Cellulose Beads as Novel Support of Copper Active Site for the Catalytic Abatement of Water Emerging Contaminant

Alejandra Devard

INCAPE: Instituto de Investigaciones en Catalisis y Petroquimica

M. Claudia Taleb

Instituto de Tecnología Celulósica, ITC

Graciela V. Olmos

Instituto de Tecnología Celulósica, ITC

F. Albana Marchesini

INCAPE: Instituto de Investigaciones en Catalisis y Petroquimica

Laura B. Gutierrez (✉ lbgutier@fiq.unl.edu.ar)

INCAPE: Instituto de Investigaciones en Catalisis y Petroquimica <https://orcid.org/0000-0001-5717-611X>

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Abstract

Different regenerated cellulose (RC) beads were synthesized as supports of copper as the active site for catalytic degradation of emerging contaminants (ECs) in water. Starting from a commercial dissolving pulp, RC beads were prepared from the direct dissolution and from both cellulose carbamate and viscose solutions. Copper was added to the supports by a simple green method. The material characterization by FTIR, TGA, SEM and XPS confirmed the successful incorporation of copper in all the prepared supports.

Phenol was adopted as EC test molecule, and catalytic wet peroxide oxidation (CWPO) at 70°C was used to analyse the Cu-cellulosic beads catalytic performance.

The novelty and importance of preparing bead-shape catalysts with cellulose reside in the use of an economic, renewable and biodegradable matrix, and the simple separation of the structured catalyst from the heterogeneous solid/liquid reaction media.

1. Introduction

Low concentrations of Emerging contaminants (ECs) are frequently found in the aqueous effluents of chemical, pharmaceutical and petrochemical industries; and they are usually associated with the development of various adverse effects in ecology and/or organisms (Stuart, Lapworth, Crane, & Hart, 2012). They are the result of the use of personal hygiene products, industrial and hospital waste, and therapeutic medicines consumed at home, such as anti-inflammatories and analgesics, antibiotics, and antidepressants. The development of new powerful and sensitive analytical techniques (e.g., LC-MS, Liquid Chromatography - Mass Spectroscopy) has allowed the detection of extremely low concentrations of these compounds in complex matrices. Actually, ECs are eliminated from water using different technologies for instance oxidation processes (Gautam, Kumar, & Lokhandwala, 2019). The Advanced Oxidation Processes (AOPs) including photo-catalysis and catalytic wet peroxide oxidation (CWPO), are among the most employed and suitable methods for the removal of organic products from water (Hachemaoui et al., 2021; Miklos et al., 2018). In the CWPO procedure, highly reactive oxidizing radicals are generated resulting in the mineralization of ECs, i.e., their degradation and carbon dioxide and mineral salts production (Valkaj et al., 2011). The ECs catalytic oxidation involves the design of catalytic materials with optimal activity and selectivity, together with good long-term stability and low production costs (Chiron, Fernandez-Alba, Rodriguez, & Garcia-Calvo, 2000; Rizzo et al., 2019). The presence of catalytic materials represents substantial improvements in the ECs degradation process, such as lower temperatures and residence time (Levec & Pintar, 2007).

Although many efforts have been made, the design of such materials is still a real challenge (Giwa et al., 2021). In this sense, the synthesis of metallic nanoparticles (NPs) used as catalytic entities is of great interest because of their derived properties. Nevertheless, whatever the case, it is necessary to immobilize the catalytic nanoparticles on solid substrates. There are many inorganic materials that could be used for supporting NPs, but they are either expensive or nonrenewable. Consequently, low-cost and sustainable

natural organic materials could be considered. Among them, cellulose appears as an attractive matrix because it is a natural, abundant, and available material on earth. Among the many advantages of using this natural polymer we can mention: (i) its surface structure allows to be physicochemical modified reaching new properties that could be used in specific applications, such as in the field of adsorbents and catalysts (Eyley & Thielemans, 2014; Hokkanen, Bhatnagar, & Sillanpää, 2016; Roy, Semsarilar, Guthrie, & Perrier, 2009) (ii) the possibility of producing structured supports with different shapes (fibers, films, membranes, sponges, and beads) through different dissolution methods (Heinze, Seoud, & Koschella, 2018; Navard, 2012). However, it should be taken into account that because the cellulose melting point is higher than its degradation temperature, its use as catalysts is restricted to lower than 200°C catalytic reactions.

Phenol is generally used as a model molecule of organic contaminant for ECs studies, and copper and iron supported in several matrices have been proved for its degradation by the CWPO method. Zeolites and mesoporous materials were reported for this aim (Maduna et al., 2018; Y. Wu, Zhang, & Yan, 2020; Yan, Wu, & Zhang, 2016).

