Kinetics of Catalytic Wet Peroxide Oxidation of Phenolics in Olive Oil Mill Wastewaters over Copper Catalysts

Karolina Maduna,†,‡ Narendra Kumar,‡ Atte Aho,‡ Johan Wärnà,‡ Stanka Zrnčević,† and Dmitry Yu. Murzin*†

Faculty of Chemical Engineering and Technology, Department of Reaction Engineering and Catalysis, University of Zagreb, Marulicev trg 19, 10000 Zagreb, Croatia
Faculty of Science and Engineering, Laboratory of Industrial Chemistry and Reaction Engineering, Åbo Akademi University, Biskopsgatan 8, FI 20500 Turku-Åbo, Finland

Supporting Information

ABSTRACT: During olive oil extraction, large amounts of phenolics are generated in the corresponding wastewaters (up to 10 g dm$^{-3}$). This makes olive oil mill wastewater toxic and conventional biological treatment challenging. The catalytic wet peroxide oxidation process can reduce toxicity without significant energy consumption. Hydrogen peroxide oxidation of phenolics present in industrial wastewaters was studied in this work over copper catalysts focusing on understanding the impact of mass transfer and establishing the reaction kinetics. A range of physicochemical methods were used for catalyst characterization. The optimal reaction conditions were identified as 353 K and atmospheric pressure, giving complete conversion of total phenols and over 50% conversion of total organic carbon content. Influence of mass transfer on the observed reaction rate and kinetics was investigated, and parameters of the advanced kinetic model and activation energies for hydrogen peroxide decomposition and polyphenol oxidation were estimated.

1. INTRODUCTION

Phenols are important industrial chemicals widely used as reactants and solvents in numerous commercial processes and therefore are often present in industrial effluents. The major anthropogenic sources of phenol-contaminated wastewaters are petrochemical, pharmaceutical, wood, pulp, and paper and food processing industries as well as landfill and agricultural area leachate waters.1 There are several environmental concerns regarding phenols; thus, they are considered to be hazardous in industrial wastewaters, harmful even at low concentration levels (ppm range). Wastewaters containing phenols should therefore undergo a special treatment. In EU, the current limits for wastewater emission of phenols are 0.5 mg dm$^{-3}$ (0.5 ppm) for surface waters and 1 mg dm$^{-3}$ (1 ppm) for sewage systems with maximum allowed concentration levels in potable and mineral waters of 0.5 mg dm$^{-3}$ (1 ppm) for surface waters and 1 mg dm$^{-3}$ (1 ppm) for sewage systems with maximum allowed concentration levels in potable and mineral waters.

Significant quantities of phenolics are generated in olive oil mill wastewater (OOMW) including organic contaminants such as lignin, tannins, and polyphenolic compounds. Significant amounts of olive oil mill wastewater exceeding several million tons are produced in Europe alone despite stringent legislation1 and are not properly treated. The properties of OOMWs depend on the method of extraction, feedstock properties, and region and climate conditions. In general, OOMW is a dark brown acidic effluent (pH = 4.0–5.5), with a distinctive odor and high conductivity, comprising besides water (80–85%) organic compounds (15–18%) and inorganic elements (2%, potassium salts and phosphates). The concentration of phenols and polyphenols in OOMW can be as high as 20 wt %.3 Although several studies were reported on removal of phenolics in OOMW,4 significant efforts are still needed. Often separation-based technologies are suggested as an alternative to biological processes, however, their effective application can be hindered by high operational costs and sustainability concerns such as generation of secondary toxic wastes because the toxic compounds are not destroyed but only separated.5 Therefore, in the current work, the focus was on catalytic approaches to diminish the content of phenolics in OOMW.

In particular, the catalytic wet peroxide oxidation (CWPO) process is a suitable method6 generating hydroxyl radicals during hydrogen peroxide decomposition. Hydrogen peroxide is generally considered as a nontoxic and ecologically attractive oxidant. Application of heterogeneous catalysts, such as zeolites,7 in CWPO of organic compounds has been reported. Transition metal-exchanged (mostly iron and copper) zeolites of FAU or MFI morphology showed promising results; however, there are still some open issues such as resistance to leaching of the active metal during the reaction. Apart from few recent reports8–11 most of the studies describe application...
of powdered catalysts for which mass transfer limitations can be neglected.\textsuperscript{7,12,13} It is apparently clear that scaling up of a commercial CWPO process requires detailed studies with the pelletized catalysts. In this case, external and internal mass transfers (i.e., diffusion processes in the boundary layer surrounding the catalyst pellet and in the pores of the catalyst) should be properly considered.

In this work, the activity of copper-containing catalysts was tested in catalytic wet peroxide oxidation of OOMW with a special attention to the stability of copper during the reaction, namely, its resistance to leaching. The influence of interparticle and intraparticle diffusion was investigated, and the reaction kinetics parameters of the proposed pseudo-second-order kinetic model were estimated.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. A series of copper-containing 13X zeolite catalysts were prepared by postsynthesis ion-exchange from the sodium form of the commercial 13X zeolite acquired from UOP Italy (13X-APG Molsiv, SiO$_2$/Al$_2$O$_3$ = 3.2, w$_{Na}_2$O = 20 wt %, d$_{B,range}$ ≤ 2 mm).

Depending on the bead size, between 2.5 and 10 g dm$^{-3}$ zeolite was ion-exchanged with a 0.05 M copper acetate solution under agitation at 298 K for 0.5 to 3 h, followed by filtration of the samples and drying overnight at room temperature to obtain copper-bearing zeolites with a similar metal content. The detailed preparation method was described previously.\textsuperscript{14} After copper ion-exchange, postsynthesis thermal treatment was performed consisting of calcination at 1273 K for 3 h (ramp 2 K min$^{-1}$) to achieve materials exhibiting a higher stability against the loss of the active metal component during the reaction. The list of prepared catalysts and their designated names is presented in Table 1.

| sample | bead size range mm | preparation method | copper content, wt % (UV–vis) |
|--------|-------------------|--------------------|-----------------------------|
| Cu/13X-1 | 0.40–0.63 | ion exchange (10 g dm$^{-3}$, 2 h) | 8.6 |
| Cu/13X-K1273-1 | 0.80–3.03 | ion exchange + calcination at 1273 K | 7 |
| Cu/13X-2 | 0.315–0.40 | ion exchange (10 g dm$^{-3}$, 0.5 h) | 8 |
| Cu/13X-K1273-2 | 0.63–0.80 | ion exchange + calcination at 1273 K | 7 |
| Cu/13X-3 | 0.10–1.00 | ion exchange (10 g dm$^{-3}$, 3 h) | 7 |
| Cu/13X-K1273-3 | 1.25–2.00 | ion exchange + calcination at 1273 K | 7 |

The crystalline structures of the parent zeolite- and prepared zeolite-based catalysts containing copper were evaluated by powder X-ray diffraction (XRD) analysis on a XRD 600, Shimadzu instrument. Cu K$_\alpha$ was used as the radiation source at the wavelength of 0.154 nm with 2θ from 5 to 60° with a 0.02° step size. The peak identification was performed using X’Pert HighScorePlus software.

The morphology of the fresh- and spent-zeolite-based copper catalysts Cu/13X and Cu/13X-K1273 was studied using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM analysis was performed on carbon-coated samples using a LEO Gemini 1530 instrument equipped with a Thermo Scientific UltraDry Silicon Drift Detector. The transmission electron microphotographs were taken by a JEM-1400 Plus transmission electron microscope (TEM) operated at 120 kV acceleration voltage. The powdered samples were suspended in 100% ethanol under ultrasonic treatment for 10 min. For each sample, a drop of ethanol suspension was deposited on a Cu fiber carbon grid (200 mesh) and evaporated, after which the images were recorded.

