Peroxide Oxidation of Olive Oil Mill Wastewater over Zeolite Based Catalyst

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Olive oil mill wastewater (OOMW) – the liquid waste generated in the process of olive oil extraction contains significant amounts of phenolics. Their high polluting charges that are measured in BOD_5 and COD levels up to 35 g dm^{-3} and the presence in the concentrations up to 10 g dm^{-3} are of special concern to the environment. These compounds make OOMW biorefractory in nature and unsusceptible to a conventional biological treatment. Reducing their toxicity prior to the conventional treatment is therefore of the uttermost importance. The non-selective catalytic wet peroxide oxidation (CWPO) process is one of the methods that can be used for that purpose in practice. With the use of catalysis the process can be successfully operated under mild conditions with low energy consumption. In this work, the influence of the reaction parameters and the catalyst preparation method on the activity and stability of zeolite (13X) based catalyst in the reaction of hydrogen peroxide oxidation of phenolic compounds present in wastewater from industry for processing olives and olive oil was examined. The reaction was carried out in a batch reactor at different stirring speed, particle sizes, temperatures, catalyst loadings and initial concentrations of hydrogen peroxide. The catalyst Cu/13X was prepared by ion exchange of commercial 13X zeolite. Characterization of the catalyst included N_2 physisorption, XRD, $TPD-CO_2$ and FTIR-Pyridine desorption. In order to increase the catalyst's stability, it was subjected to a thermal post-synthesis treatment at 1273 K. The justification for post synthesis treatment of the catalyst is reflected in the enhanced stability of the catalytically active material which is removed from the carrier, i.e. larger resistance of Cu/13X - K1273 to leaching. Examining the effect of the mixing rates and catalyst particle sizes on reaction rate it was found that the reaction is carried out in the kinetic regime, with the total phenols content diminished by more than 80 % with a 20 % decrease in wastewater's TOC content and leaching below 3 wt. %.

1. Introduction

To this day numerous scientific investigations have been conducted in order to develop new technologies for most effective purification of wastewaters polluted with organic compounds such as phenol and its derivatives (Gogate and Pandit, 2004). Phenols are important industrial chemicals of environmental concern and are some of the major hazardous compounds in industrial wastewater due to their poor biodegradability, phytotoxic and antimicrobial properties, as well as their suspected carcinogenic and mutagenic properties. Phenolic wastewater therefore requires a special consideration prior to its release into the environment. One example of industrial effluent that contains significant amounts of phenolics is olive oil mill wastewater (OOMW) – the liquid waste generated in the olive oil production process. During the extraction process excessive amount of phytotoxic wastewater that contains a number of harmful organic contaminants such as lignin, tannins and polyphenolic compounds is produced. It is estimated that more than 4.6 Mt of olive-mill wastewater is produced each year at the European level alone as reported by Herve (2010). Even though the

European Commission has adopted the legislation that prohibits the release of untreated OOMW into the environment, over 90 % of olive mills releases its wastes directly to streams (58 %), sea (11.5 %) and soil (19.5 %) without any prior treatment. Its high polluting charges that are measured in BOD_5 and COD levels up to 35 g dm^{-3} as well as the presence of phenols that can constitute up to 20 wt. % of total organic content make this wastewaters challenging for treatment. Conventional biological treatment is not applicable for the treatment of OOMW 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 OOMW and improve the biodegradability of such effluents as described by La Cara et al. (2012). Catalytic wet peroxide oxidation (CWPO) process is one of the methods that can be used for that purpose in practice (Giordano et al., 2007). The non-selective oxidation of organic compounds is the consequence of the presence of hydroxyl radicals that are formed during the decomposition of hydrogen peroxide. With the use of catalysis the process can be successfully operated under mild conditions with low energy consumption.

Based on the previously conducted research reported in Maduna Valkaj et.al. (2011), literature overview and current trends in development of new catalytic oxidation processes for treatment of wastewaters burdened with organic pollutants, commercial FAU zeolite (type X) was selected as catalyst support for copper Cu^{2+} cations. Activity and stability of such prepared catalysts was tested in catalytic wet peroxide oxidation of OOMW. Influence of reaction parameters and post-synthesis thermal treatment on their catalytic properties was investigated.

