Research Article

Removal of recalcitrant organic compounds from an industrial complex effluent by heterogeneous Fenton-type treatment[†]

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Graphical abstractGraphical abdstract

Industrial chemi-mechanical pulping effluents are not affected by conventional treatment. The main parameters involved in Fenton-type treatment were determined. Factorial experiments were applied to evaluate the most favorable range of conditions for $CuO/\gamma-Al_2O_3$ application. The highest reduction of all parameters was obtained at the superior level of all variables, achieving reductions of COD and TOC between 40 and 50%.

Abstract

Because of their chemical complexity, industrial chemi-mechanical pulping effluents are evaporated and burned, in spite of the high associated cost involved in these processes. The aim of this study was to remove recalcitrant compounds from this kind of wastewater using a Fenton-type treatment. The main parameters involved in the process and their influence on the results were determined. Homemade catalysts based on CuO, Fe_2O_3, NiO and ZnO, supported on γ-Al_2O_3 have been tested for catalytic oxidation, and the CuO/γ-Al_2O_3 catalysts showed the greatest effect on total organic carbon (TOC) reduction (52.7%). A series of two-level factorial experiments was subsequently applied to evaluate the most favorable range of conditions for CuO/γ-Al_2O_3 application. The studied variables were hydrogen peroxide concentration ($[H_2O_2]$, g/L), active phase content (metal oxide supported on alumina, %), mass of catalyst (metal oxide/alumina system, g), and reaction temperature (°C). The highest reduction of all parameters was obtained at the superior level of all variables with CuO/γ-Al_2O_3, achieving reductions of chemical oxygen demand (COD) and TOC between 40 and 50%. Increasing catalyst mass did not produce additional benefit. This variable has a significant effect only on the reduction of aromatic compounds. At its low level, reduction in aromatic content exceeded 80%. Color reduction was influenced only by temperature (maximum reduction of 90%).

Abbreviations: AOP, advanced oxidation process; **BAT**, best available technology; **BET**, Brunauer, Emmet, and Teller, **BOD**, biochemical oxygen demand; **CMP**, chemi-mechanical pulping process; **COD**, chemical oxygen demand; **EDS**, energy dispersive X-ray; **HYP**, high yield pulping process; **HPLC**, high performance liquid chromatography; **SD**, standard deviation; **SEM**, scanning electron microscopy; **tc**, treatment combination; **TOC**, total organic carbon; **XRD**, X-ray diffraction

Keywords: Advanced oxidation, Chemi-mechanical pulping effluent, Factorial experimental design, Heterogeneous type Fenton reactions, Recalcitrant compounds

1. Introduction

In Fenton reactions of model compounds, the evolution of oxidation mechanism of the system and its intermediates is widely understood [1--6]. On the contrary, in the case of real industrial streams, the catalytic parameters and catalytic conditions of the treatment are barely known.

Generally, the untreated liquid streams that result from processing of lignocellulosic materials have high biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (mainly fibers), fatty acids, tannins, resin acids, lignin and its derivatives. Some contaminants are natural and other are xenobiotic, i.e. formed during the pulp and paper process, and recalcitrant to degradation [7, 8]. In alkaline sulfite chemi-mechanical pulping processes (CMP), wastewater contains low molecular weight hemicelluloses, sugars, organic acids and several compounds that are recalcitrant to microbiological treatment, such as aromatic derivatives from wood extractives and labile lignin fractions. As CMP processes do not have a chemical recovery system, diluted spent liquors are generally treated in conventional effluent treatment systems, but

recalcitrant compounds are not affected and are discharged as they are [9--11]. A proper effluent treatment is therefore mandatory.

In these processes (as in many other cases), the chemical structure of wastewater is scarcely established, which makes the design of an effluent treatment system very difficult. Since this effluent is recalcitrant to biological degradation and it might be toxic to aquatic species [12, 13], conventional treatment systems are not enough and pulp and paper mills are forced to adopt technologically advanced treatments [14, 15].

Advanced oxidation processes (AOP) exploit the high oxidation potential of hydroxyl radicals, which attack most of organic molecules [16]. The high reactivity of these radicals and their low selectivity during the oxidation process are useful attributes that make these technologies a promising option for the treatment of effluents containing refractory compounds [14, 17].

In many cases, the objective of the oxidation process is not complete mineralization, with the subsequent conversion from organic carbon to carbon dioxide, but the conversion of pollutants into biodegradable substances that do not cause inhibition problems in the biomass of conventional biological treatment, nor cause ecotoxicity problems in the discharge. The application of one method over the other mainly depends on the contaminant concentration and flow rate of the effluent [18, 19].

The utilization of H_2O_2 has emerged as a viable alternative among other oxidants, because it improves the efficiency of the oxidation, it is non-toxic and does not form any harmful by-products, and the reactions are carried out under non-critical conditions [20]. The process is performed at atmospheric pressure and low temperatures. Initial studies on AOP with H_2O_2 were carried out using iron salts as homogeneous catalysts in the reactions known as "Fenton reactions". The main disadvantage of homogeneous catalysts is the difficulty of the post-reaction separation of the catalysts from the product stream. It is then necessary to implement recovery operations to retrieve the used catalyst with the consequent increase of operational costs. An alternative solution to this problem is the deposition of the active phase on a porous solid, which characteristics are comparable to those of homogeneous catalysts, but that can be recovered by simple separation steps for reuse in other processes. Different variants of catalytic systems that work with active ions on a solid support are in study. In the field of heterogeneous catalysis, such reactions are known as "Fenton type reactions" [21--23]. The Fenton reagent's mechanism has not been fully explained because of the variety of complex compounds and intermediates that are formed, and their subsequent reactions. During the reaction with the solution of H_2O_2 and salts of Fe(II), organic compounds are oxidized with a radical chain mechanism [24], where hydroxyl radicals are capable of rapidly attacking organic substrates [25]. The main parameters that govern this system are: the initial concentration of H_2O_2, the concentration of Fe(II) and the temperature of the reaction [26].

High yield pulping processes (HYP) which combine chemical action prior to mechanical action are CMP. The unknown chemical structure and complexity of some contaminants in high yield pulping effluents represent a challenge. The aim of this study was to remove recalcitrant compounds from a CMP industrial effluent using a Fenton type treatment. The main parameters involved in the process and their influence on the results were

determined.

The first part of the work consisted of selecting efficient and stable metal oxides to eliminate recalcitrant substances. To select a particular catalytic system, the behavior of different catalysts consisting of metal oxides supported on alumina was evaluated, analyzing the oxidation of recalcitrant compounds in a Fenton type system. No reports on the treatment of HYP effluents treated by catalytic processes such as Fenton-type reactions have been found. Because of their chemical complexity, "best available technologies" (BAT) practice consists of evaporation and burning, in spite of the high associated cost involved in these processes. An experimental design consisting in a series of two-level factorial experiments was applied to evaluate the most favorable range of conditions for the oxidation of recalcitrant compounds.

Materials and methods

2.1 Black liquor

The spent liquor came from Papel Prensa S.A. integrated mill, located in San Pedro, Argentina, which produces 132 000 tons/year of soda-sulfite chemi-mechanical pulps from a mixture of willows, poplar and eucalyptus, and newspaper. In alkaline sulfite CMP wood chips are impregnated with sodium hydroxide and sodium sulfite (pH 9--10), and they are subsequently treated mechanically in a refiner. Chemical treatment is slight and lignin is not removed, but only softened. This type of pulping allows the use of low-density hardwoods as a fiber raw material. The actual effluent comprises several streams: 1) liquid waste from deinking plant; 2) water from wood treatment; 3) black liquor from the chemical treatment of wood (pH 7-8, deep red color, mainly composed by extractive and lignin derived from the product of the chemical reaction between wood and pulping liquor); 4) effluent from chemi-mechanical pulp washing; 5) effluent from the bleaching plant; and 6) white water from the paper making section of the mill.