Copper loading was measured using a UV/vis spectrometer (UV1600PC, Shimadzu) at 270 nm for the parent solution of copper acetate applied during ion exchange and later confirmed by energy-dispersive X-ray microanalysis (EDXA) during SEM analysis and by inductively coupled plasma-optical emission spectrometry (ICP-OES) (PerkinElmer, Optima 5300 DV) after dissolution in HF.

The basicity of the prepared catalysts was elucidated using temperature-programmed desorption (TPD) of CO$_2$ on AutoChem 2010 (Micromeritics Instruments) in the temperature range of 373–1173 K according to the method described by Kumar et al.\textsuperscript{15}

Infrared spectroscopy (ATI Mattson FTIR) was applied to elucidate the strength of Bronsted and Lewis acid sites using the KBr pellet technique working in the range of wavenumbers of 4000–400 cm$^{-1}$ with pyridine as the probe molecule. A detailed description of the analytical procedure is available.\textsuperscript{16}

2.3. Catalytic Experiments. The catalytic experiments were carried out under atmospheric pressure in a 250 cm$^3$ glass batch reactor equipped with a pH electrode and a temperature sensor. The stirring speed in the range between 50 and 800 min$^{-1}$ and catalyst particle sizes from ca. 0.3 to 2.0 mm were

| pH | $r_{DOC}$ g dm$^{-3}$ | COD, g O dm$^{-3}$ | $r_{TPh}$ g dm$^{-3}$ | total solids, g dm$^{-3}$ |
|----|----------------------|---------------------|----------------------|----------------------|
| 4.79 | 10.7 | 36 | 1.8$^{\#}$ | 27 |

$^{\#}$Total phenols content constitutes 17 wt % total organic carbon (TOC) content of the OOMW.

The OOMW Properties at Source (293 K)

| Total Phenols Content | 17 wt % | TOC, g dm$^{-3}$ | pH | $r_{TPh}$ g dm$^{-3}$ |
|----------------------|---------|-----------------|----|----------------------|
| 4.79 | 10.7 | 36 | 1.8$^{\#}$ | 27 |
varied to address the impact of mass transfer. For elucidation of reaction kinetics, the catalyst loading, reaction temperature, and hydrogen peroxide concentration were varied. OOMW was supplied by a private oilery (Dalmatia Region, Croatia) from a three-phase extraction process of olive oil production from green olive stock mixture (local sort *Olea europaea* var. *obllica*). Basic properties of the wastewater are presented in Table 2.

Prior to reactions, OOMW was filtered through a 100 μm nylon filter bag and diluted with distilled water (v/v = 50:50). UV−vis absorbance was applied to monitor the concentration of phenolics and hydrogen peroxide. The standard Folin−Ciocalteu method at 765 nm described in the literature was used to measure the total phenol concentration. A standard curve of gallic acid was used for quantification, and the results were expressed as gallic acid equivalent (GAE) concentrations. The ammonium metavanadate spectrophotometric method at 324.9 nm. X-ray powder diffraction (XRD) was evaluated with a TOC-V CSN Shimadzu analyzer using diluted reaction mixtures, and chemical oxygen demand (COD) of the selected samples was measured by a UV/vis spectrometer using the dichromate colorimetric method at 605 nm (Hach-Lange cuvette tests). The copper content in the reaction mixture was determined by atomic absorption spectrometry of diluted reaction mixture solutions on Shimadzu AAS 6300 using a Cu hollow cathode at λ = 324.9 nm. X-ray powder diffraction analysis and N$_2$ physisorption measurements were conducted to reveal potential structural changes and coking.

### 3. RESULTS AND DISCUSSION

#### 3.1. Catalyst Characterization

After testing all prepared catalysts having different sizes, it was concluded (see below) that Cu/13X-1 with the size range of 0.4−0.63 mm is the most appropriate for CWAO. Table 3 thus contains results obtained from N$_2$ physisorption analysis of Cu/13X-1 and its thermally treated counterpart. The incorporation of copper in 13X zeolite did not have a significant effect on the measured surface area.

The thermal treatment resulted in a decrease of both specific surface area and pore volume with a shift of the pore size distributions (Figure 1) from the microporous (Cu/13X-1) to the mesoporous range (Cu/13X-K1273-1). Such pronounced differences in the physical properties for the catalyst calcined at 1273 K can be attributed to structural changes during thermal treatment.

XRD diffractograms of Cu/13X-1 already presented in ref 19 confirm the FAU structure as no shifts in the peak positions and no significant diffraction lines assigned to any new or impurity phase were observed. XRD suggested high crystallinity of the copper-containing material as incorporation of copper into the zeolite framework via ion exchange does not influence the crystal structure. In agreement with the literature, the obtained results indicate that Cu$^{2+}$ ions are well dispersed in the zeolite framework and that the size of copper particles is below the detection limit for the XRD measurement (<2−4 nm). In fact, from the TEM image of a Cu/13X-1 catalyst (Figure 2a), very small metal particles highly dispersed in single zeolite crystals can be observed. Their average size calculated using TEM analysis was 1.7 nm.

The copper-bearing zeolite calcined at 1273 K exhibited phase transformations from a zeolite to a silicate-based material upon heating. As previously reported, several phases were determined for Cu/13X-K1273-1, including magnesium silicate, copper oxide, anorthoclase (Na$_{0.65}$K$_{0.16}$Al$_{12}$Si$_{18}$O$_{46}$), and andesine (Na$_{0.68}$Ca$_{0.34}$Al$_{1.46}$Si$_{2.54}$O$_{12}$). Changes in crystal phases upon thermal treatment were in line with a decrease of the surface area and pore volume (Table 3). The size of CuO in Cu/13X-K1273-1 according to the Debye−Scherrer equation was 26.0 and 25.1 nm for the respective peaks at 35.5 and 38.6°. An average metal particle size analysis using TEM was not applicable for the Cu/13X-K1273-1 catalyst because of a poor resolution between the dark metal particles and the dark surface of single catalyst crystals (Figure 2b). The increase in the size of the metal particles in the Cu/13X-K1273-1 catalyst is most probably a consequence of metal sintering and clustering of smaller metal particles into larger ones that occurs during thermal treatment.

The morphology, shape, and size of crystals of Cu/13X-1 and Cu/13X-K1273-1 catalysts were additionally characterized.

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Table 3. Specific Surface Areas, Pore Volumes, and Copper Loadings of Prepared-Zeolite-Based Catalysts

| Sample          | Copper content, wt % | Specific surface area, m$^2$ g$^{-1}$ | Pore volume, cm$^3$ g$^{-1}$ | Average pore size, nm |
|-----------------|----------------------|---------------------------------------|-----------------------------|------------------------|
| 13X-APG Molv    |                      |                                       |                             |                        |
| Cu/13X-1        | 8.6                  | 594$^{19}$                           | 0.31$^{19}$                  | 2                      |
| Cu/13X-K1273-1  | 11.5$^{b}$           | 618$^{19}$                           | 0.34$^{19}$                  | 2                      |

$^{a}$ Calculated using $d_{PORE} = 4V_{PORE}/S$. $^{b}$ Calculation based on a 25% reduction of the catalyst’s mass during postsynthesis thermic treatment.

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Figure 1. Pore size distributions in Cu/13X-1 and Cu/13X-K1273-1 catalysts.
by SEM. From the transmission electron micrograph (Figure 2a) and the scanning electron micrograph (Figure 3a) of the Cu/13X-1 catalyst, specific needle-shaped crystals were identified.