2. Experimental

The catalysts were prepared by ion exchange from commercial 13X zeolite (13X-APG Molsiv™ UOP Italy, SiO_2/Al_2O_3 = 3.2, w_{Na_2O} = 20 wt. %) of different particle sizes by a conventional method as described in paper by Maduna Valkaj et al. (2011). Postsynthesis thermal treatment consisted of calcination of prepared Cu/13X samples at 1,273 K for 5h (ramp 2 K min^{-1}).

Textural characterization of the catalyst samples was performed by means of nitrogen adsorption/desorption isotherms (Sorptomatic 1900, Carlo Erba) at 77 K. The specific surface area calculations were performed using Dubinin´s and B.E.T. equations for microporous and mesoporous samples. Crystalline structures of all prepared catalysts were verified by X-ray diffraction analysis (XRD 600, Shimadzu) using CuKα radiation in the $5° < 2\theta < 60°$ range, step size of 0.02. Copper content on the catalysts were determined by UV/VIS (UV1600PC, Shimadzu) at 270 nm from the copper acetate solutions used during ion exchange. The basicity of the prepared catalysts was investigated using the temperature programed desorption (TPD) of CO_2 (AutoChem 2010, Micromeritics Instruments) according to the method described by Kumar et al. (2012) and Leino et al. (2013). The strength of Brønsted and Lewis acid sites of the catalysts was measured with infrared spectroscopy (ATI Mattson FTIR) using pyridine as a probe molecule. Detailed description of the measurement procedure was provided by Aho et al. (2007).

The catalytic tests were carried out in a 250 cm^3 glass reactor in batch operation mode equipped with pH meter at atmospheric pressure. Influence of different stirring speed (50 – 800 min^{-1}), particle sizes (0.314 – 2.0 mm), temperatures (323 – 353 K), catalyst loadings (0 – 5 g) and initial concentrations of hydrogen peroxide (0 – 1.34 mol dm^{-3}) on catalytic activity and stability of prepared catalysts in the catalytic wet peroxide oxidation of OOMW were investigated. The OOMW was supplied by a private oilery (Dalmatia Region, Croatia) with the following properties at 298 K: pH 4.79, total phenols concentration of 1.8 g dm^{-3} (gallic acid equivalent) and TOC and COD levels of 10.7 g dm^{-3} and 36 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 the standard Folin-Ciocalteau method at 765 nm and ammonium metavanadate method at 450 nm. Total organic carbon (TOC) was determined with TOC-V CSN Shimadzu analyzer from diluted reaction mixture. Stability of the used catalysts was monitored through the extent of copper leaching as well as the stability of the zeolite support. Copper content in the reaction mixture was measured by atomic absorption spectrometry. The structural integrity of the spent catalysts and deactivation of the catalyst due to coke formation were studied by X-ray powder diffraction and N_2 physisorption.

3. Results and Discussion

The results obtained from N_2 physisorption of prepared catalysts are shown in the Table 1. 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, the thermal treatment resulted in the decrease of both specific surface area and pore volume. The change of physical properties is

well pronounced in the catalyst calcined at 1273 K, which can be attributed to structural changes during thermal treatment.

Table 1: Specific surface area and pore volume of prepared zeolite based catalysts

Sample	Preparation method	Copper content, wt. %	Specific surface area, m² g⁻¹	Pore Volume, cm³ g⁻¹
13X-APG Molsiv™	-	-	594 (Dubinin)	0.31
Cu/13X	Ion Exchange	9	618 (Dubinin)	0.34
Cu/13X-K1273-1	Ion Exchange + Calcination	9	26 (B.E.T.)*	0.03

*B.E.T. equation was used because of the mesoporous nature of Cu/13X-K1273-1 catalyst