As effluent 3) contains the highest polluting load, dilutions of liquor 3) were performed with a liquor/water ratio of 1:50 to simulate the final mill effluent. The liquor was stored in plastic containers and was used without filtration. Oxidative processes were applied to this simulated effluent.

The main characteristics of the industrial spent liquor are shown in Table 1.

2.2 Catalyst preparation and characterization

Samples of several metal oxides supported on alumina were tested at 70°C. Pellets of γ-Al_2O_3 (Alfa SASOL) were used as support and were impregnated using aqueous solutions of $Cu(NO_3) \cdot 2.5\ H_2O$ (Riedel-de Haën, pa), $Ni(NO_3) \cdot 2.6\ H_2O$ (Baker, pa), $Zn(SO_4) \cdot 7\ H_2O$ (Riedel-de Haën, pa), citrate Fe(III) (BioPack, pa) as precursors. The incipient wetness impregnation method comprises mixing the support with an aqueous solution containing an appropriate amount of salt so that, after calcination, the catalyst contains the required metal content. The volume of the solution that is prepared is equal or slightly smaller than the pore volume of the support. The maximum load is limited by the solubility of the precursor in the solution. Solids were air dried during 24 h, then oven dried at 120 °C, and finally calcined at 900 °C in air atmosphere.

To select the metal system, γ-Al_2O_3 (I) pellets of 2.5 mm in diameter and 190 m^2/g of surface area (determined by the Brunauer, Emmet, and Teller method (BET) method) were used. The final charge of the

four catalysts (CuO/Al_2O_3, NiO/Al_2O_3, ZnO/Al_2O_3 and Fe_2O_3/Al_2O_3) was 5% by weight. In addition, experiments were carried out using two commercial pellets catalyst: Haldor-Topsoe (52% CuO, 25% ZnO) and Engelhard (12.5% CuO, 0.3% NiO) for comparison.

To evaluate the factors that influence the process, γ-Al_2O_3 (II) pellets 1.8 mm in diameter and 200 m^2/g of surface area (according to the manufacturer) were used. The final load of catalysts used in this stage was established according to the experimental design.

The support and the catalysts were characterized using the following techniques:

- Surface areas were calculated from nitrogen adsorption at −196 °C by using a Micromeritics FlowSorb II 2300.
- Oxide structures and cluster size of the synthesized metal oxides supported on alumina were determined by techniques of powder X-ray diffraction (powder XRD) using PANanalytical, X'Pert Pro equipped with Cu Kα radiation. The patterns were recorder over a range of $10° < 2\theta < 70°$ and compared to the JCPDS files to confirm phase identities.
- The surface morphology of the catalysts was examined by means of a scanning electron microscopy (SEM).

The elemental composition of the catalysts was determined by energy dispersive (EDS) X-ray spectroscopy using an EDAX Genesis XM4-Sys 60 equipment, equipped with a EDAX multichannel analyzed model EDAM IV, sapphire detector Si(Li) and Be window, super ultra-thin, software EDAX Genesis version 5.11.

2.3 Experimental design

To determine the magnitude of the effect of each variable (factor) on the studied system, experiments were conducted according a 2^4 factorial design. In this design, the number of combinations of treatments (tc) is given by 2^n, where n corresponds to the number of the analyzed experimental variables. In this study, $n = 4$, therefore tc $= 2^4 = 16$ treatments. The studied variables were hydrogen peroxide concentration [H_2O_2] in g/L, active phase content, that is, content of metal oxide supported on alumina (%), mass of catalyst, i.e. metal oxide/alumina system (g) and reaction temperature (°C). The analysis of each experiment was performed using coded levels (+1 and --1 values), which arise from the true values converted to independent unit values of the factors. The real and coded values of each level of the experimental factors are shown in Table 2.

The H_2O_2 dosage was based on the stoichiometric ratio with respect to COD. This was calculated assuming complete oxidation of COD to CO_2 and H_2O. The H_2O_2 stoichiometric concentration respect to COD value was 1.98 g/L. To set H_2O_2 levels, the feasibility of reducing the treatment cost was assessed, so the lowest (sub-stoichiometric I) and uppermost (upper-stoichiometric II) values of the experimental design correspond to H_2O_2/COD ratios of 0.9:1, and 1.2:1, respectively.

2.4 Catalytic activity

A 250 mL PYREX glass batch reactor with a glass stopper equipped with a condenser, a thermocouple, and pH meter were used. To minimize external mass transport effects, experiments were carried out with a high-

speed magnetic stirrer (1200 rpm). Testing was performed in contact with air at atmospheric pressure. The reaction volume was 100 mL (with a dilution of 1:50 such as initial values of COD and TOC of the diluted liquor were 931 and 433 mg/L, respectively). The experiments were conducted using γ-Al$_2$O$_3$. The H$_2$O$_2$/COD ratio for the selection of the metallic system analysis was fixed as 9.4:1. H$_2$O$_2$ in excess (18.6 g/L) was used to select the most suitable catalyst metal system, since the extent of recalcitrance of this effluent was not known. The oxidation reaction was carried out at 70°C and with 1 g catalyst in all assays. All catalytic reactions were developed without pH adjustment to record the natural tendency of each catalyst system, allowing to avoid pH control systems and to compare the activity of the different catalyst systems.

Once the catalyst was added to the liquid mixture in the reactor, and the system reached the reaction temperature, initial time was recorded ($t = 00$, corresponding to the sample M00). At this point the corresponding amount of H$_2$O$_2$ was added, initiating the oxidation reaction (time zero, $t = 0$, corresponding to the sample M0). 2.5 mL samples were taken at different time intervals such as 0, 15, 30, 60, 120, 180 and 240 min (each sample was labeled from M0 to M6 according to time intervals) and were kept in plastics vials and then analyzed. The total oxidation reaction time was 240 min (M6). The analyzed responses throughout the reaction were: percentage of TOC reduction (TOC % reduction), percentage of aromatic content reduction (aromatic % reduction), percentage of COD reduction (COD % reduction), percentage of color reduction (color % reduction) and H$_2$O$_2$ consumption.

TOC conversion in blank trials (Al$_2$O$_3$ + H$_2$O$_2$ + effluent; H$_2$O$_2$ + effluent; Al$_2$O$_3$ + effluent) was negligible.

2.5 Analytical Techniques

Solids were determined according to Tappi T629 [27]. Inorganic content was assessed by determining the ashes at 525°C according to Tappi T211 [28]. The color of the effluent was measured by spectroscopy, measuring the absorbance at 450 nm (TECHCOMP spectrometer). COD was measured following the technique SM 5220-B (Standard Methods for the Examination of Water and Wastewater) [29]. To assess oxidation, total organic carbon (TOC) was measured using a TOC analyzer (Shimadzu, TOC-VCPN model). The evolution of aromatic compounds and the acids present in liquors, and peroxide consumption during the reaction, were quantified by high performance liquid chromatography (HPLC) (Waters, Massachusetts, USA) using an Aminex-HPX87H column under the following conditions: 4 mM H$_2$SO$_4$ as eluent, flow rate of 0.6 mL/min, 35°C, and UV diode array detector (organic acids at 210 nm and aromatic compounds at 254 nm).

2.6 Statistical evaluation

All results were statistically analyzed using the Statgraphics software at 95% of confidence level.