Although agglomerated, these can be associated with X zeolite morphology similar to that reported previously.22 Single crystals in Cu/13X-K1273-1 were observed to be larger in size and of irregular shapes and a broad crystal size range (Figures 2b and 3b) in agreement with XRD, showing the presence of several crystal phases.

To evaluate metal dispersion across the surface, SEM imaging in a backscattering mode of the pellets and the cross sections of pellets was performed (Figure 4).

The brighter areas in the backscattering images are representative of the higher densities of the more heavy elements (copper). It can be noticed that copper is consistently spread over the surface of the Cu/13X-1 catalyst (Figure 4a,b), whereas in the case of the Cu/13X-K1273-1 catalyst (Figure 4c,d), copper is mainly located on the outer catalyst surface and in the narrow band close to the pellet surface several micrometers in width. Migration of copper from inside of the pellet to its outer surface is most probably a consequence of the structural changes during thermal postsynthesis treatment.

XPS analysis was used for the identification of the oxidation state of copper cations in Cu/13X-1 and Cu/13X-K1273-1. From the XPS spectra presented in Figure 5, characteristic peaks were identified for Cu 2p, O 1s, Al 2p, and Si 2p for both catalysts. Differences in the high-resolution spectra of Cu 2p and O 1s indicate that the nature of copper species is different in Cu/13X-1 and thermally treated Cu/13X-K1273-1 catalysts.

The first exhibits only two main peaks at 934 (Cu 2p3/2) and 953.3 eV (Cu 2p1/2), confirming the presence of Cu1+ as in Cu2O. In the high-resolution Cu 2p spectra of the latter, strong Cu2+ satellite peaks at 943.3 and 964.2 eV were present, contributing to the presence of the CuO phase, as previously identified by XRD.23 Differences in O 1s signals additionally confirm the distinction between copper oxides found on the surface of Cu/13X-1 and Cu/13X-K1273-1 catalysts. It should be noted that reduction of finely dispersed Cu2+ under exposure to the X-ray beam during XPS analysis in the case of the Cu/13X-1 catalyst cannot be excluded. Therefore, a difference between the catalysts can also be related to difficulties in reduction of larger CuO particles in the case of Cu/13X-K1273-1 during the XPS measurements.

During catalyst preparation, the influence of metal incorporation into the zeolite support as well as the influence of postsynthesis thermal treatment on the acid–base properties of the parent and copper-bearing zeolites has been investigated. CO2-TPD profiles of the parent zeolite as such (13X), calcined form (13X-K1273), copper zeolite (Cu/13X-1), and the calcined material (Cu/13X-K1273-1) were presented previously.19 The calculated amounts of desorbed CO2 are given in Table 4.

Weak, medium, and strong basic sites were identified in 13X and copper-modified 13X zeolites,19 which is explained by the application of the sodium form of the commercial zeolite for catalyst preparation as well as with the intrinsic (structural) basicity of oxygen atoms present in the zeolite.24 Copper-containing zeolite Cu13X-1 exhibited much higher quantities of desorbed CO2 related to strong basic sites (>750
indicating a more pronounced basicity of copper-exchanged zeolite. High temperature, however, can in general also lead to structural changes of the zeolite, thus preventing a straightforward assignment of high-temperature peaks to strong basic sites. This possibility was ruled out because only strong basic sites were seen for thermally stable Cu/13X-K1273-1.

Acidity measurements were reported previously showing that copper-containing catalysts exhibited Lewis acidity, which can be explained by the presence of copper.

Thermal treatment of Cu/13X-1 resulted in a decrease in acidity. Bronsted acid sites are degraded upon severe heat treatment above 773 K, whereas Lewis acidity from Cu²⁺ present in Cu/13X was diminished by the formation of copper

Table 4. Basicity of the Prepared Catalyst Measured by TPD-CO₂

| sample       | weak 320–500 K | medium 500–750 K | strong >750 K | total basicity |
|--------------|----------------|-----------------|--------------|----------------|
| Cu13X-1      | 0.036          | 0.009           | 0.580        | 0.625          |
| Cu13X-K1273-1| 0.105          | 0.105           |              |                |

Figure 4. Backscattering SEM images of pellets and cross sections of pellets: Cu/13X-1 (a, b) Cu/13X-K1273-1 (c, d).

Figure 5. XPS survey and high-resolution spectra of Cu/13X-1 (a) and Cu/13X-K1273-1 (b).
oxide, showing a more basic character. As reported previously,\textsuperscript{19} higher acidity was measured for Cu/13X-K1273-1 compared to that for the copper-free counterpart.

3.2. Preliminary Catalytic Experiments and Analysis of Internal Mass Transfer. Catalytic wet peroxide oxidation of OOMW was performed under mild reaction conditions. During preliminary studies, the extent of thermal decomposition of polyphenols present in the OOMW was investigated as well as the influence of catalyst addition on the reactant conversion rates. The possible catalytic activity of the parent Na-13X zeolite in the CWPO of phenol was excluded during our previous investigations of a model catalytic system.

Preliminary results on catalytic oxidation were already reported,\textsuperscript{19} confirming the role of catalysts in reducing the amount of phenolics and decomposing hydrogen peroxide (Figure 6a,b). Thermal treatment of the catalyst at high temperature was effective in decreasing hydrogen peroxide decomposition, improving also the conversion of total phenols.

These results indicate that the oxidant is probably inefficiently used in the reaction on Cu/13X-1 and that hydrogen peroxide is mainly consumed in the reactions where hydroxyl radicals are lost and are not used for degradation of the polyphenols. In CWPO, oxidation of organic compounds is attributed to the presence of hydroxyl radicals that are generated when hydrogen peroxide is decomposed. Reaction pathways can be presented with Reactions 1–6. In the initial stages of the reaction, hydroxyl and perhydroxyl radicals are produced by hydrogen peroxide decomposition on the catalyst\textsuperscript{25}

\[
\begin{align*}
\text{Cu}^+ + \text{H}_2\text{O}_2 & \rightarrow \text{Cu}^{2+} + \text{OH}^* + \text{OH}^- \\
\text{Cu}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Cu}^+ + \text{HO}_2^* + \text{H}^+ \\
\text{ROH} + \text{OH}^* & \rightarrow \text{intermediates} \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\end{align*}
\]

Both radical species are capable of oxidizing the organic compounds; however, the reactivity of hydroxyl radicals is dominant. Catalytically produced hydroxyl radicals react with phenolic compounds, oxidizing them through a series of intermediates to carbon dioxide and water when complete mineralization is achieved

Hydroxyl radicals are very reactive, and they are involved in a number of competing side reactions such as scavenging hydrogen peroxide and termination between the hydroxyl and perhydroxyl radicals\textsuperscript{7}

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{OH}^* & \rightarrow \text{HO}_2^* + \text{H}_2\text{O} \quad (4) \\
\text{H}_2\text{O}_2 + \text{HO}_2^* & \rightarrow \text{OH}^- + \text{H}_2\text{O} + \text{O}_2 \quad (5) \\
\text{HO}_2^* + \text{OH}^* & \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad (6)
\end{align*}
\]