To confirm structure and crystallinity, the samples were studied by X-ray diffraction and the XRD difractograms are presented in Figure 1a. In the patterns of 13X and Cu/13X all peak positions matched those reported for FAU structure by Treacy et al. (2001). No shift in the peak positions and no significant diffraction lines assigned to any new or impurity phase are observed. The high intensities of peaks and low background lines suggest high crystallinity of copper bearing 13X zeolite meaning that incorporation of copper into the zeolite framework via the ion exchange method does not have an influence on the crystal structure of the zeolite. According to the report from Benaliouche et al. (2008) these results indicate that Cu^{2+} ions seem to be well dispersed in the zeolite framework in the Cu/13X catalyst and that the size of copper particles is below detection limit for XRD measurement (< 2 nm). Copper bearing zeolite calcined at 1,273 K exhibits a change in number, intensity, and position of peaks indicating that upon heating Cu/13X catalyst undergoes phase transformations. In a diffractogram of Cu/13X-K1273-1 catalyst four new crystalline high temperature stabile phases have been identified: magnesium silicate (Mg_2SiO_4), copper oxide (CuO), anorthoclase ($Na_{0.85}K_{0.14}AlSi_3O_8$) and andesine ($Na_{0.685}Ca_{0.347}Al_{1.46}Si_{2.54}O_8$). The change in dominant crystal phases of thermally treated sample is accompanied by a significant drop in the measured surface area and pore volume as presented in Table 1. The size of CuO particles on a Cu/13X-K1273-1 catalyst was estimated from the XRD difractogram using Debye-Scherrer equation using full-width at half maximum (FWHM) from the two main peaks in the spectra attributed to copper oxide (2θ = 35.5 ° and 38.6 °) according to the procedure described by Muhamad et al. (2007). The calculated copper oxide particle size was 26.01 and 25.13 nm for the peaks at 35.5 ° and 38.6 °.
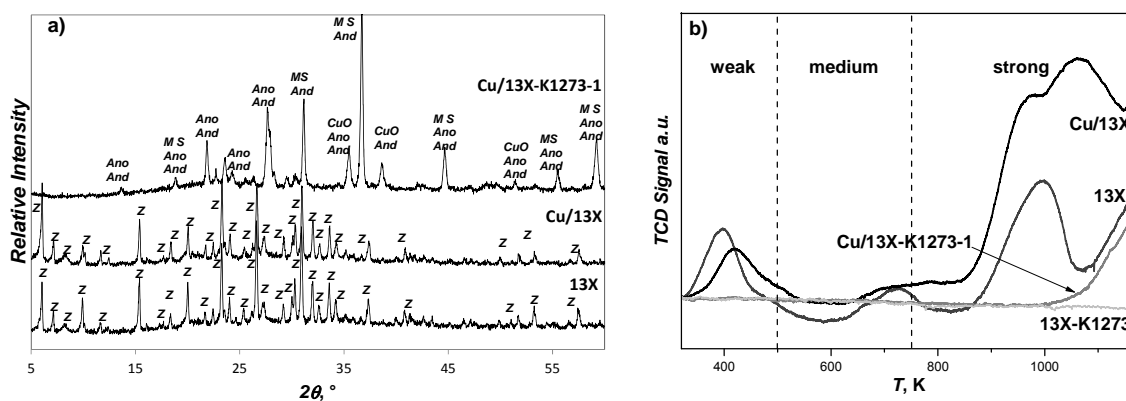

Figure 1: a) XRD difractograms of 13X, Cu/13X and Cu/13X-K1273-1 samples (Z – zeolite, MS – magnesium silicate, CuO – copper oxide, Ano – Anothoclase, And – Andesine) b) CO₂-TPD profiles of 13X, Cu/13X, Cu/13X-K1273-1 and 13X-K1273 samples

During the preparation of catalysts, the influence of incorporation of metal to the zeolite support as well as the influence of postsynthesis thermal treatment on the acid-base properties of parent and copper bearing zeolites has been investigated. Temperature programed desorption of CO_2 was used as a method for evaluation of basicity of the zeolite support (13X), copper zeolite (Cu/13X), calcined copper zeolite (Cu/13X-K1273-1) and the calcined zeolite support (13X-K1273-1). From the CO_2-TPD profiles presented in Figure 1b weak, medium and strong basic sites can be identified in the 13X and copper modified 13X zeolite which correlates with the fact that a sodium form of commercial zeolite was used for the preparation of the catalysts. The incorporation of copper into the zeolite framework gave a significant increase in the total amount of desorbed CO_2 in the