3   Results and discussion

3.1 Characterization of the catalysts

The characterization results of the γ-alumina and tested catalysts are summarized in Table 3. Both the impregnation process and the thermal treatment induced a decrease in the surface areas [30], but despite the

calcination temperatures, the results show acceptable surface areas after calcination, which provides the ability to achieve high oxidation values in further catalyst experiments. Therefore, the key point in producing high-performance catalysts is to increase or maintain the surface area [31]. BET values from Table 3 also indicate that the use of γ-Al_2O_3 is very important to provide high surface areas [32]. The performance of metal oxides as catalyst supports depends on their crystalline structure and textural properties. Although porosity of the catalyst was not measured, it can be assumed that porosity was slightly affected by calcination. Mesoporous materials such as γ-Al_2O_3 are preferred because they offer the advantage of avoiding pore plugging [33]. Mesopores are the paths for reactants and products, rendering high dispersion of active phase [34] and increase the amount of accessible active sites, improving catalytic reactions [35].

X-ray diffraction analysis revealed the presence of the characteristic peaks of the γ-Al_2O_3 phase (see Fig. 1). No peaks of other metals-containing phases were detected, only the main peaks corresponding to the γ-alumina phase, which are $2\theta = 66.7°$ (100), $46.1°$ (80), $37.4°$ (60), and $39.7°$ (30). This result shows that the support is thermally stable and no structural changes occurred during the preparation of the catalyst, at least measurable by this technique [36]. From the absence of diffraction lines associated with the studied metal oxides, it can also be deduced that the concentration of impregnated active phase is quite low and the formed particles are well dispersed oxides [37], preventing its detection by XRD, as reported for Fe_2O_3/Al_2O_3 [30], CuO/Al_2O_3 [38], NiO/Al_2O_3 [39], and ZnO/Al_2O_3 [40].

The dispersion of metal species on the surface of the catalysts was analyzed by SEM-EDAX. Figure 2 shows SEM pictures, EDS spectra and the quantitative analysis (active phase content) obtained for CuO/Al_2O_3(I), NiO/Al_2O_3(I), and ZnO/Al_2O_3(I) catalysts. Fe_2O_3/Al_2O_3(I) SEM and EDAX spectra are not shown, but the quantification gave 7.37% of Fe_2O_3. This difference of 5% can be attributed to experimental errors, mostly of the equipment of measure. For all catalyst systems analyzed by SEM, the supported particles are well dispersed and distributed homogeneously over the substrate. The composition of each catalyst via spectrometry and EDX was determined as the average of four replicas. Catalysts based on Zn and Fe presented sulfur and chlorine impurities, respectively. The presence of the impurities was due to precursors used in both cases, which were not fully eliminated by thermal treatment during calcination.

3.2 Selection of the metallic system

Catalytic activity tested on different systems is summarized in Fig. 3 (as TOC % reduction). The NiO/Al_2O_3 catalyst (reduction of 3.7%) showed a statistically similar behavior to that of the blank test ($p < 0.05$); i.e. which means that does not produce a significant effect on percentage of TOC reduction. These results differ from those observed by other authors [37, 41], who confirmed the high oxidizing power of supported nickel applied to several types of compounds and the strong interaction between the metal particles and the support. These differences could be explained by the low active phase content and low working temperature used in this work. The catalyst NiO/Al_2O_3, and Engelhard (39.6% of TOC reduction), showed significant differences in their behavior ($p < 0.05$), but it is presumed that the high conversion rate achieved by the bimetallic catalyst is not the result of nickel action. Haldor-Topsoe and ZnO/Al_2O_3 (47.1 and 38.7% of TOC reduction,

respectively) showed no significant differences in their behavior ($p < 0.05$). Copper and zinc appear to have a synergistic effect. In addition, CuO/Al_2O_3 and Fe_2O_3/Al_2O_3 catalysts presented a significant effect on TOC (52.7 and 30.10%, respectively). The oxidative action of Fe_2O_3/Al_2O_3 was not significantly different from ZnO/Al_2O_3 ($p < 0.05$). Therefore, CuO/Al_2O_3, ZnO/Al_2O_3 and Fe_2O_3/Al_2O_3 catalysts have the greatest effect on the oxidation of recalcitrant compounds, and consequently, the highest values on the percentages of TOC reduction. The maximum conversion values achieved were generally low. This may be due to the high value of the initial concentration of peroxide, since H_2O_2 in excess can generate radical capturing compounds (scavenging effect), decreasing the oxidation efficiency [42].

Leaching of the active phase was not observed in any of the tests when working with an excess of H_2O_2, possibly also due to the slight variation of pH of the solutions, which remained near neutrality [43, 44]. This trend can be explained by the formation of sodium carbonate, whereas the reaction proceeds because of the oxidation of liquor components. It should be noted that alumina used as support gives the catalyst certain chemical properties that influence pH, among other conditions of the reaction. The pH values of the oxidation reactions were close to 7.3, the value in the blank trials using only the support (alumina as catalyst). In cases when homemade catalyst was used, the pH was also close to this value (see Table 4), indicating that the pH of the reaction medium is also controlled by the support [45]. Acid and basic sites at the surface of γ-Al_2O_3 behave exactly as acid and basic substances in solution, probably buffering the reactions with the alkaline liquor. Therefore, they respond reversibly to a change in the pH of the solution with the concomitant variation of the total surface charge [46]. Thus, it is possible that the higher catalytic activity of a catalyst based on copper is also based on the favorable pH of the reaction [47]. On the contrary, optimal pH for an iron based catalyst is between 3 and 4, which discourages their use for practical applications [48].

Copper oxide was selected as oxidation catalyst for the rest of the work, as it generated one of the highest percentages of mineralization. Moreover, the pH range of the reaction media (near neutral) is considered optimal for its use [49], which represents an additional advantage when working with alkaline liquors because pH control is not needed.

3.3 Effect of temperature, hydrogen peroxide concentration, active phase content, and mass of catalyst

The results of the analysis of the factorial design at 240 min of reaction (M6) are shown in Table 5.

The effect of factors is defined as the change in the studied response as a consequence of the change in factor level, from the lower to the upper level and vice versa. The effect of the studied factors (and their levels) on the percentage of TOC reduction, aromatic compounds reduction, and COD reduction can be seen in Fig. 4. Standard deviations (SD) for the means of TOC, aromatic compounds and COD were ±1.83, ±2.22, and ±1.28 respectively. The percentage of TOC reduction, aromatic compounds reduction, and COD reduction can be seen in Table 6.

Temperature was the most important factor for TOC reduction over the studied range (*p*-value: 0.0002). The oxidation degree reached a maximum at the highest temperature, as shown in Fig. 4 (70°C). A potential solution to improve mineralization degree with the same dose of H_2O_2 is to increase temperature, because it determines the radicals generation rate [50, 51], reducing reaction costs [52, 53]. The detrimental effect of

competitive reactions and scavenging, which appears when the ratio of oxidizing agent is not correct (for example, when hydrogen peroxide concentrations is above the optimum), is partly offset by the positive action of increasing temperature [26]. Temperature is also the most influential factor in COD and aromatic compounds reduction (p-value of 0), as shown in Fig. 4. The greatest percentages of reduction were achieved at the highest value of the variable (70°C). Discoloration of the effluent showed the same behavior (p-value: 0.0084).

Hydrogen peroxide concentration showed significant influence on TOC conversion rates (p-value: 0.0243), COD (p-value: 0.0336) and aromatic content (p-value: 0.0005). Even if the best oxidation rates were attained working with the highest H_2O_2 concentration, conversion rates were not as high as expected (Fig. 4). Peroxide did not have significant effect on discoloration of the effluent. This behavior is not in agreement with findings of other authors [54, 55], but H_2O_2 concentrations used in the present study were low.