If the latter reactions of hydroxyl radicals are dominant, hydrogen peroxide will be consumed fast and majority of the generated hydroxyl radicals will be spent ineffectively in undesired side reactions. This could be considered a preferred reaction pathway if the intraparticle diffusion resistances for the phenolic molecules are present. In this case, only hydrogen peroxide would be adsorbed and decomposed on the catalytically active sites on the internal catalyst surface, whereas adsorption of polyphenols would be limited mostly to the outer surface of the catalyst. In the absence of organic compounds, the hydroxyl radicals formed inside the catalyst would for the most part react with one another and hydrogen peroxide. Taking into account the average pore sizes in the Cu/13X-1 catalyst (2 nm) and cross sections of hydrogen peroxide (0.15 nm) and polyphenols (1–2 nm), configurational diffusion limitations could be expected for the phenolic compounds found in the OOMW. In addition to configurational limitations, intraparticle resistances for hydrogen peroxide and polyphenols could be present. They were verified using the Weisz–Prater criterion\textsuperscript{26}

\[
\Psi = \frac{r_{\text{obs}}R^2}{c_sD_e} \begin{cases} < 6, & n = 0 \\ < 0.6, & n = 1 \\ < 0.3, & n = 2 \end{cases}
\]

where \( r_{\text{obs}} \) is the observed reaction rate, \( R \) is the particle radius, \( c_s \) is the molar concentration of the solute at the catalyst surface, \( D_e \) is the effective diffusion coefficient of the solute, and \( n \) is the reaction order. For the porous media and the random pore model, the effective diffusion coefficient is defined as \( D_e = D^* \varepsilon \), where \( D \) is the diffusion coefficient, \( \varepsilon \) is the porosity, and \( r \) is the tortuosity, which are connected to the structural characteristics of the catalyst and pore geometry. For

\[ \text{Figure 6. Kinetic curves for hydrogen peroxide (a) and total phenols (b) \( \left( c_{\text{HP},0} = 0.25 \text{ M, } T = 353 \text{ K, } N = 600 \text{ min}^{-1}, m_{\text{CAT}} = 2.5 \text{ g, } d_b = 0.4–0.63 \text{ mm} \right) \).}\]
the liquid–solid catalytic systems, only molecular diffusion was taken into account, \( D \approx D^\text{static}_{AB} \). The molecular diffusion coefficient was calculated from the Wilke–Chang equation \(^{27}\)

\[
D^\text{static}_{AB} = \frac{7.4 \times 10^{-5} (\Phi M_b)^{1/2} T}{\mu_b V_{b(A)}^{0.6}} \text{ (cm}^2 \text{ s}^{-1})
\]

(8)

where \( \Phi \) is the dimensionless association factor of the solvent (\( \Phi = 2.6 \) for water), \( M_b \) is the molar mass of the solvent, \( \mu_b \) is the dynamic viscosity of the solvent in cP at temperature \( T \) (K), and \( V_{b(A)}^{0.6} \) is the liquid molar volume at the solute normal boiling point. For the purposes of this study, the liquid molar volumes at the solute’s normal boiling point were calculated from the Tyn and Calus equation

\[
V_b = 0.285 V_1^{0.408} \text{ (cm}^3 \text{ mol}^{-1})
\]

(9)

The calculations of the diffusion coefficients were performed for hydrogen peroxide and phenol diffusing in water using the data and expressions obtained from the thermodynamic properties databank.\(^{28}\) In the absence of thermodynamic data at the critical point for polyphenols such as hydroxytyrosol or tyrosol that are most commonly found in the OOMW, phenol was chosen as a model compound for the calculations. Because polyphenols are more complex and larger molecules than phenol, it is reasonable to expect that if the internal transfer limitations exist for phenol they would be even more pronounced for polyphenols. The obtained values of the diffusion coefficients at 353 K and normal pressure (typical reaction conditions) were \( 6.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \) for hydrogen peroxide and \( 3.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \) for phenol. Application of the Weisz–Prater criterion (eq 7) for the observed initial reaction rates of hydrogen peroxide decomposition \( (r_{\text{HP,obs}} = 3.7 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}) \) and polyphenols oxidation \( (r_{\text{TPh,obs}} = 5.3 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}) \) and their corresponding surface concentrations with the mean catalyst particle diameter of 0.515 mm and \( \frac{f}{c} \) ratio of 0.1 (generally valid for zeolites) resulted in the values of the dimensionless Weisz modulus of 0.15 for hydrogen peroxide diffusion and 2.25 for phenol. With this result, the presence of intraparticle diffusion for hydrogen peroxide can be eliminated, whereas the same cannot be concluded for the phenolics, especially for the reaction orders higher than zero. For polyphenols in OOMW, larger pore diffusion limitations can be expected being the most probable cause of an inefficient use of hydrogen peroxide. Because there are no pore diffusion limitations for the oxidant, hydrogen peroxide mainly decomposes inefficiently inside the Cu/13X-1 catalyst pores where negligible amounts of polyphenols are present.

On the other hand, because of the larger pore sizes of the calcined Cu/13X-K1273-1 catalyst (average pore size of 5 nm), the internal diffusion in this reaction should not be as significant as in the case of the Cu/13X-1 catalyst and faster decomposition of hydrogen peroxide and oxidation of polyphenols should be expected. However, this is not the case. The reason for a much slower radical generation rate lies in the fact that the postsynthesis thermal treatment induced migration of the catalytically active species (copper) toward the pellet surface, which was confirmed by SEM imaging in the backscattering mode of the cross sections of Cu/13X-1 and Cu/13X-K1273-1 pellets, as presented in Figure 5 b,d. Hydrogen peroxide decomposition in the Cu/13X-K1273-1 catalyst takes place only in a narrow ring of few micrometers from the particle surface where the presence of copper is identified and where polyphenols are also present. In this case, it can be considered that the pore diffusion for polyphenols is not as significant as in the case of the Cu/13X-1 catalyst and that most of the generated hydroxyl radicals are reacting with the organic compounds and are not inefficiently spent in fast scavenging reactions inside the catalyst pellet (eqs 4–6). As a result, the rates of polyphenol oxidation are comparable for both catalysts with a higher extent of oxidation for Cu/13X-K1273-1 resulting in an almost complete removal of the phenolic content after 180 min of reaction.

Comparison of Cu/13X and Cu/13X-K1273 during preliminary studies included also the investigation of their behavior in CWPO of OOMW, namely, measuring the extent of copper leaching during the reaction as well as by analyzing potential changes of the zeolite support after the reaction. XRD diffractograms of both catalysts prior and after catalytic experiments are close to each other (Figure 7a,b), indicating good stability of the support, while copper leaching was significantly different.

By measuring the copper content in diluted reaction mixtures using atomic absorption spectroscopy, it was determined that after 180 min 38 wt % copper leached from the Cu/13X-1 catalyst in a striking contrast to only 2 wt % for its counterpart calcined at high temperature, indicating severe instability of Cu/13X-1. Contribution of the leached copper in the solution to the overall catalytic performance was discussed previously,\(^{29,30}\) concluding that it can be neglected due to inactivation of copper by carboxylic acids. However, in this case, when over 20% of copper leached from the catalyst before

Figure 7. XRD diffractograms of the fresh and spent Cu/13X-1 (a) and Cu/13X-K1273-1 (b) catalysts.
the reaction was initiated by addition of hydrogen peroxide, the homogeneous contribution should not be excluded because oxidation of organic compounds catalyzed by copper cations in the liquid phase is possible. The copper leaching results were confirmed by energy-dispersive X-ray spectroscopy analysis of the fresh and spent catalysts, showing 42 wt % loss of copper for the spent Cu/13X-1 catalyst and 4 wt % loss of copper for the Cu/13X-K1273-1 catalyst. Specific surface area measurements were also supporting the superior resistance against leaching of the thermally treated catalyst.