As regards copper nanoparticles evolution on catalytic supports, wetness impregnation of metal precursors, co-precipitation, mechanical mixing, ionic exchange, and so on, are the most used conventional methods (Pinna, 1998; Schwarz, Contescu, & Contescu, 1995). However, nowadays the selection of low cost and friendly NPs precursors should also be considered in order to follow the green chemistry principles. As a result, Gioria, et al. (Gioria et al., 2019) reported that more monodisperse CuNPs were obtained by the reduction of aqueous acetate copper solution with ascorbic acid on SiO₂ support in comparison with CuO-SiO₂ mechanical mixture and with suspensions in organic solvents.

Cellulose is insoluble in regular organic solvents because of its stable supramolecular structure. Consequently, the cellulose dissolution involves the disruption of strong hydrogen bonding (inter and intramolecular) networks. Then, the solvents should be capable of interacting with the hydroxyl groups of the AGU (anhydrous glucose unit), in order to break down, totally or partially, the strong inter-molecular hydrogen-bonding between the polymeric chains. There are two basic procedures for cellulose dissolution: (i) from physical interactions between cellulose and the solvent (aqueous inorganic complexes, NaOH solution, mineral acids, among others); and ii) from the chemical derivatization of cellulose with different reactants such as trifluoroacetic acid (CF₃COOH), formic acid (HCOOH), NaOH/CS₂ (viscose process), NaOH/urea (carbamate method), among others. In the latter case the derivatized material should be dissolved in suitable solvents (El Seoud & Heinze, 2005; Fink, Ganster, & Lehmann, 2014; Heinze et al., 2018).

The well-known viscose method for cellulose dissolution is used efficiently in industrial processes, however it presents serious pollution problems since carbon sulphide is used as a solvent (Kotek, 2007). Similar to viscose technology, the Carbacell® process (cellulose carbamate process) represents a “friendlier” alternative (Qi, 2017) as carbon sulphide is replaced by urea. In order to find easy, cheap and non-hazard routes for the cellulose dissolution and the moulding without derivatization, the use of

aqueous sodium hydroxide at low temperature in combination with different additives (urea, thiourea) has been discussed (Egal, Budtova, & Navard, 2008; Navard, 2012). Nowadays, the regenerated products from dissolved cellulose have gained interest since they are easy to obtain, biocompatible, biodegradable, sustainable, and chemically and thermally stable (Hou et al., 2018; Luo & Zhang, 2010; Wang, Lu, & Zhang, 2016).

As a result, the syntheses of copper/cellulose composites by different methods have been reported for antibacterial proposals (Muthulakshmi et al., 2017; Yoosefi Booshehri, Wang, & Xu, 2015) and for water treatment catalytic reactions (Hamzavi, Gerivani, Saeedi, Naghdipari, & Shahverdizadeh, 2020).

The main goal of this work consists of studying the synthesis of novel catalysts based on regenerated cellulose (RC) beads supporting copper nanoparticles for the removal of organic contaminants in water. Cellulosic beads obtained from different dissolution methods (NaOH/urea solution, viscose and carbamate solution) were proved for the incorporation of copper. Phenol was proposed as a contaminant test molecule to be decomposed on the synthesized copper/cellulose material.

2. Experimental

2.1. Production of cellulose solutions

Commercial dissolving pulp (95 % α cellulose, 428 mL/g intrinsic viscosity, 0.7 mmol/g carboxyl group), produced from Eucalyptus (Solucell®) was provided by Bahia Specialty Cellulose S.A. company (Camacari, Brazil). Analytical grade chemical reagents and deionized water were used in all experiments.

Starting from the dissolving pulp, three cellulose solutions were prepared: Direct Dissolution (D), Cellulose Carbamate (C), and Viscose (V). The synthesis protocols are described and schematized in Scheme S1 in the supplementary data.

2.1.1. Direct Dissolution (D)

According to previously reported methods, a mechanical refining and an enzymatic treatment were performed in order to improve the reactivity and accessibility of the as-received pulp (Grönqvist et al., 2015; Olmos, 2016). The direct dissolution cellulosic pulp (D) was carried out by stirring a mixture of 7 wt.% NaOH (Cicarelli Pro-analysis ACS) and 12 wt.% urea (Cicarelli Pro-analysis) in a thermostatic bath (-5°C) for 30 min. Then the undissolved cellulose was removed by centrifugation during 15 min at 12000 rpm. Finally, the material was stored at 6°C in closed containers until its later use (Egal et al., 2008; Medronho & Lindman, 2014; Olmos, 2016; Qin, Lu, Cai, & Zhang, 2013).

