



Nanofiltration of partial oxidation products and copper from catalyzed wet peroxidation of phenol

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HIGHLIGHTS

- The Cu-chitosan/Al₂O₃ catalyst gave a 90% TOC reduction.
- Essential total phenol removal was obtained in 2 h.
- Nanofiltration of the real CWPO effluent gave a high copper recovery of 97%.
- Only a 5% loss of the initial steady flux was observed after 4 h.
- Coupling nanofiltration and CWPO successfully reduces the toxicity of the effluent.

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ABSTRACT

The aim of this work is to study the combination of Catalytic Wet Peroxide Oxidation (CWPO) and nanofiltration processes in the treatment of phenol solutions. A home-made Cu-chitosan/Al₂O₃ catalyst was applied for this purpose. The effluent from CWPO usually contains some metal leached from the catalyst in addition to latter oxidation intermediates (short chain organic acids). Downstream nanofiltration is used to retain the metal leached from the catalyst, which would result in secondary pollution and negatively impact on a possible subsequent biological treatment step.

The CWPO was performed in a batch recycle trickle bed reactor packed with the catalyst. The final distribution of intermediates was identified by HPLC. Cross flow filtration experiments using either model solutions containing phenol and the main intermediates (succinic, malonic, maleic and oxalic acid), with and without Cu(II) or the effluent of the CWPO reaction were performed using a NF90 membrane. When all intermediates were combined, the rejection of copper reached over 95% while an acceptable maximum of 10% of permeate flux loss, compared with the initial flux, was maintained.

Nanofiltration of a real CWPO effluent gave a higher copper recovery of 97%. Thus, the permeate toxicity was highly reduced. In addition, after 4 h of filtration, only a 5% of flux loss was observed, which guarantees a stable filtration for days.

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1. Introduction

Catalytic Wet Peroxide Oxidation (CWPO) using heterogeneous catalysts based on low-valence transition metals (Fe, Cu) has emerged as a clean and effective alternative among other processes to treat phenol contaminated wastewaters [1–3]. However, the process is accompanied with some metal leaching that would result in secondary pollution and negatively impact on a possible subsequent biological treatment step. Metal lixiviation is caused by the exposure of the catalyst to hot acid aqueous media, a scenario difficult to avoid since the latter oxidation intermediates are short chain acids. This effect,

which can be neglected when iron is used, can be critical if other metals are applied, e.g. copper. In addition, the CWPO of phenol generates other intermediates with different levels of toxicity and recalcitrance against further oxidation. Hence, the toxicity of those partially oxidized organic intermediates as well as that resulting from metal loss by leaching must still be eliminated before the effluent is discharged into a municipal Wastewater Treatment Plant.

In principle, many partially oxidized intermediates and metal leached could be recovered, concentrated and recirculated to the oxidation reactor by the coupling of a membrane separation process system to the CWPO process. Nanofiltration (NF), which is in the transition between ultrafiltration (UF) and reverse osmosis (RO) processes, has properties of high rejection of multivalent ions and organic matter with molecular weights (MW) larger than 200 Da [4–7]. Therefore, coupled CWPO and NF processes could enhance mineralization giving more treatable final

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products, and most importantly, assuring the rejection of the metal leached.

Several authors studied the combination of some Advanced Oxidation Processes with filtration [8–12]. Urriaga et al. [8] employed hollow fibers as membrane contactors for the recovery of copper from WPO processes. Hellenbrand et al. [9] studied wet oxidation and NF in an integrated system for the treatment of polyethylene glycol. The partial oxidation products formed during a brief period of pretreatment in a low pressure WO reactor were separated by NF, and larger molecules were recycled into the reactor where they underwent further oxidation. The results demonstrate that by using a combination of an oxidative and a separation step, a higher selectivity of the overall process towards partial oxidation products can be achieved. López-Muñoz et al. [10] reported the performance of NF and reverse osmosis membranes (NF-90 and TFC-HR) to retain the intermediate products of phenol chemical oxidation in aqueous solution. Experiments evidenced that selective separation between phenols and dicarboxylic acids can be achieved at solution pH around 5.

Jae-Hyuk Kim et al. [11] presented a novel hybrid system combining NF with homogeneous catalytic oxidation for the degradation of bisphenol-A in sources of drinking water. Iron(III)–tetrasulphophthalocyanine (Fe(III)–TsPc) was used as a homogeneous metal catalyst to degrade BPA in the presence of hydrogen peroxide. In the NF-hybrid system, BPA removal was above 95% throughout the entire duration of operation due to continuous decomposition of BPA in the retentate by catalytic oxidation.