For the Cu/13X-1 catalyst, the specific surface area and pore volume decreased from the initial \( S_{\text{FRESH}} = 618 \text{ m}^2 \text{ g}^{-1} \) and \( V_{p,\text{FRESH}} = 0.34 \text{ cm}^3 \text{ g}^{-1} \) to \( S_{\text{SPENT}} = 434 \text{ m}^2 \text{ g}^{-1} \) and \( V_{p,\text{SPENT}} = 0.30 \text{ cm}^3 \text{ g}^{-1} \), respectively, whereas the values for the Cu/13X-K1273-1 catalyst did not significantly change before and after the reaction: \( S_{\text{FRESH}} = 26 \text{ m}^2 \text{ g}^{-1} \) and \( V_{p,\text{FRESH}} = 0.03 \text{ cm}^3 \text{ g}^{-1} \) to \( S_{\text{SPENT}} = 24 \text{ m}^2 \text{ g}^{-1} \) and \( V_{p,\text{SPENT}} = 0.04 \text{ cm}^3 \text{ g}^{-1} \), respectively.

One of the possible explanations for large variations in stability between calcined and noncalcined catalysts could be the different copper speciation, namely, the presence of Cu\(^+\) in Cu/13X-1 as revealed by XPS. To our knowledge, no report on the differences in the stability of Cu\(^+\) and Cu\(^{2+}\) in the CWPO of phenolics has been published. However, different coordination of copper inside the zeolite lattice for Cu\(^+\) and Cu\(^{2+}\) cations was reported by Vanelderen et al.,\(^{31}\) which could have an impact on their catalytic properties as well.

An alternative explanation was proposed by Taran et al. based on a study of Cu-ZSM-5.\(^{13}\) The authors have shown that copper catalysts with 1–2 wt % loading possessed the highest activity and reasonable stability, whereas an increase in copper resulted in a lower activity and stability. In the current work, for the noncalcined catalysts, the amount of Cu could have been too high to allow formation of a stable material. After calcination, the zeolitic structure has been destroyed, giving several new phases. It could be due to the fact that partial encapsulation of CuO particles makes the catalyst less prone to leaching.

Whatever the explanation, elucidation of mass transfer influence and kinetic analysis was done for the Cu/13X-K1273 catalyst in which the more efficient use of the oxidant was proven to take place.

3.3. Mixing Efficiency and External Mass Transfer. In the case of catalytic wet peroxide oxidation of polyphenols over a solid pellet catalyst, following mass transfer processes should be considered: transport of the dissolved reactants from the liquid bulk to the catalyst outer surface and transport inside the pores of the pellet. These effects result in the concentration gradients of reactants and products across phase boundaries and within the catalyst particle, as present in Figure 8.

To evaluate all possible mass transfer limitations, a combined theoretical/experimental approach was adopted in this study. Mass transfer coefficients through the external boundary layer and inside the pores were calculated for hydrogen peroxide and model compound phenol, and the presence of diffusion limitations was evaluated by the application of external mass transport and internal pore diffusion criteria for the Cu/13X-K1273-1 catalyst. Additionally, the efficiency of mixing in the reactor was verified and evaluation of reaction conditions for achieving total suspension of the catalyst was performed.

External mass transfer or the mass transfer in the thin boundary layer around the solid catalyst particle depends on hydrodynamic conditions in the reactor (stirring speed), physical properties of the liquids, and the size of the catalyst particles. In the catalytic reactions in which the suspended solid catalyst is used, external mass transfer resistances can be minimized by efficient mixing that establishes thorough dispersion of reactants and catalyst in the liquid and the use of the smaller catalyst particles. The first step in achieving this is ensuring that under the conditions of the catalytic experiments the solid catalyst is completely suspended in the liquid and no particles remain at the bottom of the reactor for longer than 1 s. The minimum stirrer speed necessary for total
Figure 9. Influence of the stirring speed on hydrogen peroxide (a) and total phenol (b) content with time (N = 50−800 min⁻¹, ω₀P,0 = 0.25 M, T = 353 K, n_Cu/13X-K1273-1 = 2.5 g, d_b = 0.4−0.63 mm).

The absence of external mass transfer for the stirring speed of 600 rpm was verified by applying the external mass transport criterion that can be derived considering the mass transfer rate or the maximum specific mixing power was calculated from

\[ Sh = 1.0Re^{1/3}Sc^{1/3} \]  

where \( Re \) number is expressed as \( Re \propto (\frac{ω}{r})^{1/3} \) based on the Kolmogorov theory of turbulence. By rearranging eq 13, the following expression for estimating liquid/solid mass transfer coefficient \( k_{LS} \) can be derived

\[ k_{LS} = \frac{(cD_j)^{1/6}}{(\eta d_b)} \]  

In eq 14, \( \epsilon \) denotes the energy of dissipation, \( D \) is the diffusion coefficient of the diffusing compound, \( d_m \) is the impeller diameter, \( \rho \) and \( \eta \) are the density and dynamic viscosity of water, and \( d_p \) is the particle diameter. The energy of dissipation or the maximum specific mixing power was calculated from

\[ \epsilon = \frac{P}{\rho_L V_L} = \frac{N_d \rho_L N^3 d_s^3}{\rho_L V_L} \]  

where \( P \) is the mixing power that depends on the impeller type and stirring speed, \( N_d \) is the power number of the impeller, and \( \rho_L \) and \( V_L \) are the density and volume of the liquid. For a 45° pitched four-blade turbine impeller 4.5 cm wide with \( N_d = 1.3 \) in the turbulent region \( (Re > 10^3) \) at a stirring speed of 600 rpm mixing the volume of 250 cm³, the maximum specific mixing power was calculated to be 0.96 W kg⁻¹. The mutual diffusion coefficients of solutes in water were calculated using the Wilke–Chang equation (eq 8), resulting in the values of \( 6.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \) for hydrogen peroxide and \( 3.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \) for phenol. Next, the external mass transfer coefficients for hydrogen peroxide and phenol were calculated from eq 14, resulting in \( k_{LS,HP} = 5.6 \times 10^{-4} \text{ m} \text{ s}^{-1} \) and \( k_{LS,Ph} = 3.8 \times 10^{-4} \text{ m} \text{ s}^{-1} \).

The above theoretical approach results were experimentally verified by adopting the published procedures for the elimination of external mass transfer. To confirm the specific conditions under which the reaction was operating with negligible external mass transfer resistances, the influence of
the stirring speed and particle size on the reaction rates of hydrogen peroxide decomposition and polyphenols oxidation was investigated. The results are presented in Figures 9, 10, and S1. From the results presented in Figure 9, it can be seen that already above 100 rpm there are no significant changes in the reaction rates of hydrogen peroxide decomposition and polyphenols oxidation and that the increase in the stirring speed above 600 rpm does not further increase them. This indicates that for the stirring speed above 600 rpm the external mass transfer resistances are minimized and that the mass transfer through the boundary layer proceeds faster than the surface reaction.

From the above-presented results, it can be concluded that the reaction mixture is most effectively mixed at the stirrer speed of 600 rpm and that decreasing the particle size below 0.8 mm resulted in only a slight improvement in the observed rate of phenol oxidation excluding the presence of external mass transfer limitations that could influence the reaction kinetics.

3.4. Influence of Catalyst Loading, Initial Concentration of Hydrogen Peroxide, and Temperature.

Figure 10. Influence of catalyst bead size on hydrogen peroxide (a) and total phenol (b) content with time \((N = 600 \text{ min}^{-1}, c_{\text{HP},0} = 0.5 \text{ M}, T = 353 \text{ K}, m_{\text{Cu/13X-K1273}} = 2.5 \text{ g}, d_B = 0.315–2.00 \text{ mm})\).