Only the catalyst mass had a significant effect on the reduction of aromatic compounds (p-value: 0.0207). The highest reduction was achieved with 0.5 g of catalyst load (Fig. 4). Increasing catalyst mass within the studied range (0.5–1 g) did not result in an additional benefit in COD and TOC reduction, although active sites for H_2O_2 decomposition and for organic compounds adsorption are increased [56]. Significant reductions of TOC and COD were achieved by increasing active phase content (p-values: 0.0179 and 0.0002 for TOC and COD, respectively), suggesting that the active phase (catalyst after calcination) is not in the bulk of the support but on the surface (Fig. 4).

The interaction between active phase and temperature showed to be highly significant ($p = 0.0183$). A synergistic effect can be observed in TOC, COD, and aromatic reduction when both variables were at their uppermost level (2.5 % and 70°C). The interactions between [H_2O_2] and active phase ($p = 0.0194$), and [H_2O_2] and catalyst mass ($p = 0.0077$) were only significant on percentage of COD reduction.

The significance of each factor over the response varied along the oxidation reaction, so this must be taken into account to select and optimize the catalytic system. The effect of each significant factor on the percentages of TOC and of aromatic compounds reductions is shown in Fig. 5 (non-significant factors and interactions are not shown). Figure 5 shows that maximum removals were produced at high levels of temperature, hydrogen peroxide, and active phase for TOC, whereas in the case of aromatic compounds, high levels of temperature and peroxide, and low level of catalyst mass were necessary.

According to Table 5, final pH remained almost constant despite the different tested conditions. Similar final pH values probably are an indication that there are similar distribution of intermediates and/or similar accumulation of carboxylic acids at the end of each oxidation reaction [57]. As the only identified species were acetic acid, oxalic acid, sulfur compounds, sodium carbonate and other salts [10, 11], probably these last ones buffered the oxidation reaction and avoid higher degree of mineralization. It is known that those compounds are recalcitrant and interfere the Fenton oxidation process [58, 59].

Since H_2O_2 consumption is critical in this catalytic process, the oxidation reactions were also evaluated using the "η parameter" (Table 5). This parameter, as defined by several authors [60], represents the reagent consumption considered as the amount of TOC (mg/L) and COD (mg/L) converted per unit of decomposed H_2O_2 (g/L). From the comparison of treatment conditions which differ only in the temperature of reaction, the

efficiency of H_2O_2 does not decrease when increasing temperature as should be expected if H_2O_2 is decomposed due to thermal instability. On the contrary, a higher temperature implies a faster, and more efficient cooper-catalyzed H_2O_2 conversion into radicals, enhancing mineralization. Other authors [54] also found that H_2O_2 conversion into hydroxyl radicals is accelerated as the temperature increases, and the amount of H_2O_2 available to scavenge these radicals is accordingly small, allowing a higher H_2O_2 consumption yield for a given conversion of TOC and COD.

The long-term stability of a catalyst is essential for industrial applications. A catalyst batch was retained and reused again at the same conditions (tc: 12 of the experimental design), without treatment between runs maintaining a similar alkaline liquor concentration. The solid was just recovered from the solution after the reaction, dried at room temperature and tested again. The TOC removal achieved and the H_2O_2 consumed were similar after five consecutive cycles, indicating that it is possible to reuse the catalyst without affecting its efficiency. The analysis of TOC reduction profiles in the repeated experiments showed a slight induction period which marginally lengthened the consecutive runs. Nevertheless, the results observed for the fifth reuse of the catalyst showed that it was still active and able to be used.

3.4 Effect of the initial concentration of hydrogen peroxide and active phase in conditions out of the design

Fenton systems using Cu^{2+} catalysts require a larger stoichiometric excess of H_2O_2, compared to conventional Fenton systems, to overcompensate the competitive scavenging by O_2 (this treatment needs to work under aerobic conditions) [49]. To verify if this is the case in the current study, hydrogen peroxide concentrations much higher than stoichiometric values were tried (Fig. 6). Under these conditions (large excess of oxidizing agent) differences in mean reductions of TOC and COD were 34 and 40%, respectively, of those obtained with upper-stoichiometric II concentration, respectively (p-value < 0.05), as shown in Fig. 6. The three studied H_2O_2 concentrations resulted in significant differences on the reduction of aromatic compounds (p-value < 0.05). As H_2O_2 concentration increases, the amount of hydroxyl radicals available for the oxidation of pollutants also increases and the removal of recalcitrant compounds increases as well. Nevertheless, the efficiency of a dose of H_2O_2 80% higher than that of the initial trials was very low (only 15--20% of TOC reduction). It is possible that the excess of H_2O_2 has promoted scavengers generation (radical capture compounds), decreasing the oxidation efficiency [61]. Final TOC conversions were 37, 40, and 62% for peroxide concentrations corresponding to sub-stoichiometric I, upper-stoichiometric II, and in excess, respectively.

Increasing the active phase induces the oxidant to generate more free radicals [62]. A correct balance between the mass of catalyst and the supported metal oxide is essential to maximize the amount of radicals generated in these systems [63]. Oxidation reactions using 5% of active phase were carried out (in addition to the design), but there were no statistically significant differences in COD and aromatic reductions between the three amounts of active phase tried (Fig. 6). TOC conversion decreased by 39.2% with respect to the other amounts of active phase when 5% was used (p-value < 0.05). Even if it is generally assumed that the concentration of the active phase has a strong influence on free radicals generation and it has also a great

influence on the kinetics reaction of TOC reduction [64, 65], it was not the case in this study. The relative difference between aromatic compounds and TOC removal was higher when using 5% of active phase. The results suggest that an important amount of the organic intermediates remain in the reaction mixture [66]. In conventional Fenton processes, the organic matter competes with the metallic substance for the hydroxyl radicals. It is then assumed that with 5% of active phase, the TOC at the end of the catalytic reaction is low, as the ratio metal content/ oxidizing agent decreased [42, 67].

Concluding Remarks

Catalytic oxidation in the presence of hydrogen peroxide could be an efficient alternative to treat effluents from chemi-mechanical pulp processes.

It was found that NiO/Al_2O_3 catalyst was not active, since it did not produce a significant effect on the TOC reduction.

Catalysts based on Cu, Fe, and Zn showed the best results in terms of TOC reduction and aromatic reduction along the oxidation reaction. Copper did not generate active phase leaching when working with an excess of H_2O_2.

When working with the Cu catalyst, temperature showed to be the most important factor for TOC, COD, and aromatic reduction of the simulated effluent in the studied range, being the only factor that significantly affected the effluent discoloration. The highest values of oxidation and discoloration were achieved at the uppermost temperature level (70°C).

Hydrogen peroxide concentration significantly reduced TOC and COD, although the achieved conversion (40--50%) was lower than expected in its uppermost level (2.5 g/L). However, reduction of the aromatic content was near 80%. The inability of the catalyst to achieve higher oxidation of refractory compounds was not a consequence of the availability of oxidizing agent.

Catalyst mass affected only the reduction of aromatic compounds, showing its greatest effect at its lowest level (0.5 g).

The highest level of active phase tested in the experimental design (2.5%) produced maximum reductions of TOC and COD. Working with high percentages of active phase (5%) did not produce any improvement.

The authors have declared no conflict of interest.

References

[1]   P. Massa, M. A. Ayude, F. Ivorra, R. Fenoglio, P. Haure, Phenol oxidation in a periodically operated trickle bed reactor, *Catal. Today* 2005, *107–108*, 630–636.

[2]   M. Pera-Titus, V. García-Molina, M. a Baños, J. Giménez, S. Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: a general review, *Appl. Catal., B* 2004, *47 (4)*, 219–256.

[3]   S. Karthikeyan, V. K. Gupta, R. Boopathy, a. Titus, G. Sekaran, A new approach for the degradation of high concentration of aromatic amine by heterocatalytic Fenton oxidation: Kinetic and spectroscopic

studies, *J. Mol. Liq.* 2012, *173,* 153–163.