Banerjee et al. [12] combined a Fenton process with NF to treat a synthetic solution of eosin dye. Three combinations of Fenton and NF were studied: the first one was Fenton followed by NF, the second one was NF followed by Fenton while the third one was two-step NF. The time required to reduce the concentration of dye to the level of 1 mg/L by Fenton was large, even though the initial rate of dye degradation was fast. Similarly, a one step NF could not reduce the dye concentration below 1 mg/L. Thus, a combined process like the first or the third one makes the removal of the dye more feasible.

Overall, Fenton process conducted at mild conditions requires a high concentration of homogeneous catalyst to obtain a good degree of mineralization of the pollutant. This generates a huge amount of Fenton sludge to treat at the end of the reaction and the continuous addition of metal salt. Heterogenization of the catalyst overcomes this problem or at least reduces it, since some leaching of the active elements cannot be completely avoided. Then, the coupling of a membrane separation process system to the CWPO process is recommended in order to prevent the occurrence of metal in the exiting effluent.

In the current work, we report the use of combined oxidative and separation processes applied to the detoxification of phenol solutions. The CWPO was performed in a fixed bed recirculating reactor packed with a home-made Cu-chitosan/ Al_2O_3 catalyst. Phenol disappearance, distribution of partial oxidation products and copper leaching were examined.

Cross flow filtration experiments were conducted using a NF90 membrane in a lab-scale filtration cell. The rejection of phenol, main final intermediates (succinic, malonic, maleic and oxalic acids) and copper leached was determined.

2. Experimental

2.1. Catalyst preparation and characterization

The Al_2O_3 /chitosan-Cu(II) catalyst was prepared by coprecipitation of the Cu-chitosan complex onto alumina spheres. The $\gamma\text{-Al}_2\text{O}_3$ (provided by Sasol, average particle diameter of 1.76 mm) was added into the chitosan- Cu^{2+} solution (10 g/L of copper and 5 g/L of chitosan) while stirring. The solid was filtered and rinsed with distilled water and contacted with a 0.1 mol/L NaOH solution. Then, the solid was filtered,

Table 1
Catalyst characterization.

Copper content (%)	1.2
BET area (m^2/g)	167
Chitosan content (% wt)	2.6
Particle diameter (mm)	1.76

washed again and finally dried at room temperature for 48 h and later at 323 K for 24 h.

The copper content of the catalyst was determined by soaking the sample in 65% HNO_3 solution and then analyzing the copper concentration using Atomic Absorption Spectroscopy (AAS) in an ANALYST 300 Perkin-Elmer Spectrophotometer. Copper leached from the catalyst during oxidation tests was also measured by AAS.

The specific surface area (BET) was measured with a Micromeritics ASAP 2000 instrument using N_2 adsorption at 77 K.

Thermogravimetric analysis (TGA) was performed to confirm the existence of the complex Cu-Chitosan onto the γ -alumina. Data were captured using a TGA (Shimadzu, model TGA-50) instrument with a constant airflow of 20 mL/min. The heating rate applied was 10 °C/min and the temperature was increased from 25 °C to 900 °C. However, the temperature was first kept constant at 110 °C for 30 min in order to assure the complete removal of water contained in the sample.

Table 1 presents the results from the catalyst characterization.

Fig. 1 presents curves from TGA analysis.

2.2. Catalytic wet peroxide oxidation

A load of 41 g of the Cu(II)-chitosan/alumina catalyst was used in the CWPO of a phenol solution of 1 g/L (Panreac, 99%) in a recirculating jacketed packed bed glass reactor (60 cm long and 2.35 cm of internal diameter) operated at 323 K and 1 atm in co-current downwards operation. This set-up presents some advantages over the continuous one-step reactor configuration. It is a smaller device that uses fewer catalyst and reactants and, although the one-pass conversion is lower (differential reactor), much higher conversions can be achieved through prolonged exposure to the catalyst within the fixed bed. Additionally, as one-pass conversion does not require to be large, there is no need of a significant liquid residence time in the reactor and this allows extension of the examined liquid velocity range, using a reasonable amount of catalyst; consequently, conditions attained at high and low velocities can be studied without changing the set-up.

Air was introduced at the top of the reactor at a flow rate of 50 mL/min, since it was observed that catalyst wetting was more uniform and liquid flow was more stable under gas flow conditions. Furthermore, we confirmed through results obtained in slurry batch reactors

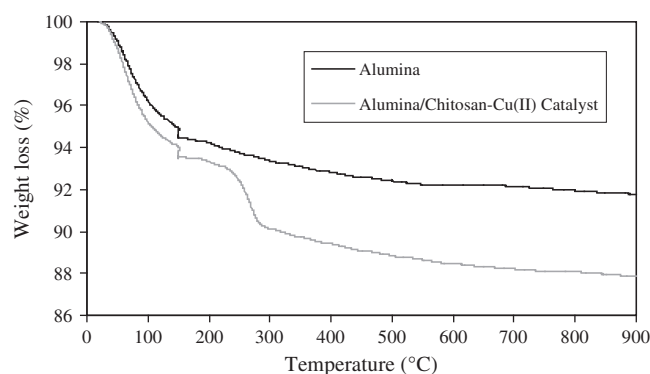


Fig. 1. Thermogravimetric analysis of the catalyst and the alumina support.