Figure 11. Time dependence of hydrogen peroxide decomposition (a–c) and total phenol content (d–f) with points representing the experiment and lines representing the kinetic model. In (a) and (d), \(c_{\text{HP},0} = 0–1.34 \text{ M}, T = 353 \text{ K}, m_{\text{Cu/13X-K1273}} = 2.5 \text{ g}, d_B = 0.4–0.63 \text{ mm}\); in (g), (b), and (e), \(c_{\text{HP},0} = 0.5 \text{ M}, T = 353 \text{ K}, m_{\text{Cu/13X-K1273}} = 0–5 \text{ g}\); and in (c) and (f), \(c_{\text{HP},0} = 0.5 \text{ M}, T = 323–353 \text{ K}, m_{\text{CAT}} = 2.5 \text{ g}\). In all cases, \(N = 600 \text{ min}^{-1}\) and \(d_B = 0.4–0.63 \text{ mm}\).
subsequent experiments aimed at revealing the optimal initial concentration of hydrogen peroxide, catalyst loading, and reaction temperature were performed under the above-mentioned reaction conditions. The results of these studies presented in Figure 11 showed that the most significant influence on the extent of total phenols and TOC removal had the initial hydrogen peroxide concentration.

By increasing the initial content of the oxidant, the rate and the extent of the total phenols, TOC, and COD removal increased. At higher initial concentrations of hydrogen peroxide (above 0.75 M), when all total phenols that constitute approximately 17 wt % in TOC loading are eliminated, no significant increase in the oxidation rate of polyphenols can be observed. This is considered to be the consequence of the intensification of side reactions of hydroxyl radicals and the scavenging effect of the oxidant as described earlier (eqs 4–6). However, oxidation of intermediates that are formed by polyphenol conversion becomes significant, further decreasing the organic content of the reaction mixture. The best results were obtained in the reaction conducted with the initial hydrogen peroxide concentration of 1.34 mol dm$^{-3}$ at 353 K and with 2.5 g of catalyst when ~97% of total phenols and 47% of TOC reduction were achieved with a rather small copper leaching (Figure 12).

A higher catalyst bulk concentration gave more prominent hydrogen peroxide decomposition, and total phenol oxidation increased as expected (Figure 11b,e).

In contrast to the reports published for similar catalytic systems, no limit of catalyst loading was observed and the reaction rates increased proportionally with the mass of the catalyst added to the reactor.

The increase in the reaction temperature (Figure 11c,f) had a similar beneficial effect on the catalyst activity, yielding higher conversions of both reactants at elevated temperatures.

3.5. Kinetic Analysis. In heterogeneous catalysis, intrinsic kinetics can be evaluated only if the external or internal mass transfer resistances are not affecting the surface reaction rate. The above-presented results and discussion of the diffusion influence in CWPO of polyphenols from OOMW over the Cu/13X-K1273-1 catalyst indicate that for a stirring speed of 600 rpm, catalyst size of 0.4–0.63 mm, and the catalyst loading of 2.5 g the external and internal mass transfer resistances for both the oxidant and the polyphenols are minimized and that the surface reaction can be presumed to be the slowest step in the overall reaction rate.

As mentioned before, the CWPO reaction mechanism is very complex, consisting of numerous parallel and serial reactions involving different molecular and radical species. However, the following main reaction steps can be identified: initiation of catalytic decomposition of hydrogen peroxide, which results in the generation of hydroxyl radicals (eq 1), followed by the oxidation of polyphenols and intermediates (propagation, eq 3), and finally a loss of hydroxyl radicals in the undesired side reactions (termination, eq 4–6). In a very simplistic form, the oxidation pathway can be represented as

$$\text{ROH} + \text{H}_2\text{O}_2 \rightarrow \text{intermediates} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \tag{16}$$

Because of the complexity of the system, performing a detailed kinetic analysis is challenge even for the model wastewaters where most of the organic compounds present in the reaction mixture are known. The composition of the real wastewater effluent produced during olive oil extraction depends on the production process used, olive species, and climate region, but, in general, OOMW contains more than 30 different polyphenols as well as other prone to oxidation organic acids that can engage in the reaction with hydrogen peroxide and hydroxyl radicals.

The presence of inorganic salts such as chlorides and phosphates complicates the matter further. The heterogeneity of the OOMW composition as well as the reaction scheme complexity make carrying out the detailed kinetic study next to impossible that would incorporate all individual reactions with all of the initial and intermediate compounds and radicals. Because of this, the kinetic modeling is often limited to some parameter that represents the group of targeted compounds or major constituents of the wastewater such as COD, TOC, or total phenol content.

On the basis of the kinetic regularities and literature data for similar catalytic systems, the following kinetic model for polyphenol oxidation and decomposition of hydrogen peroxide was proposed

$$\begin{align*}
\frac{dc_{\text{TPh},1}}{dt} &= \left(k_{\text{TPh},1}c_{\text{TPh},1}c_{\text{Ph},1} + k_{\text{TPh},2}c_{\text{TPh},2}c_{\text{Ph},1}\right)\gamma_{\text{CAT}} \tag{17} \\
\frac{dc_{\text{HP}}}{dt} &= \left(k_{\text{HP},1}c_{\text{HP},1} + k_{\text{HP},2}c_{\text{TPh},1}c_{\text{Ph},1} + k_{\text{TPh},2}c_{\text{TPh},2}c_{\text{Ph},2}\right)\gamma_{\text{CAT}} \tag{18}
\end{align*}$$

where $c_{\text{TPh}}$ is the molar concentration of total phenols expressed as gallic acid equivalent, $c_{\text{HP}}$ is the molar concentration of hydrogen peroxide, and $\gamma_{\text{CAT}}$ is the catalyst loading in g dm$^{-3}$. The total phenol content was divided into two fractions: more reactive ($c_{\text{TPh},1}$) and less reactive ($c_{\text{TPh},2}$) based on preliminary analysis of the obtained experimental data. In all performed experiments, two reaction phases could clearly be distinguished: a fast decrease of the total phenol content, which occurred within the first 30–60 min of the reaction, and slow oxidation of the remaining less-reactive fraction of total polyphenols present in the reaction mixture. The initial value of the concentration ratio of the two polyphenol fractions was set as 0.5 during parameter
estimation analysis. Reaction constants (k_{TPH1}, k_{TPH2}, and k_{HP}), reaction orders in reactants and the catalyst (n_1, n_2, n_3, n_4), and concentration ratio of the polyphenol fractions are the kinetic parameters that were estimated during modeling. These expressions take into account that the oxidation rate of polyphenols depends on the concentrations of both reactants and the catalyst loading and that the decomposition rate of hydrogen peroxide considers the contribution of not only the reaction with polyphenols but also the side reactions of hydrogen peroxide decomposition. The contribution of the noncatalytic hydrogen peroxide decomposition and polyphenol oxidation was also considered based on the data acquired from hydrogen peroxide decomposition. The estimation of the kinetic parameters was carried out by nonlinear regression analysis using simulation and parameter estimation software MODEST. Ordinary differential equations (eqs 17 and 18) were solved with the backward differential method. The sum of residual squares (Q)

\[ Q = \sum_{i=1}^{nobs} \sum_{j=1}^{nsets} \left( y_{\text{exp},ijk} - y_{\text{est},ijk} \right)^2 w_{ij} \]  

was minimized with the hybrid Simplex–Levenberg–Marquardt method, where y_{exp} represents experimental data and y_{est} represents the estimated values, i.e., the concentrations.