range of strong basic sites (>750K). However, it must be mentioned here that the peaks detected above 1,073 K in the CO_2-TPD profiles of 13X and Cu/13X samples cannot be attributed solely to the desorption of carbon dioxide adsorbed on the strong basic sites due to the thermally induced structural changes of the zeolite support that arise at such high temperatures. On the other hand, CO_2-TPD profile of a high temperature stable Cu/13X-K1273-1 catalyst exhibits the presence of only strong basic sites which can be attributed exclusively to the presence of copper oxide and not the structural changes since the desorption of CO_2 over calcined support without copper (13X-K1273) was not observed. FTIR using pyridine as a probe molecule was used to determine the amount of weak (523 K), medium (623 K) and strong (723 K) Brønsted (1545 cm^{-1}) and Lewis acid sites (1450 cm^{-1}) in the 13X, Cu/13X, Cu/13X-K1273-1 and 13X-K1273 samples. From the calculated data presented in Table 2 it can be observed that the most acidic materials in terms of both Brønsted and Lewis acidity are 13X and Cu/13X in which the Lewis acid sites are more dominant. The Lewis acid sites in these samples can be attributed to the Na^+ that act as Lewis acid sites as suggested by Benaliouche et al. (2008). During the incorporation of copper cations in 13X zeolite in the ion exchange a part of sodium cations are exchanged with the copper cations resulting in decrease of Lewis acidity, and in the same time an increase in the strength of Brønsted acid sites. Thermal treatment of Cu/13X catalyst however, induced a significant decrease in total acidity of the catalyst what is no doubt connected with the structural changes of the material. When compared to acidity of thermally treated support (13X-K1273 K), Cu/13X-K1273-1 catalyst exhibits somewhat higher acidity that can only be attributed to the presence of copper oxide phase. These results are in accordance with the XRD and N_2 physisorption analyses results.

Table 2: Acidity of the prepared catalyst measured by FTIR-Pyridine TPD

Sample	Brønsted acid sites (µmol g^{-1})			Lewis acid sites (µmol g^{-1})		
	523 K (weak)	623 K (medium)	723 K (strong)	523 K (weak)	623 K (medium)	723 K (strong)
13X	25	11	0	274	28	0
Cu13X	47	4	3	183	3	1
Cu13X-K1273-1	10	7	16	8	9	6
13X-K1273	8	7	7	6	5	4

Activity and stability of the prepared catalysts was tested in catalytic wet peroxide oxidation of OOMW under mild reaction conditions. The wastewater was obtained from mechanical green olives processing during the two phase extraction of olive oil from a private oilery in the coastal region of Croatia. Prior to conducting experiments the OOMW was filtered through a 100 µm filter bag and diluted with distilled water in a 1:1 ratio. A preliminary set of experiments was performed in order to investigate the extent of thermal decomposition of OOMW and to compare uncatalyzed and catalyzed peroxidation reactions. In the experiment when only OOMW was heated to 353 K (without the catalyst and without the oxidant) the total phenols content decreased by 21 % after 180 min of heating under agitation. When hydrogen peroxide was added to OOMW the total phenols conversion increased to 51 % with the total organic carbon conversion of 8 %. The presence of a catalyst in the reaction mixture had a significant effect on the reaction rate drastically increasing the rate and the extent of hydrogen peroxide decomposition and total phenols removal as presented in Figure 2a and b. The decomposition of hydrogen peroxide over Cu/13X catalyst proceeds fast resulting in total consumption within the first 30 minutes of the reaction. Oxidation of phenolics proceeds until all oxidant is spent. On the other hand, when the calcined Cu/13X-K1273-1 catalyst was used, the decomposition rate of hydrogen peroxide was slowed down which was accompanied with a prolonged oxidation step of the phenolic compounds. The residual concentrations of total phenols after 180 minutes of the reaction were 140.1 mg dm^{-3} with Cu/13X catalyst (X_{TPh} = 84 %) and 84.7 mg dm^{-3} with Cu/13X-K1273-1 catalyst (X_{TPh} = 88 %). Conversions of total organic carbon content were $X_{TOC, Cu/13X}$= 14 % and $X_{TOC, Cu/13X-K1273-1}$= 18 % confirming the observation about prolonged oxidation with the calcined catalyst. Stability of used Cu/13X and Cu/13X-K1273-1 catalysts was monitored through the extent of copper leaching during the reaction as well as by monitoring the stability of the zeolite support. Even though the XRD difractograms of both catalysts appear very similar before and after reactions (data not presented here) the amount of copper leaching from the catalysts was substantially different: 38 wt. % for the Cu/13X catalyst and only 2 wt. % for the Cu/13X-K1273-1 catalyst. It was found that in the reaction with Cu/13X 24 wt. % of copper leached from the catalyst even before the reaction was initiated with the addition of hydrogen peroxide. These results indicate that the observed catalytic activity should not be attributed solely to the heterogeneous catalysis, but to the leached copper cations as well (homogeneous catalysis). The results of the specific surface area measurements for the spent catalysts additionally confirm the better stability of the thermally treated catalyst ($S_{Cu/13X, FRESH}$ = 618 m^2 g^{-1}; $S_{Cu/13X, SPENT}$ = 434 m^2 g^{-1}; $S_{Cu/13X-K1273-1, FRESH}$ = 26 m^2 g^{-1}; $S_{Cu/13X-K1273-1, SPENT}$ = 24 m^2 g^{-1}).