Table 2
Characteristics of NF90 membrane.

MWCO (Da)	200
Support	Polysulfone
Active layer	Polyamide
Isoelectric point	4
Pure water permeance ($\text{dm}^3 \text{h}^{-1} \text{m}^{-2} \text{bar}$)	5.6

that the presence of air does not influence CWPO outcomes in terms of mineralization or product distribution.

The liquid feed consisted of 600 mL of a phenol solution, which was kept in a flask inside a thermostatic bath, and recirculated at a flow rate of 45 mL/min. A dose of 11.65 mL of H_2O_2 (30% wt) was added into the phenol solution flask to initiate the reaction. Once it was consumed, a second dose of 11.65 mL was added. The total amount of added oxidant was 2.57 times the stoichiometric amount required.

Two tests of 4 h each, at identical conditions, were performed, using the same load of catalyst but a fresh phenol solution each time. Catalyst leaching was evaluated over a total period of 8 h. Phenol, Total Organic Carbon (TOC) and H_2O_2 concentrations and pH values were measured along the reaction time.

2.2.1. Analytical methods

During CWPO tests, liquid samples were taken at different time intervals and immediately analyzed. Phenol was detected and measured by a standard colorimetric method [13]. Hydrogen peroxide was detected by an iodometric titration method [13].

Total Organic Carbon values were obtained by a TOC Analyser (Analytic Jena, model NC 2100). The samples were acidified with 50 mL HCl 2 mol/L, then were bubbled with synthetic air for 3 min to eliminate the inorganic carbon content and finally injected.

Phenol, TOC and H_2O_2 conversions were evaluated at different times up to 240 min. Data shown here represent an average of at least three experiments, which showed satisfactory repeatability.

Identification of intermediates was carried out in a HPLC (Agilent Technologies, model 1100) with a C18 reverse phase column (Agilent Technologies, Hypersil ODS). The analyses were performed using a mobile phase with a gradient mixture of methanol and ultra pure water (Milli-Q water, Millipore) from 0/100 v/v to 40/60 v/v. The flow rate increased from 0.6 at the fifth minute to 1.0 mL/min at the seventh minute. The pH of the water was previously adjusted at 1.41 with sulphuric acid. A diode array detector was used for detecting the organic

compounds analyzed at 254 nm or 210 nm, depending on the compound to be identified.

2.3. Nanofiltration

2.3.1. Membrane and chemicals

For filtration solutions, the following chemicals were used: oxalic acid dihydrate (Aldrich, 99%), malonic acid (Fluka, 99%), maleic acid (Fluka, >99%), succinic acid (Fluka, 99%), phenol (Panreac, >99%), copper sulfate (Aldrich).

The NF90 membrane was manufactured by DOW-Filmtec (Minneapolis, USA) and was gently provided free of charge. Table 2 gives the most important characteristics of the selected membrane.

2.3.2. Crossflow filtration experiments: set-up and procedure

A schematic representation of the filtration process is presented in Fig. 2. A 1.2 L jacketed glass tank contained the filtration solution, where the temperature was set constant to 30 °C. Filtration tests were conducted in crossflow mode, because fouling is expected to be lower than in dead-end mode thanks to the tangential flow of the feed stream. Tangential flow velocities of 8.3 cm/s were achieved using a Sterlitech module (model CF042) hosting coupons of 42 cm² of filtration area. The transmembrane pressure was set to 6 bar. pH was neither adjusted nor controlled. Filtration was monitored for 4 h. Both permeate and retentate streams exiting the membrane were recycled back to the feed tank to maintain the feed solution concentration constant during the filtration experiment. Only a small fraction of permeate was not recycled to the feed tank because permeate samples were periodically withdrawn to characterize them. The permeate flux was measured with a balance (A&D Instruments, model GF-1200). A membrane pump (Prominent, model Vario) was selected for feeding the solutions to be filtered to the membrane module. A pulse dampener (Hydracar S.A., model U002A18V1-AI) was installed before the membrane module in order to transform the pulsing flow to nearly continuous flow reproducing a real membrane operation. The pulse dampener was actuated by means of a backpressure valve installed after it. Before every test, the membrane was soaked in water for 1 day and then subjected at 8 bar of pressure for 1 h.