[4]   J.-H. Sun, S.-P. Sun, M.-H. Fan, H.-Q. Guo, L.-P. Qiao, R.-X. Sun, A kinetic study on the degradation of *p*-Nitroaniline by Fenton oxidation process, *J. Hazard. Mater.* 2007, *148 (1–2)*, 172–177.

[5]   N. Kang, D. S. Lee, J. Yoon, Kinetic modeling of Fenton oxidation of phenol and monochlorophenols, *Chemosphere* 2002, *47 (9)*, 915–924.

[6]   S. Esplugas, J. Giménez, S. Contreras, E. Pascual, M. Rodríguez, Comparison of different advanced oxidation processes for phenol degradation, *Water Res.* 2002, *36 (4)*, 1034–1042.

[7]   European Commission, *Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques in the Pulp and Paper Industry*, Publications Office of the European Union, Luxembourg **2001**.

[8]   A. Muna, T. Sreekrishnan, Aquatic toxicity from pulp and paper mill effluents: a review, *Adv. Environ. Res.* 2001, *5 (2)*, 175–196.

[9]   P. Meza, F. E. Felissia, M. C. Area, Reduction of the recalcitrant COD of high yield Pulp mills effluents by AOP, Part 1. Combination of Ozone and activated sludge, *Bioresources* 2010, *6 (2)*, 1053–1068.

[10]   M. C. Area, J. L. Valade, Revisión de la composición de los licores residuales de los procesos de pulpado y su aprovechamiento, *Papel. Rev. Pap. Esp. Am. Lat.* 1998, 67–70.

[11]   M. C. Area, J. L. Valade, Hacia una utilización integral de la madera. Revisión de los procesos de pulpado con acción química, *Papel. Rev. Pap. Esp. Am. Lat.* 1998, 47–51.

[12]   C. Baptista, D. Robert, A. P. Duarte, Effect of pulping conditions on lignin structure from maritime pine kraft pulps, *Chem. Eng. J.* 2006, *121 (2–3)*, 153–158.

[13]   L. Hou, Y. Xie, G. Ying, Z. Fang, Developmental and reproductive characteristics of western mosquitofish (*Gambusia affinis*) exposed to paper mill effluent in the Dengcun River, Sihui, South China, *Aquat. Toxicol.* 2011, *103 (3–4)*, 140–149.

[14]   K.-H. Kim, S.-K. Ihm, Heterogeneous catalytic wet air oxidation of refractory organic pollutants in industrial wastewaters: a review, *J. Hazard. Mater.* 2011, *186 (1)*, 16–34.

[15]   L. G. Covinich, D. I. Bengoechea, R. J. Fenoglio, M. C. Area, Advanced Oxidation Processes for Wastewater Treatment in the Pulp and Paper Industry : A Review, *Am. J. Environ. Eng.* 2014, *4 (3)*, 56–70.

[16]   R. Munter, Advanced oxidation processes – current status and prospects, *Proc. Est. Acad. Sci. Chem.* 2001, *50 (2)*, 59–80.

[17]   S. Sharma, J. P. Ruparelia, M. L. Patel, A general review on Advanced Oxidation Processes for waste water treatment, *Inst. Technol. Nirma Univ. Ahmedabad* 2011, 8–10.

[18]   A. R. Fernández-Alba, P. Letón García, R. Rosal García, M. Dorado Valiño, S. Villar Fernandez, J. M. Sanz García, Tratamientos avanzados de aguas residuales industriales. Informe de vigilancia tecnológica Madrid, in *Universidad de Alcála, Círculo de Innovación en Tecnologías Medioambientales y Energía (CITME)*, *J. M., Colección vt2*, CEIM Dirección General de Universidades e Investigación, Madrid **2006**.

[19]   R. Alnaizy, A. Akgerman, Advanced oxidation of phenolic compounds, *Adv. Environ. Res.* 2000, *4 (3)*, 233–244.

[20]   P. Massa, A. Dafinov, F. Medina Cabello, R. Fenoglio, Catalytic wet peroxide oxidation of phenolic

solutions over Fe_2O_3/CeO_2 and WO_3/CeO_2 catalyst systems, *Catal. Commun.* 2008, *9 (7)*, 1533–1538.

[21]   P. Massa, A. Dafinov, R. Fenoglio, F. Medina Cabello, Degradación catalítica de fenol con peróxido d e hidrógeno : sistemas fenton heterogéneo. Catalytic degradation of phenol with hydrogen peroxide: heterogeneous fenton-like systems, *Rev. Soc. Quím. Perú* 2009, *75 (2)*, 194–200.

[22]   H. Al-Sheeha, M. Marafi, A. Stanislaus, Reclamation of alumina as boehmite from an alumina-supported spent catalyst, *Int. J. Miner. Process.* 2008, *88 (3–4)*, 59–64.

[23]   G. Cao, M. Sheng, W. Niu, Y. Fei, D. Li, Regeneration and reuse of iron catalyst for Fenton-like reactions, *J. Hazard. Mater.* 2009, *172 (2–3)*, 1446–1449.

[24]   L. F. Liotta, M. Gruttadauria, G. Di Carlo, G. Perrini, V. Librando, Heterogeneous catalytic degradation of phenolic substrates: catalysts activity, *J. Hazard. Mater.* 2009, *162 (2–3)*, 588–606.

[25]   M. S. Lucas, J. A. Peres, Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation, *Dye Pigm.* 2006, *71 (3)*, 236–244.

[26]   F. Torrades, M. Pérez, H. D. Mansilla, J. Peral, Experimental design of Fenton and photo-Fenton reactions for the treatment of cellulose bleaching effluents, Chemosphere 2003, 53 (10), 1211–1220.

[27]   TAPPI Test Methods, *Tappi T629 wd-80, Analysis of Spent Sulfite Liquor*, TAPPI PRESS, Atlanta **2000**.

[28]   TAPPI Test Methods, *Tappi T211 om-93, Ash in wood, pulp, paper and paperboard: combustion at 525°C*, TAPPI PRESS, Atlanta **2000**.

[29]   L. S. Clesceri, A. E. Greenberg, A. D. Eaton, *APHA Standard Methods for the Examination of Water and Wastewater*, 17th Ed., American Public Health Association, American Water Works Associaction, Water Pollution Control Federation, Washington, DC **1998**.

[30]   C. Di Luca, F. Ivorra, P. Massa, R. Fenoglio, Alumina Supported Fenton-Like Systems for the Catalytic Wet Peroxide Oxidation of Phenol Solutions, *Ind. Eng. Chem. Res.* 2012, *51*, 8979–8984.

[31]   F. Schiith, W. Sing, J. Weitkamp, *Handbook of Porous Solids*, Wiley-VCH, Weinheim, Germany **2002**.

[32]   Y. S. Wu, J. Ma, F. Hu, M. C. Li, Synthesis and Characterization of Mesoporous Alumina via a Reverse Precipitation Method, *J. Mater. Sci. Technol.* 2012, *28 (6)*, 572–576.

[33]   A. Khaleel, S. Al-Mansouri, Meso-macroporous γ-alumina by template-free sol–gel synthesis: The effect of the solvent and acid catalyst on the microstructure and textural properties, *Colloids Surf., A* 2010, *369, (1–3)*, 272–280.

[34]   M. Akia, S. M. Alavi, M. Rezaei, Z.-F. Yan, Optimizing the sol–gel parameters on the synthesis of mesostructure nanocrystalline γ-Al_2O_3, *Microporous Mesoporous Mater.* 2009, *122 (1–3)*, 72–78.

[35]   J. C. Groen, W. Zhu, S. Brouwer, S. J. Huynink, F. Kapteijn, J. A. Moulijn, J. Pe, Direct Demonstration of Enhanced Diffusion in Mesoporous ZSM-5 Zeolite Obtained via Controlled Desilication, J. Am. Chem. Soc. 2007, *6*, 2003–2008,.