Subsequent studies were performed with a more stable Cu/13X-K1273-1 catalyst. The influence of stirring speed, particle size, catalyst mass, initial concentration of hydrogen peroxide and reaction temperatures on the catalysts´ activity and stability was investigated (data not presented here, submitted). In short, increase in stirrer speed above 600 rpm does not have further influence on the observed reaction rate while decreasing the particle size below 0.8 mm results in only a slight improvement in the observed rate of oxidation of phenols. The increase in the catalyst loading in the range from 0 – 5 g in the reactor show that above 2.5 g the reaction rates of hydrogen peroxide decomposition and total phenols oxidation did not increase significantly. These results indicate that when a stirrer speed of 600 rpm, catalyst with the particle size range from 0.4 - 0.63 mm and catalyst loading of 2.5 g are used the interphase resistances are minimized and that the reaction is operated in the kinetic regime (surface reaction being the slowest step in the overall reaction rate). The most significant influence on the extent of total phenols and TOC removal has the increase in the reaction temperature and initial hydrogen peroxide concentration.
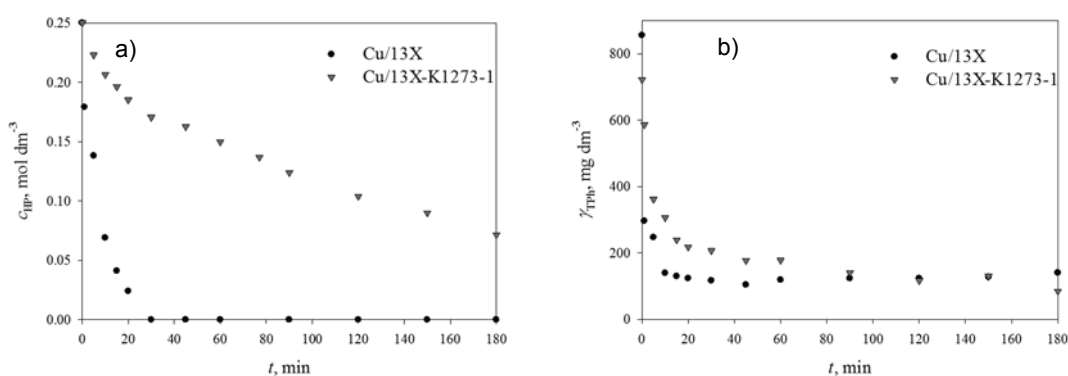