The rejection coefficients (R) of the compounds were evaluated from initial feed concentrations (C_f) and permeate concentrations (C_p) as usual: $R(\%) = 1 - C_p/C_f$.

As the permeate flux ($\text{dm}^3 \text{h}^{-1} \text{m}^{-2}$) initially decreased as a result of concentration polarization and fouling phenomena, permeate flux decline is reported instead of absolute flux. Permeate flux decline is expressed by the ratio between the actual permeate flux (J_p) and

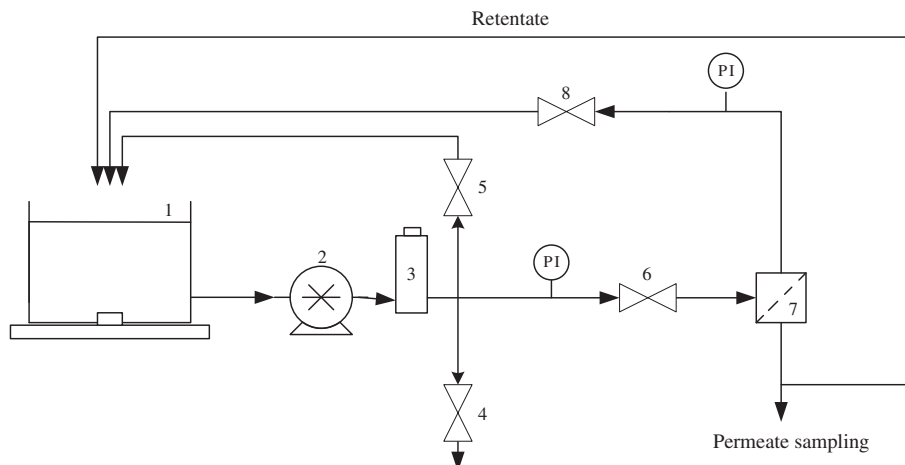


Fig. 2. Filtration experimental set-up. (1) Jacketed feed tank; (2) pump; (3) dampener; (4) relief valve; (5) bypass valve; (6) and (8) backpressure valves; (7) membrane module; (PI) pressure gauges.

the original water permeate flux (J_w), evaluated before starting the filtration run. In addition, J_a is the water permeate flux after the filtration test ($L/h^{-1} m^{-2}$) once the membrane is subjected to softly rinsing with deionised water. Thus, the ratio J_a/J_w indicates the level of severe fouling, which can only be eliminated with specific cleaning, if possible.

Final oxidation products in phenol pathway are short chain organic acids. Maleic, malonic, succinic and oxalic acids were identified by HPLC. Therefore, tests were performed with model solutions of these intermediates. Phenol was also included as a model compound for the aromatics.

The following solutions were tested: Cu^{2+} 14 mg/L, phenol 1000 mg/L, succinic acid 100 mg/L, malonic acid 100 mg/L, maleic acid 100 mg/L and oxalic acid 30 mg/L. The tests with each intermediate were repeated at the same concentration but in the presence of 14 mg/L of copper, which is the amount of copper leached during the second test in the fixed bed recycle reactor. Finally, a sample containing all the intermediates plus copper and a sample of the actual supernatant from a selected CWPO test were filtrated. The supernatant presented a final TOC of 80 mg/L, copper concentration of 14 mg/L and a pH of 5.7.

Physico-chemical properties of studied compounds are listed in Table 3. The solution containing all the intermediates plus copper displayed a pH of 2.8.

3. Results and discussion

3.1. CWPO tests

A preliminary blank experiment was performed with the Al_2O_3 support alone and in the absence of oxidant, to discriminate the effect of adsorption. In the absence of copper, phenol removal took place essentially by adsorption, with phenol and TOC conversions of around 17%.

The catalyst was used in two tests of 4 h each, under the same conditions, using a fresh phenol solution each time, proving to be active for phenol oxidation at 323 K. Performance of the catalyst, namely phenol and TOC conversions, H_2O_2 consumption and pH evolution at different times are respectively presented in Figs. 3 and 4.