[36]   U. Laska, C. G. Frost, G. J. Price, P. K. Plucinski, Easy-separable magnetic nanoparticle-supported Pd catalysts: Kinetics, stability and catalyst re-use, *J. Catal.* 2009, *268 (2)*, 318–328.

[37]   C.-L. Chen, C.-H. Wang, H.-S. Weng, Supported transition-metal oxide catalysts for reduction of

sulfur dioxide with hydrogen to elemental sulfur, *Chemosphere* 2004, *56 (5)*, 425–431.

[38]   S.-K. Kim, K.-H. Kim, S.-K. Ihm, The characteristics of wet air oxidation of phenol over CuO$_x$/Al$_2$O$_3$ catalysts: effect of copper loading, *Chemosphere* 2007, *68 (2)*, 287–292.

[39]   A. Alejandre, F. Medina, P. Salagre, A. Fabregat, J. Sueiras, Characterization and activity of copper and nickel catalysts for the oxidation of phenol aqueous solutions, *Appl. Catal., B* 1998, *18 (3–4)*, 307–315.

[40]   L. Paulhiac, O. Clause, Surface Coprecipitation of Co(II), Ni(II), or Zn(II) with Al(II1) Ions during Impregnation of y-Alumina at Neutral pH, *J. Am. Chem. Soc* 1993, *115*, 11602–11603.

[41]   H.-W. Kim, K.-M. Kang, H.-Y. Kwak, J. H. Kim, Preparation of supported Ni catalysts on various metal oxides with core/shell structures and their tests for the steam reforming of methane, *Chem. Eng. J.* 2011, *168 (2)*, 775–783.

[42]   S. G. Schrank, H. J. José, R. F. P. M. Moreira, H. F. Schröder, Applicability of Fenton and H2O2/UV reactions in the treatment of tannery wastewaters, *Chemosphere* 2005, *60 (5)*, 644–55.

[43]   N. Inchaurrondo, J. Cechini, J. Font, P. Haure, Strategies for enhanced CWPO of phenol solutions, *Appl. Catal., B* 2012, *111–112*, 641–648.

[44]   J. Herney-Ramirez, M. A. Vicente, L. M. Madeira, Heterogeneous photo-Fenton oxidation with pillared clay-based catalysts for wastewater treatment: A review, *Appl. Catal., B* 2010, *98 (1–2)*, 10–26.

[45]   J. G. Carriazo, L. F. Bossa-benavides, E. Castillo, Actividad catalítica de metales de transición en la descomposición de peróxido de hidrógeno, *Quim. Nov.* 2012, *35 (6)*, 1101–1106.

[46]   M. Trueba, S. P. Trasatti, γ-Alumina as a Support for Catalysts: A Review of Fundamental Aspects, *Eur. J. Inorg. Chem.* 2005, *17*, 3393–3403.

[47]   M. J. Ndolomingo, R. Meijboom, Kinetic analysis of catalytic oxidation of methylene blue over γ-Al2O3 supported copper nanoparticles, *Appl. Catal., A* 2015, *506*, 33–43.

[48]   E. G. Garrido-Ramírez, B. K. Theng, M. L. Mora, Clays and oxide minerals as catalysts and nanocatalysts in Fenton-like reactions — A review, *Appl. Clay Sci.* 2010, 47, 182–192.

[49]   A. D. Bokare, W. Choi, Review of iron-free Fenton-like systems for activating H$_2$O$_2$ in advanced oxidation processes, *J. Hazard. Mater.* 2014, *275*, 121–135.

[50]   F. Zeinaly, J. Shakhes, N. Zeinali, Multi stage peroxide and activated peroxide bleaching of kenaf bast pulp, *Carbohydr. Polym.* 2013, *92 (2)*, 976–981.

[51]   M. S. F. Santos, A. Alves, L. M. Madeira, Paraquat removal from water by oxidation with Fenton's reagent, *Chem. Eng. J.* 2011, *175*, 279–290.

[52]   G. Pliego, J. A. Zazo, J. A. Casas, J. J. Rodriguez, Case study of the application of Fenton process to highly polluted wastewater from power plant, *J. Hazard. Mater.* 2013, *252–253*, 180–185.

[53]   M. Xu, Q. Wang, Y. Hao, Removal of organic carbon from wastepaper pulp effluent by lab-scale solar photo-Fenton process, *J. Hazard. Mater.* 2007, *148 (1–2)*, 103–109.

[54]   E. C. Catalkaya, F. Kargi, Color, TOC and AOX removals from pulp mill effluent by advanced oxidation processes: a comparative study, *J. Hazard. Mater.* 2007, *139 (B)*, 244–253.

[55]   S. Karimi, A. Abdulkhani, A. H. B. Ghazali, F.-R. Ahmadun, A. Karimi, Color remediation of chemimechanical pulping effluent using combination of enzymatic treatment and Fenton reaction,

Desalination 2009, *249*, 870–877.

[56] J. H. Ramirez, F. J. Maldonado-Hódar, A. F. Pérez-Cadenas, C. Moreno-Castilla, C. A. Costa, L. M. Madeira, Azo-dye Orange II degradation by heterogeneous Fenton-like reaction using carbon-Fe catalysts, *Appl. Catal., B* 2007, *75*, 312–323.

[57] N. S. Inchaurrondo, P. Massa, R. Fenoglio, J. Font, P. Haure, Efficient catalytic wet peroxide oxidation of phenol at moderate temperature using a high-load supported copper catalyst, *Chem. Eng. J.* 2012, *198–199*, 426–434.

[58] E. Brillas, A review on the degradation of organic pollutants in waters by UV photoelectro-Fenton and solar photoelectro-Fenton, *J. Braz. Chem. Soc.* 2014, *25 (3)*, 393–417.

[59] J. A. Zazo, J. A. Casas, C. B. Molina, A. Quintanilla, J. J. Rodriguez, Evolution of Ecotoxicity upon Fenton ' s Oxidation of Phenol in Water, Environ. Sci. Technol. 2007, *41 (20)*, 7164–7170.

[60] J. A. Zazo, G. Pliego, S. Blasco, J. A. Casas, J. J. Rodriguez, Intensification of the Fenton Process by Increasing the Temperature, *Ind. Eng. Chem. Res* 2011, *50*, 866–870.

[61] H. Zangeneh, A. A. L. Zinatizadeh, M. Feizy, A comparative study on the performance of different advanced oxidation processes (UV/O3/H2O2) treating linear alkyl benzene (LAB) production plant's wastewater, *J. Ind. Eng. Chem.* 2014, *20 (4)*, 1453–1461.

[62] J. Sotelo, G. Ovejero, F. Martínez, J. Melero, A. Milieni, Catalytic wet peroxide oxidation of phenolic solutions over a LaTi1−xCu$_x$O$_3$ perovskite catalyst, *Appl. Catal., B* 2004, *47*, 281–294.

[63] M. F. Sevimli, E. Deliktas, S. Serkan, A comparative study for treatment of white liquor by different applications of Fenton process, *Arab. J. Chem.* 2013, *7*, 1116–1123.

[64] M. J. Farré, X. Doménech, J. Peral, Assessment of photo-Fenton and biological treatment coupling for Diuron and Linuron removal from water, *Water Res.* 2006, *40*, 2533–2540.

[65] R. C. Martins, A. F. Rossi, R. M. Quinta-Ferreira, Fenton's oxidation process for phenolic wastewater remediation and biodegradability enhancement, *J. Hazard. Mater.* 2010, *180*, 716–721.

[66] B. Y. Jibril, A. Y. Atta, Y. M. Al-Waheibi, T. K. Al-Waheibi, Effect of copper loadings on product selectivities in microwave-enhanced degradation of phenol on alumina-supported copper oxides, *J. Ind. Eng. Chem.* 2013, *19*, 1800–1804.