Figure 2: Concentrations of hydrogen peroxide (a) and total phenols (b) with time in the reactions with Cu/13X and Cu/13X-K1273-1 catalysts (c_{VP}= 0.25 M, T= 353 K, N= 600 o min^{-1}, m_{CAT}= 2.5 g, d_P= 0.4 - 0.63 mm)
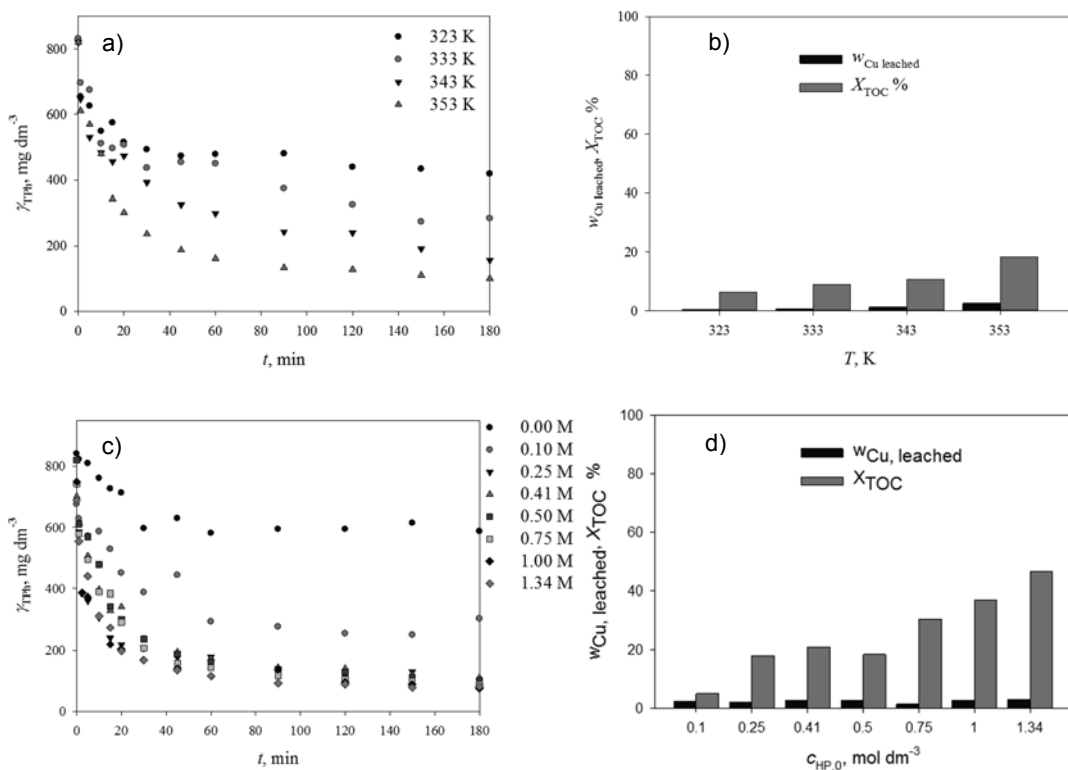

Figure 3: Influence of reaction temperature (a and b) and initial concentration of hydrogen peroxide (c and d) on total phenols content with time, TOC conversions and copper leaching in the reactions with Cu/13X-K1273-1 catalyst (c_{VP} = 0 - 1.35 M, T = 323-353 K, N= 600 o min^{-1}, m_{CAT} = 2.5 g, d_P= 0.4 - 0.63 mm)

As can be seen from Figure 3a-d the best results were obtained in the reaction conducted at 353 K with the initial hydrogen peroxide concentration of 1.34 mol dm^{-3} when 88 % of total phenols and 46.5 % in TOC reduction were achieved with copper leaching never exceeding more than 3 wt. %.

4. Conclusions

In this work influence of post synthesis thermal treatment and reaction parameters was investigated on the catalytic properties of zeolite catalysts. Physical, textural and chemical properties changed significantly after the calcination at 1273 K yielding a profoundly more stable catalyst in terms of active metal component leaching in the catalytic wet peroxide oxidation of OOMW. Even though the catalyst activity decreases after thermal treatment with respect to H$_2$O$_2$ decomposition rate, the extent of total phenols removal and the TOC abatement increased. The rate of phenol oxidation and hydrogen peroxide decomposition increased with the increase of reaction temperature.

The best results were obtained in the reaction with Cu/13X-K1273-1 catalyst operated at 353 K with the initial hydrogen peroxide concentration of 1.34 mol dm^{-3} and the reaction time of 3 hours when over 88 % removal of total phenols and acceptable TOC conversions were achieved without significant leaching of copper ions from the zeolite based support.

Acknowledgements

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