In the first iteration, the polyphenol oxidation reaction orders in polyphenols and hydrogen peroxide concentration were identified in a run with all of the kinetic parameters set as floating. In most cases, the polyphenol oxidation reaction order with respect to phenol (n_1), hydrogen peroxide (n_2), and catalyst concentration (n_3) were close to 1, whereas the order of hydrogen decomposition reaction with respect to hydrogen peroxide was close to 2 (n_4). The second iteration of modeling was performed with fixed reaction orders, and the results are shown in Table 5 and Figures 11 and 13.

**Table 5. Kinetic Modeling Results (n_1 = n_3 = n_4 = 1, n_2 = 2)**

| Estimated Parameter | Value | Standard Error | Relative Standard Error (%) |
|---------------------|-------|----------------|-----------------------------|
| k_{TPH1} (dm^6 mol^{-1} min^{-1} g_{CAT}^{-1}) | 14.9 | 2.9 | 19.5 |
| k_{TPH2} (dm^6 mol^{-1} min^{-1} g_{CAT}^{-1}) | 3.16 | 0.025 | 0.8 |
| k_{HP} (dm^6 mol^{-1} min^{-1} g_{CAT}^{-1}) | 0.186 | 0.00344 | 1.8 |
| E_{TPH1} (kJ mol^{-1}) | 62.2 | 19.6 | 31.5 |
| E_{TPH2} (kJ mol^{-1}) | 90.1 | 0.7 | 0.8 |
| E_{HP} (kJ mol^{-1}) | 30.1 | 1.8 | 6.1 |
| \(v_{TPH1}/v_{TPH2}\) | 0.345 | 0.00186 | 0.5 |

Taking into account the complexity of the reaction mixture and limitations of the analytical methods, the obtained results show good agreement of the experiment and the proposed kinetic model for both hydrogen peroxide decomposition and polyphenol oxidation. In general, the fit is better for hydrogen peroxide decomposition, whereas the worst agreement for the polyphenol oxidation was achieved for the reactions in which the initial concentration of hydrogen peroxide was the lowest, indicating that for these reactions one of the kinetic model assumptions does not hold.

Activation energies for hydrogen peroxide decomposition and polyphenol oxidation over the pelletized Cu/13X-K1273-1 catalyst were determined from the temperature dependencies of the calculated rate constants described by a modified Arrhenius equation

\[ k = k_{av} \exp \left( -\frac{E}{RT} \left( \frac{1}{T'} - \frac{1}{T_{av}} \right) \right) \]  

where \(k_{av}\) is the constant at the average temperature of the experiments \(T_{av}\). The obtained values of activation energies for hydrogen peroxide decomposition and polyphenol oxidation of \(E_{HP} = 30.1\) kJ mol\(^{-1}\), \(E_{TPH1} = 62.2\) kJ mol\(^{-1}\) and \(E_{TPH2} = 90.1\) kJ mol\(^{-1}\) are in the range of values reported for similar model reaction systems using powdered catalysts, i.e., 45–140 kJ mol\(^{-1}\).

**3.6. Catalyst Testing in Olive Oil Mill Wastewater Treatment.** The catalyst performance was finally tested in the prolonged reaction over 10 h to determine whether the catalyst gets deactivated with prolonged use. From the results presented in Figure 14, it can be seen that the oxidation of organic content continues after phenolics are eliminated, demonstrating the catalyst ability to enhancing peroxidation of not only phenols but also other organic compounds present in the olive oil mill wastewater, resulting in complete conversion of total phenols and 52% conversion of TOC. The Cu/13X-K1273-1 catalyst preserved its stability even after 10 h of reaction when only 3.3 wt % copper leached from the catalyst. By a comparison of the fresh and spent catalysts, it was observed that the catalyst maintained its initial surface area and pore volume (\(S_{FRESH} = 26\) m\(^2\) g\(^{-1}\) and \(V_{p,FRESH} = 0.03\) cm\(^3\) g\(^{-1}\) to \(S_{SPENT} = 25\) m\(^2\) g\(^{-1}\) and \(V_{p,SPENT} = 0.03\) cm\(^3\) g\(^{-1}\). Although the loss of 3.3 wt % of the initial copper content from the catalyst is negligible, this result is very encouraging when compared to that of similar catalytic systems described in the literature. The extent of leaching of the Cu/13X-K1273 pelletized catalyst is generally lower when compared to that of other zeolite or zeolite-based catalysts, and is comparable to leaching of copper-containing pillared clay catalysts according to the work of Inchaurreondo et al. However, most of these results are connected to CWPO studies of model or often highly diluted wastewaters, which should be taken into account when comparing them with the results of this study where a real industrial effluent was used because the extent of metal leaching from the catalyst depends not only on the catalyst type or support material but also very strongly on the reaction conditions such as temperature, pH, and particular organic compound species and their concentrations.

**4. CONCLUSIONS**

Postsynthesis thermal treatment was beneficial for catalytic behavior of the copper-containing 13X zeolite in catalytic wet peroxide oxidation of OOMW as it resulted in an increased stability against leaching, allowing better removal of total phenols TOC due to the presence of pore diffusion limitations for polyphenols in the noncalcined Cu/13X-1 catalyst. Results of mass transfer and diffusion investigation for the calcined Cu/13X-K1273-1 catalyst excluded the influence of both external and internal mass transfer limitations. It was found that the rate of phenol oxidation and hydrogen peroxide decomposition increased with the increase of stirrer speed, catalyst loading, initial hydrogen peroxide concentration, and reaction temperature and with the decrease of catalyst bead...
size. Kinetic analysis of the catalytic system was preformed, the reaction orders in reactants and in the catalyst were identified, and parameters of the proposed kinetic model and activation energies were determined. By treating the industrial olive oil mill wastewater in a catalytic wet peroxide oxidation process over thermally stabilized copper-containing zeolite-based catalyst under mild reaction conditions (353 K and atmospheric pressure), it is possible to achieve complete conversion of total phenols and over 50% conversion of TOC, substantially minimizing copper leaching.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00948.

Observed reaction rate dependence on the stirring speed and catalyst bead size (PDF)

AUTHOR INFORMATION

Corresponding Author
*E-mail: dmurzin@abo.fi.

ORCID

Dmitry Yu. Murzin: 0000-0003-0788-2643

Notes
The authors declare no competing financial interest.

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REFERENCES

(1) Busca, G.; Berardinelli, S.; Resini, C.; Arrighi, L. Technologies for the removal of phenol from fluid Streams: A short review of recent developments. J. Hazard. Mater. 2008, 160, 265–288.
(2) Herve, M. 2010. *LIFE Focus, LIFE Among the Olives, Good Practice in Improving Environmental Performance in the Olive Oil Sector*. European Commission Environment, Directorate General: Brussels, Belgium. 2018. http://ec.europa.eu/environment/life/publications/lifepublications/lifefocus/documents/oliveoil.pdf (accessed June 14, 2018).

(3) Ouzounidou, G.; Zervakis, G. I.; Gaitis, F. Raw and microbiologically detoxified olive mill waste and their impact on plant growth. *Terra. Aquat. Environ. Toxcol.* 2010, 4, 21–38.

(4) Gogate, P. R.; Pandit, A. B. A review of imperative technologies for water waste treatment I: Oxidation technologies at ambient conditions. *Adv. Environ. Res.* 2004, 8, 501–551.

(5) Wang, H.; Guan, Q.; Li, J.; Wang, T. Phenolic waste water treatment by an electrocatalytic membrane reactor. *Catal. Today* 2014, 236, 121–126.