[67] E. Neyens, J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique, *J. Hazard. Mater.* 2003, *98 (B)*, 33–50.

Figure 1: XRD pattern. A) Fresh catalyst used in the selection of metal system. B) Fresh catalyst used in the experimental design

Figure 2: SEM images (2000×) and EDS spectra, a) CuO/Al$_2$O$_3$(I), b) ZnO/Al$_2$O$_3$(I), c) NiO/Al$_2$O$_3$(I)

Figure 3: TOC reduction (%) for different catalytic systems. Blank trial I: Al$_2$O$_3$/effluent; blank trial II: Al$_2$O$_3$/H$_2$O$_2$/effluent; blank trial III: H$_2$O$_2$/effluent (blank trials are batch reactions without active phase or

hydrogen peroxide)

Figure 4: Effect of significant factors on TOC reduction (%), aromatic compounds reduction, and COD reduction.

Figure 5: Reduction (%) of: a) TOC, b) aromatic compounds, for 240 min of reaction.

Figure 6: Influence of peroxide concentration and active phase content on the TOC reduction (%), aromatic compounds reduction (%), and COD reduction (%).

Table 1: Chemical characteristics of the spent liquor

Total soluble solids (g/L)	61.1
pH	7.4
COD (mg/L)	46 550
TOC (mg/L)	21 665
Ashes at 525°C (% of total soluble solids)	52.3
Acetic acid (g/L)	23.6
Formic acid(g/L)	0.3
Propionic acid (g/L)	0.6

Table 2: Levels of each experimental factor in real and transformed values

Treatment (tc)	$[H_2O_2]$ g/L	Active phase %	Mass g	Temperature ºC	$[H_2O_2]$	Active phase	Mass	Temperature
1	1.78	1.25	0.5	45	--1	--1	--1	--1
2	2.43	1.25	0.5	45	1	--1	--1	--1
3	1.78	2.5	0.5	45	--1	1	--1	--1
4	2.43	2.5	0.5	45	1	1	--1	--1
5	1.78	1.25	1.0	45	--1	--1	1	--1
6	2.43	1.25	1.0	45	1	--1	1	--1
7	1.78	2.5	1.0	45	--1	1	1	--1
8	2.43	2.5	1.0	45	1	1	1	--1
9	1.78	1.25	0.5	70	--1	--1	--1	1
10	2.43	1.25	0.5	70	1	--1	--1	1
11	1.78	2.5	0.5	70	--1	1	--1	1
12	2.43	2.5	0.5	70	1	1	--1	1
13	1.78	1.25	1.0	70	--1	--1	1	1
14	2.43	1.25	1.0	70	1	--1	1	1
15	1.78	2.5	1.0	70	--1	1	1	1
16	2.43	2.5	1.0	70	1	1	1	1

Table 3: Characterization Results of the Support and the Catalysts

Catalyst	Metallic content (%p/p)	Calcination temperature (ºC)	BET area (m²/g)
γ-Al$_2$O$_3$(I)	--	--	190
γ-Al$_2$O$_3$(II)	--	--	200*
Haldor-Topsoe	52% CuO/25% ZnO	--	66
Engelhard	12.5% CuO/0.3% NiO	--	210
Fe$_2$O$_3$/Al$_2$O$_3$(I)	5% Fe$_2$O$_3$/Al$_2$O$_3$	900	142
CuO/Al$_2$O$_3$(I)	5% CuO/Al$_2$O$_3$	900	187
NiO/Al$_2$O$_3$(I)	5% NiO/Al$_2$O$_3$	900	186
ZnO/Al$_2$O$_3$(I)	5% ZnO/Al$_2$O$_3$	900	190
CuO/Al$_2$O$_3$(II)	2.5% CuO/Al$_2$O$_3$	900	170
CuO/Al$_2$O$_3$(II)	1.25% CuO/Al$_2$O$_3$	900	133

*According to the manufacturer

Table 4: pH values and the end of catalytic reactions

Catalyst	pH*
Haldor-Topsoe	10
Engelhard	9.8
Fe$_2$O$_3$/Al$_2$O$_3$(I)	7.8
CuO/Al$_2$O$_3$(I)	7.6
NiO/Al$_2$O$_3$(I)	7.3
ZnO/Al$_2$O$_3$(I)	7.4

*Remained almost constant during 240 min of reaction

Table 5: Variables values at the end of the reaction (240 min of reaction)

Treatment (tc)	TOC	Aromatic	COD	Color	H$_2$O$_2$ Decomposed (g/L)	pH*	η TOC/H$_2$O$_2$	COD/H$_2$O$_2$
		(% reduction)						
1	19	25	29	69	1.33	7.5	266	501
2	19	35	24	83	2.05	7.2	170	347
3	23	28	23	76	1.57	7.4	212	456
4	29	27	27	60	2.04	7.1	151	334
5	23	26	29	58	1.67	7.6	199	397
6	25	30	29	73	2.18	7.5	149	303
7	22	15	24	50	1.75	7.4	194	405
8	25	31	30	75	2.32	7.5	140	282
9	26	62	35	82	1.78	7.2	182	338
10	27	77	29	91	2.29	7.2	140	290
11	37	71	49	91	1.78	7.2	153	267
12	44	86	52	95	2.42	7.8	101	184
13	26	51	30	64	1.78	7.5	181	371
14	30	68	34	77	2.43	7.2	124	252
15	37	66	54	83	1.78	7.5	153	285
16	44	76	56	89	2.43	7.8	99	175

* Remained almost constant during 240 min of reaction

Table 6: Effect of significant factors and their levels on TOC reduction (%), aromatic compounds reduction (%), and COD reduction (%).