In the first test, a TOC conversion of 90% was obtained. Phenol and H_2O_2 were completely consumed. The H_2O_2 was rapidly decomposed into radicals that also allowed a fast mineralization of the carboxylic acids generated during the oxidation of phenol. The HPLC identification of intermediates indicated the presence of a low concentration of aromatics (hydroquinone, catechol, p-benzoquinone), which were finally oxidized into biodegradable carboxylic acids (mostly succinic, maleic, malonic and oxalic acids). The high degree of mineralization and low accumulation of acids were proven by the pH evolution, which stayed

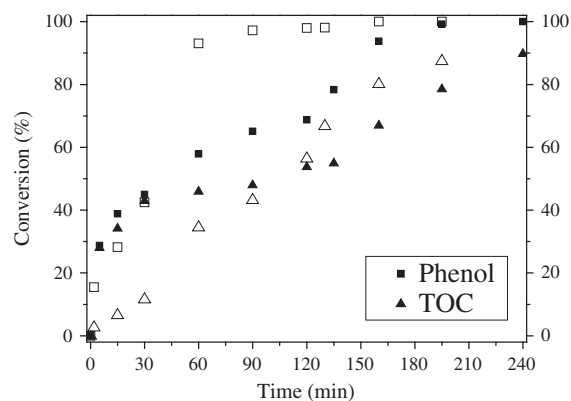


Fig. 3. Evolution of phenol and TOC conversions over time. Full symbols correspond to the first run, empty symbols to the second run. Conditions: 600 mL of 1 g/L phenol; 41 g of 1% Cu catalyst bed; phenol solution flow: 45 mL/min; temperature: 323 K; initial dose of H_2O_2 : 1.3 times the stoichiometric value.

above 6 during most of the reaction, with a minimum of 5.3. Leaching of copper was negligible. Nevertheless, some carboxylic acids were absorbed by the catalyst and this caused the initial pH value of the second test to be lower (around 5.5). Therefore, the pH evolution of the second run presented lower pH values (between 4 and 7) and measurable metal leaching from the catalyst.

Deactivation of the catalyst after the first run could be attributed to the complexation of the copper ions in the catalyst surface. Intermediates with strong complexing properties (e.g. hydroquinone, catechol, or carboxylic acids such as oxalic acid) may inactivate the catalytic properties of copper ions [14–16].

However, the activity during the second test was maintained in terms of TOC conversion and a value of 90% was obtained. In turn, essentially total phenol removal was observed after 2 h. Under these conditions, a leaching of copper of 14 mg/L was detected at the end of the reaction.

During the experiment, the color of the reaction solution turned from transparent to light brown due to the presence of p-benzoquinone and became again clear as the reaction progressed. The HPLC identification of intermediates indicated the presence of aromatics (hydroquinone, catechol, p-benzoquinone) at the first stage of reaction, which were further oxidized into biodegradable carboxylic acids, mostly succinic, maleic, malonic and oxalic acids.

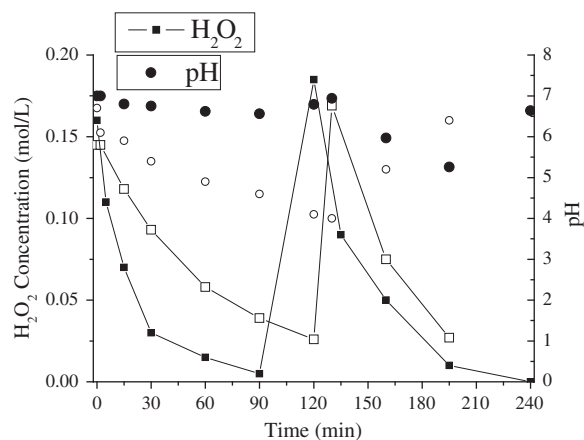


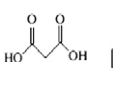
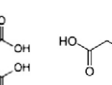
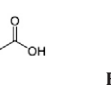


Fig. 4. Evolution of pH and H_2O_2 concentration over time. Full symbols correspond to the first run, empty symbols to the second run. Conditions: 600 mL of 1 g/L phenol; 41 g of 1% Cu catalyst bed; phenol solution flow: 45 mL/min; temperature: 323 K; initial dose of H_2O_2 : 1.3 times the stoichiometric value.

Table 3
Physico-chemical properties of the studied compounds.

Compounds	Phenol	Oxalic acid	Malonic acid	Maleic acid	Succinic acid
MW (g/mol)	94.11	90.03	104.06	116.08	118.09
pK_a^1 at 25 °C	9.9	1.25	2.85	1.91	4.21
pK_a^2 at 25 °C		4.27	5.70	6.33	5.64
Log K_{ow}	1.46	−2.22	−0.81	−0.48	−0.591
Solution pH	6.4	3.4	3.1	3.05	3.9
Solution with Cu(II) pH	5.94	3.4	3.2	3.12	3.6
Molecular structure					
Concentration (mg/L)	1000	30	100	100	100

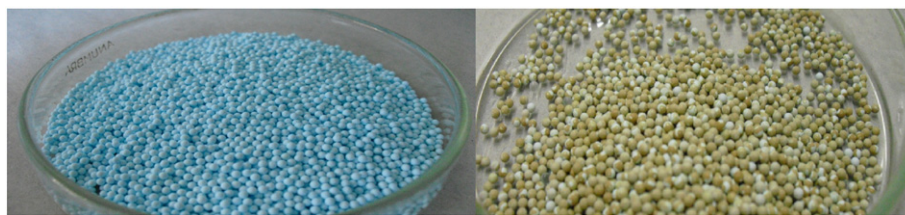


Fig. 5. Fresh and used catalysts.