(6) Giordano, G.; Perathoner, S.; Centi, G.; De Rosa, S.; Granato, T.; Katovic, A.; Siciliano, A.; Tagarelli, A.; Tripicchio, F. Fast spectrophotometric determination of H$_2$O$_2$ in photo-Fenton type of base metal. *Microporous Mesoporous Mater.* 2007, 201, 1572.

(7) Liotta, L. F.; Gruttadauria, M.; Di Carlo, G.; Perrini, G.; Librando, V. Heterogeneous catalytic degradative action of phenolic substrates: Catalysts activity. *J. Hazard. Mater.* 2009, 162, 588–606.

(8) Taran, O. P.; Zagourouko, A. N.; Ayusheev, A. B.; Yashnik, S. A.; Prihod’ko, R. V.; Ismaglov, Z. R.; Goncharuk, V. V.; Parmon, V. N. Wet peroxide oxidation of phenol over Cu-ZSM-5 catalyst in a flow reactor. Kinetics and diffusion study. *Chem. Eng. J.* 2015, 282, 108–115.

(9) Taran, O. P.; Zagourouko, A. N.; Yashnik, S. A.; Ayusheev, A. B.; Pestunov, A. V.; Prosvirnin, I. P.; Prihod’ko, R. V.; Goncharuk, V. V.; Parmon, V. N. Wet peroxide oxidation of phenol over carbon/zeolite catalysts. Kinetics and diffusion study in batch and flow reactors. *J. Environ. Chem. Eng.* 2018, 6, 2551–2560.

(10) Yan, Y.; Jiang, S.; Zhang, H. Efficient catalytic wet peroxide oxidation of phenol over Fe-ZSM-5 catalyst in a fixed bed reactor. Sep. *Purif. Technol.* 2014, 133, 365–374.

(11) Yan, Y.; Wu, X.; Zhang, H. Catalytic wet peroxide oxidation of phenol over Fe$_2$O$_3$/MCM-41 in a fixed bed reactor. Sep. *Purif. Technol.* 2016, 171, 52–61.

(12) Prihod’ko, R.; Stolyarova, I.; Gündüz, G.; Taran, O.; Yashnik, S.; Parmon, V.; Goncharuk, V. Fe-exchanged zeolites as materials for catalytic wet peroxide oxidation. Degradation of Rodamine G dye. *Appl. Catal., B* 2013, 140–141, 506–515.

(13) Murzin, D. Y. Synthesis and characterization of solid base mesoporous catalysts. *Coord. Chem. Rev.* 2012, 256, 2057–2062.

(14) Maduna Valkaj, K.; Kaseli, I.; Smolkovic, J.; Zrnčević, S. Catalytic wet peroxide oxidation of olive oil mill wastewater over zeolite based catalyst. *Catal. Eng. Trans.* 2015, 43, 853–858.

(15) Benaliouche, F.; Boucheffa, T.; Ayrault, P.; Mignard, S.; Magnoun, P. NH$_2$TPD and FTIR spectroscopy of pyridine adsorption studies for characterization of Ag- and Cu-exchanged X zeolites. *Microporous Mesoporous Mater.* 2008, 111, 80–88.

(16) Murzin, D. Y. Effect of catalyst synthesis parameters on the metal particle size. *Appl. Catal., A* 2013, 451, 251–251.

(17) Aho, A.; Kumar, N.; Muzzin, D. Y. Catalytic wet peroxide oxidation of olive oil mill wastewater over zeolite based catalyst. *Catal. Eng. Trans.* 2015, 43, 853–858.

(18) Benaliouche, F.; Boucheffa, T.; Ayrault, P.; Mignard, S.; Magnoun, P. NH$_2$TPD and FTIR spectroscopy of pyridine adsorption studies for characterization of Ag- and Cu-exchanged X zeolites. *Microporous Mesoporous Mater.* 2008, 111, 80–88.

(19) Maduna Valkaj, K.; Kaseli, I.; Smolkovic, J.; Zrnčević, S.; Kumar, N.; Murzin, D. Y. Catalytic wet peroxide oxidation of olive oil mill wastewater over zeolite based catalyst. *Catal. Eng. Trans.* 2015, 43, 853–858.

(20) Benaliouche, F.; Boucheffa, T.; Ayrault, P.; Mignard, S.; Magnoun, P. NH$_2$TPD and FTIR spectroscopy of pyridine adsorption studies for characterization of Ag-, and Cu-exchanged X zeolites. *Microporous Mesoporous Mater.* 2008, 111, 80–88.

(21) Murzin, D. Y. Evaluation of wet peroxide oxidation of phenol at moderate temperature using a high-load supported copper catalyst. *Chem. Eng. J.* 2012, 198–199, 426–434.

(22) Santos, A.; Yustos, P.; Quintanilla, A.; Ruiz, G.; Garcia-Ochoa, F. Study of the copper leaching in the wet oxidation of phenol with CuO-based catalysts: causes and effects. *Appl. Catal., B* 2005, 61, 323–333.

(23) Benaliouche, F.; Boucheffa, T.; Ayrault, P.; Mignard, S.; Magnoun, P. NH$_2$TPD and FTIR spectroscopy of pyridine adsorption studies for characterization of Ag- and Cu-exchanged X zeolites. *Microporous Mesoporous Mater.* 2008, 111, 80–88.

(24) Murzin, D. Y. Synthesis and characterization of solid base mesoporous catalysts. *Coord. Chem. Rev.* 2013, 257, 483–494.

(25) Zwietering, T. N. Suspended of solid particles in liquid by agitators. *Chem. Eng. Sci.* 1958, 8, 244–253.

(26) Sharma, R. N.; Shaikh, A. A. Solids suspension in stirred tanks with pitched blade turbines. *Chem. Eng. Sci.* 2003, 58, 2123–2140.

(27) Murzin, D. Y. *Engineering Catalysis*; De Gruyter GmbH & Co: Berlin, 2013.

(28) Perego, C.; Peratello, S. Experimental methods in catalytic kinetics. *Catal. Today* 2019, 52, 133–145.

(29) Achma, R. B.; Ghorbel, A.; Dafinov, A.; Medina, F. Copper-supported pillared clay catalysts for the wet hydrogen peroxide catalytic oxidation of model pollutant tyrosol. *Appl. Catal., A* 2008, 349, 20–28.

(30) Lucas, M. S.; Peres, J. A. Removal of COD from olive mill wastewater by Fenton’s reagent: kinetic study. *J. Hazard. Mater.* 2009, 168, 1253–1259.

(31) Rivas, F. J.; Beltrán, F. J.; Gimeno, O.; Alvarez, P. Treatment of brines by combined Fenton’s reagent—aerobic biodegradation. *J. Hazard. Mater.* 2003, 96, 259–276.

(32) Dominguez, C. M.; Quintanilla, A.; Casas, J. A.; Rodriguez, J. J. Kinetics of wet peroxide oxidation of phenol with a gold/activated carbon catalyst. *Chem. Eng. J.* 2014, 253, 486–492.

(33) Zazo, J. A.; Casas, J. A.; Mohedano, A. F.; Gilarranz, M. A.; Rodríguez, J. J. Chemical pathway and kinetics of phenol oxidation by Fenton’s reagent. *Environ. Sci. Technol.* 2005, 39, 9295–9302.

(34) Haario, H. *Mend 6.0 User’s Guide*; Profmath Oy: Helsinki, 2001.

(35) Najjar, W.; Azabou, S.; Sayadi, S.; Ghorbel, A. Screening of Fe–BEA catalysts for wet hydrogen peroxide oxidation of crude olive mill wastewater under mild conditions. *Appl. Catal., B* 2009, 88, 299–304.