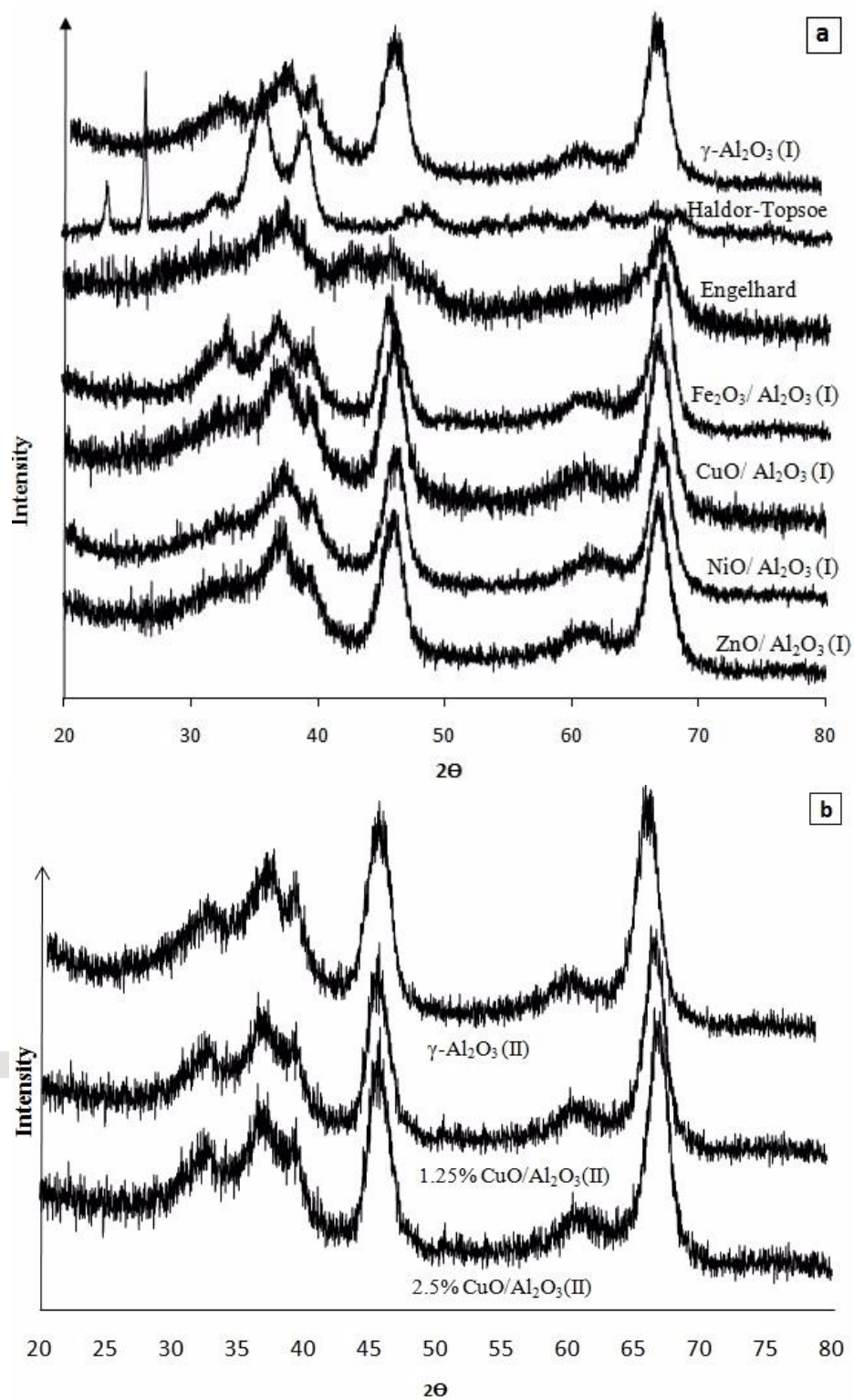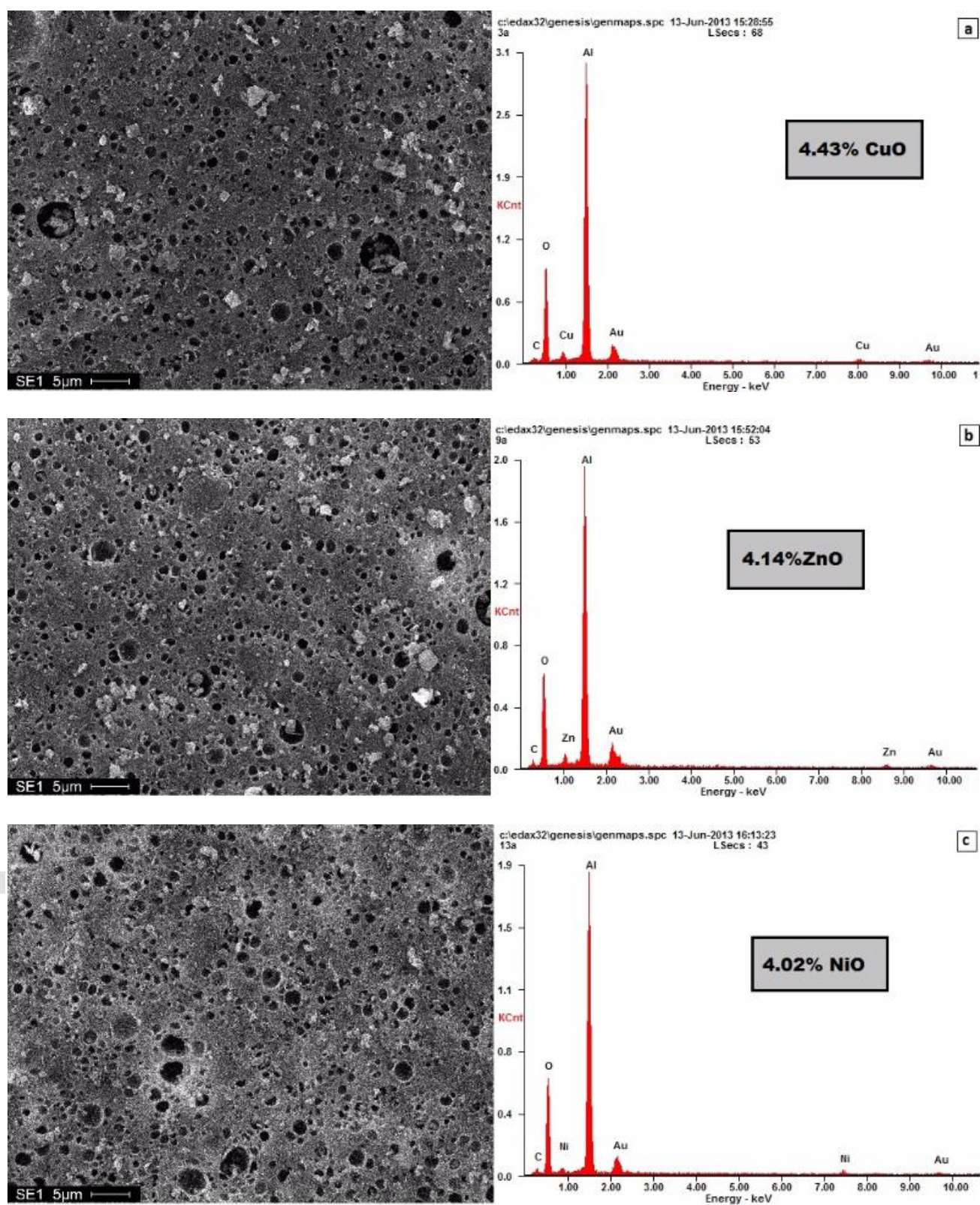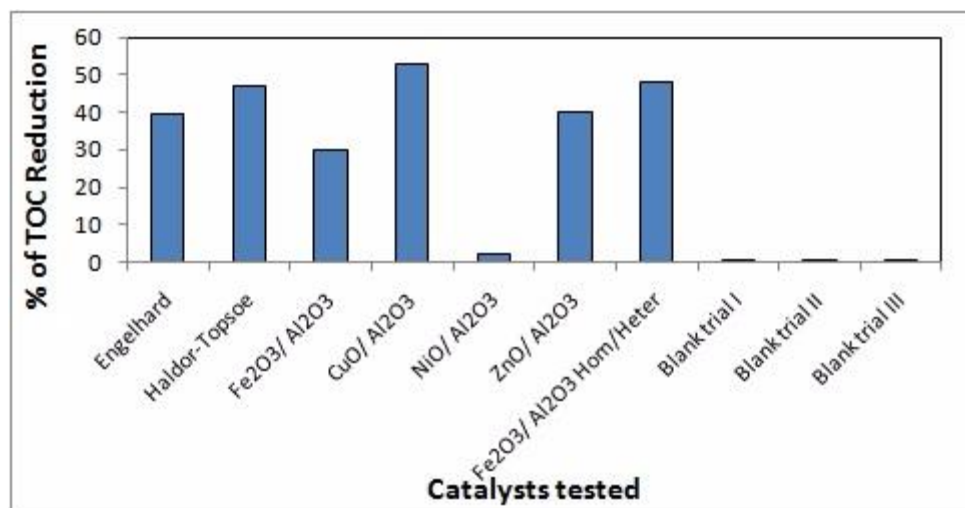| Factor	Level	% of Reduction		
		TOC	Aromatic	COD
Temperature	+	43	70	48
Temperature	--	33.5	31	37.5
H$_2$O$_2$	+	33	52	37
H$_2$O$_2$	--	25	42	31
Active phase	+	28	58.1	36
Active phase	--	23	57.8	29
Catalyst mass	+	24.1	32	32.5
Catalyst mass	--	23.8	52	33

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6