There was no substantial change in the liquid flow rate along the reaction time. Adsorbed organic compounds were not identified. After 8 h of reaction, the catalyst appearance modification is shown in Fig. 5, where a noticeable change of color is evident. There was no evidence of sludge formation, in agreement to results obtained by other authors [17,18].

A homogeneous test in a batch stirred reactor was conducted using 800 mg/L of Cu (II) and other conditions identical to the ones used here. Although results in terms of phenol, peroxide and TOC conversions are similar to those obtained with the heterogeneized catalysts, the presence of a brownish sludge was detected at the end of the reaction. This material could later cause fouling of the membrane. Therefore, the heterogeneized catalyst prevents the sludge formation during Fenton treatment, giving a solution with low cooper concentration, and is easily separated as a solid.

3.2. Nanofiltration

3.2.1. Behavior of the organic intermediates

A NF90 membrane was used to filter model liquid samples both with and without dissolved copper. The permeate flux decrease (J_p/J_w (%)) and rejection (R (%)) values are presented in Table 4 for each solution.

In the absence of copper, the rejection of all the organic compounds is low to moderate as expected according to the low molecular weight of such compounds, still away from the nominal MWCO of this membrane. However, the rejection of succinic acid, which has the largest MW (118.09 Da), is rather higher than expected. For non-charged, hydrophilic compounds, steric hindrance is most likely the driving mechanism for rejection [4,10,19]. Also, the rejection of hydrophilic, uncharged molecules should be enhanced, considering their greater affinity towards water and thus larger hydrated radius [4].

Membrane surface charge is usually quantified by zeta potential measurements. The zeta potential curve of polyamide membranes as a function of solution pH displays a shape characteristic of an amphoteric surface containing acidic and basic functional groups due to the deprotonation of carboxylic groups, and the protonation of unreacted amino functional groups, respectively [19,20]. Then, zeta potential becomes increasingly more negative as pH is increased and functional groups deprotonate. Organic acids are generally weak acids and are dissociated with regard to the pH in the solution. Changes in feed pH disturb the dissociation equilibrium of the acidic organic solutes and membrane functional groups; therefore, both the electrostatic repulsion between solute and membrane and the steric interaction inside pore walls are altered [10].

Table 4
 J_p/J_w (%) and R (%) of each model solution, after 4 h of nanofiltration.

	J_p/J_w (%)					R (%)				
	Phe	Oxa	Mln	Mlc	Suc	Phe	Oxa	Mln	Mlc	Suc
Without Cu(II)	65	83	79	75	86	16	35	27	8	45
With Cu(II)	67	81	79	75	87	19	67	23	15	33

Phe: phenol; Oxa: oxalic acid; Mln: malonic acid; Mlc: maleic acid; Suc: succinic acid.

The oxalic acid solution is more diluted than the rest and the pH value is slightly higher. Higher pH values may contribute to the increase in the rejection of negatively charged organic solutes, resulting from an increase in the electrostatic repulsion between the negatively charged oxalic acid and the membrane [4,19]. Similar results were obtained by López-Muñoz [10] who studied the rejection of several organic acids (formic, acetic, malonic and oxalic acids) with a NF90 membrane at 5.5 bar and 25 °C, with concentrations of 100 mg/L. In this study, the rejection trends agree with the size exclusion mechanism, except for oxalic acid whose rejection by both membranes is higher than that of malonic acid, despite of its lower molecular size [10]. The author justified this difference considering the amphoteric surface of the membrane containing acidic and basic functional groups due to the deprotonation of carboxylic groups, and the protonation of unreacted amino functional groups.

According to the pH and pKa values, there is an important concentration of neutral species in the malonic acid solution [10]. Therefore, the interaction between the positively charged membrane and the acid should be lower. The occurrence of significant rejection for such dicarboxylic acids can also be related to its potential capacity to form dimers of higher molecular weight by means of intermolecular hydrogen bonding. This effect can contribute to the moderate rejection of the diacids found in the study. Only maleic acid shows a very low rejection and this agrees with its capacity to form intramolecular hydrogen bonding instead of intermolecular association, avoiding the occurrence of higher MW species. In addition, unlike malonic acid, an important part of maleic acid is dissociated because of its smaller pKa. Therefore, the electrostatic interactions between the positively charged membrane and the anions are enhanced and, consequently, the rejection is somewhat reduced.

Mostly uncharged compounds such as phenols, with a slightly higher K_{ow} value, molecular weight around 100 g/mol, and hydrogen bonding ability have been found to adsorb over polyamide, increasing fouling, and then being poorly rejected [10,20]. Molecules accumulated on the membrane surface due to size exclusion could eventually diffuse through the membrane polymer matrix towards the permeate side. The phenomenon of adsorption and diffusion may be a possible explanation for slightly lower rejections [4,19]. Moreover, the phenol solution is more concentrated and concentration polarization can help to create an additional resistance to flux, resulting in a lower J_p/J_w (%). The flux of phenol solution showed a considerable decline compared with other solutions, not only due to the polarization phenomena, but also because of the adsorption of phenol over polyamide, increasing fouling [19].

On the contrary, organic acids show low affinity for the membrane material so they are not adsorbed onto the membrane surface due to their weak hydrophobic character and slightly larger MW, resulting in lower fouling and thus higher J_p/J_w (%). In this case, the decrease of J_p/J_w (%) could therefore be attributed to concentration polarization effect due to the accumulation of anions in the vicinity of the membrane surface.

When copper is added, the values of J_p/J_w do not significantly change for any of the compounds studied. In the case of succinic acid, the rejection slightly lowers when copper is added to the system. Although there is no simple explanation, this behavior can be

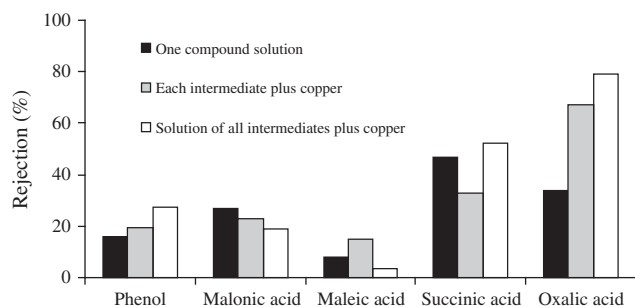


Fig. 6. Rejection of intermediates for the entire set of model solutions.

related to the inability of succinic acid to form dimers in presence of copper. On the contrary, the presence of copper favors the rejection of oxalic and maleic acids, which have quelant properties. This could be a result of positively charged complexes, such as oxalate or maleate, which are retained due to a steric factor and electrostatic repulsion. In turn, malonic acid and phenol do not show significant differences in the rejection value in the presence or absence of copper.

Fig. 6 compares the rejection of intermediates for the set of model solutions prepared. When all intermediates are combined, the rejection of phenol, succinic and oxalic acids is enhanced. This could be due, on one hand, to the formation of coupling compounds, which are retained due to a steric factor, and on the other hand to the combined polarization and fouling effect that improves de filterability. However, the rejection of malonic and maleic acid diminishes, probably because both are adversely impacted by the lower pH value.

Fig. 7 presents J_p/J_w (%) and J_a/J_w (%) values for every model solution. A maximum of 10% of permeate flux loss (J_a/J_w) remains after filtration, which is very acceptable.

The maximum drop of J_p/J_w (%) corresponds to the mixture of all compounds (54%). Progressive accumulation of solutes in the neighborhoods of the membrane surface inevitably occurs and creates solute concentration gradients in those regions. Concentration polarization is a reversible phenomenon that causes a decrease on the membrane permeate flux and can also cause a variation on the solute rejection. Concentration polarization can have either positive or negative effects on the solute rejection. For instance, the accumulation of charged solutes on membrane surface may favor the repulsion of opposite charge solutes (with respect to the membrane) and increase their rejection. On the other hand, the accumulation of solutes over the membrane

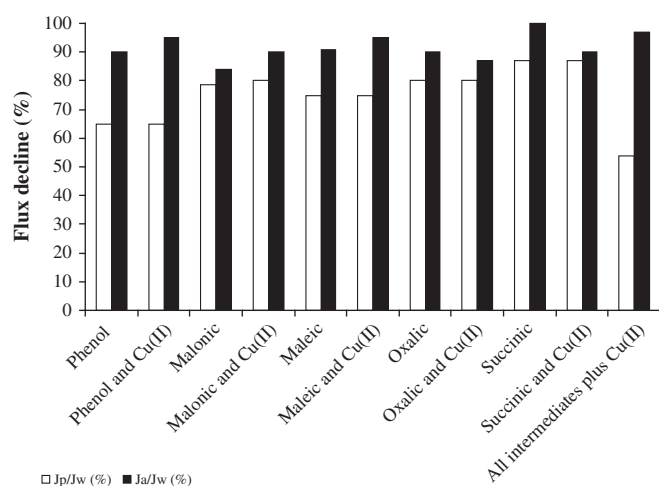


Fig. 7. J_p/J_w (%) and J_a/J_w (%) values for every model solution.

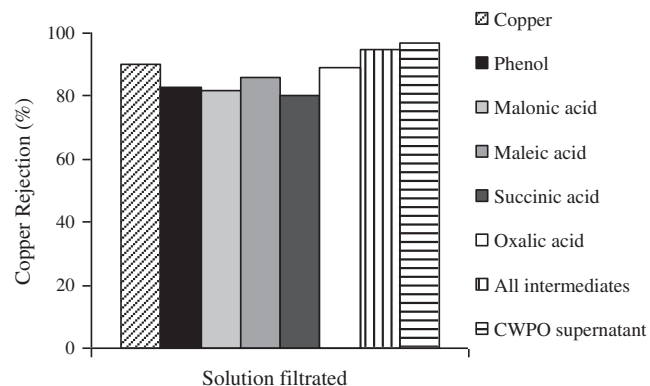


Fig. 8. Rejection of copper in all the model solutions.

surface increases the effective concentration, favoring their transport through the membrane by solution-diffusion phenomena [21,22].

3.2.2. Copper behavior

As the presence of organic acids is irrelevant for a subsequent biological treatment, since they are mostly biodegradable, copper concentration becomes the key factor for a successful combined process. Copper rejection in all the model solutions is presented in Fig. 8. The copper solution (pH 6) shows a rejection value of 90%. This value decreases to 83–85% when copper is combined with any of the compounds, except for oxalic acid. In this case, the rejection value does not change (90%). The formation of copper complexes with the dicarboxylic acids (quelant effect), decreasing the actual charge of the copper ions, fits this behavior.

When all intermediates are combined, the rejection of copper reaches 95%. This could be attributed to the formation of complexes and generation of an additional filtration film due to accumulation of species over the membrane, which helps in the filtration mechanism.

3.2.3. CWPO supernatant

Nanofiltration of the CWPO supernatant gave an overall TOC rejection between 20% and 30% and a high copper recovery of 97%, which means a TOC concentration in the permeate of around 65 mg/L.

Thus, the permeate toxicity was highly reduced as a copper concentration of less than 1 mg/L was measured in the permeate. Fig. 9 presents the J_p/J_w (%) evolution against filtration time. A final J_p/J_w (%) of 65% was detected after 4 h of filtration. However, only a 5% of flux loss with respect to the initial flux was observed, which could allow a stable filtration for days. Therefore, treated real effluents behave better than synthetic solutions; this allows affirming that

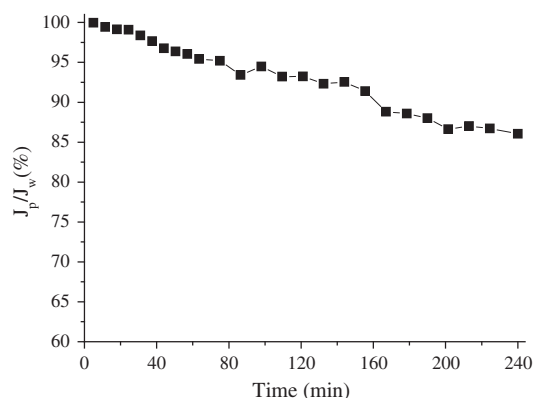


Fig. 9. J_p/J_w (%) evolution against filtration time.

the combination proposed is suitable for application on a high scale in real cases.

4. Conclusions

The real effluent from the CWPO of a phenol solution carried out using a home-made Cu-chitosan catalyst was treated by NF. The liquid sample contained mostly biodegradable carboxylic acids, such as succinic, maleic, malonic and oxalic acids as well as Cu leached from the catalyst. The coupling of both processes successfully reduces the toxicity of the effluent by retaining the copper leached from the catalyst during the oxidation reaction, even in the presence of other organic species from the phenol oxidation pathway, and leaving to pass mostly biodegradable carboxylic acids, with only a 5% of flux loss.

Additionally NF experiments were carried out using model solutions of each intermediate alone, with copper and all together. The presence of copper modifies the NF performance observed for pure compounds tested individually. When all compounds (including copper) are combined, rejection of phenol, succinic and oxalic acids is enhanced, copper rejection reaches a 95% but the rejection of malonic and maleic acids diminishes, probably because both are adversely impacted by the lower pH value. A maximum of 10% of permeate flux loss (J_a/J_w), due to irreversible fouling, was observed after filtration.

Altogether, after NF of an effluent treated by CWPO, a permeate mostly containing biodegradable organic acid and less than 1 mg/L of copper is obtained. This solution could be directed to a conventional municipal WWTP without threatening its operation.

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