2.1.2. Cellulose Carbamate Solution (C)

Cellulose Carbamate was prepared following previous reports (Fu, Guo, et al., 2014; Fu, Yang, et al., 2014; Guo, Zhou, Song, & Zhang, 2009; Guo, Zhou, Wang, Zhang, & Lin, 2010). A blend composed by cellulose pulp and a solution of 6 w/v % NaOH (Cicarelli Pro-analysis ACS) and 30 w/v % urea (Cicarelli Pro-analysis) was stirred during 120 min at 25°C. After that, the obtained material was pressed until obtaining the impregnated cellulose: cellulose pulp ratio of 4.25:1. Then, a drying treatment at 60°C for 20 h was performed. The esterification reaction was carried out in a microwave oven (160 W, 15 min). The cellulose carbamate solid was washed with deionized water until neutrality in order to remove residual reactants. Afterwards, it was dried at 60°C for 24 h.

The dried cellulose carbamate was dissolved in a mixture of 8 w/v % NaOH (Cicarelli Pro-analysis ACS) and 0.6 w/v % ZnO (Cicarelli Pro-analysis ACS) at 0°C by vigorous stirring (800 rpm) during 15 min. Then, the solution was centrifuged at 9000 rpm at 0°C for 15 min in order to remove the undissolved cellulose. In the end, the material was stored at 6°C in closed containers until its later use (Lanieri, 2017).

2.1.3. Viscose Solution (V)

The viscose solution was obtained following a similar protocol as proposed by Whistler et al. (Whistler, 1962). The dissolving pulp was firstly treated in a NaOH (Cicarelli Pro-analysis ACS) solution 18 w/v % to obtain swelled Alkali Cellulose (AC). After that, it was pressed until achieving an AC: cellulose pulp ratio of 4.25:1. Then, in order to control and reduce the cellulose polymerization degree the material was stored 48 h at 23°C. Afterwards, the xanthation reaction was conducted by the addition of CS₂ (Cicarelli Pro-analysis ACS) to the aged AC and this mixture was stirred for 3 h at 23°C. Finally, the cellulose xanthate was dissolved at 0°C in a 6 w/v % NaOH solution and it was stored at 6°C in closed containers until its later use (Kotek, 2007; Lanieri, 2017; Lanieri, Olmos, Alberini, & Maximino, 2014).

2.2 Preparation Of Regenerated Cellulose Hydrogel Beads (Rc)

The obtained cellulosic solutions (D, C and V) were used to prepare the bead-shape supports. The solutions were extruded through a syringe pump with a flow rate of 30 mL/h. The regenerated cellulose beads were prepared by coagulation followed by regeneration of the cellulose in a mixture of 5 v/v% H₂SO₄ (Cicarelli 95–98 % Pro-analysis ACS) and 5 w/v % anhydrous Na₂SO₄ (Cicarelli Pro-analysis). The beads were washed with deionized water until neutrality and stored in a refrigerator (Gericke, Trygg, & Fardim, 2013; Mao, Zhou, Cai, & Zhang, 2006; Trygg, Fardim, Gericke, Mäkilä, & Salonen, 2013).

2.3 Catalyst Preparation

The Scheme S2 (supplementary data) shows the catalyst synthesis procedure. Copper nanoparticles (CuNPs) suspension synthesized using green reagents (Xiong, Wang, Xue, & Wu, 2011), were supported

on the beads. Copper (II) acetate monohydrate (Aldrich 99.99 %) and L-ascorbic acid (AA) Biopack Pro-analysis ACS, were employed as metal precursor and reducing agent respectively.

The aqueous mixture was magnetically stirred in a reaction vessel, which was placed into a thermostatic bath (25°C or 80°C), while the pH was adjusted to 7.0 ± 0.1 (Han, Liu, Singhal, Wang, & Gao, 2012; Liu, Yasunami, Kuruda, & Okido, 2012). Then 20 mL of 0.037 M L-ascorbic acid solution was pumped dropwise into the reaction vessel using a syringe pump. After 4 hours under reaction, the pH resulted c.a. 3, and the bead's colour turned reddish, suggesting that metallic copper nanoparticles were formed on the cellulosic surface. Finally, the suspension containing the catalytic beads was filtered, and they were carefully washed with deionized water and stored in a refrigerator until their use. The copper nominal content was fixed at 5 wt. %. The catalysts prepared were labelled as Cu-T/RC, where T refers to the synthesis temperature (25°C or 80°C) and RC describes the starting regenerated cellulose (i.e. D, C or V).

2.4 Characterization Of The Synthesized Materials

Beads average diameters were determined from the images taken with an optic microscopy (OLYMPUS BX51) with an OLYMPUS E330 camera. The average value, standard deviation, and coefficient of variation were calculated. The diameter was expressed taking into account the statistical value according to the t distribution at 95 % confidence level.

Total porosity, defined as the total liquid contained in a particle related to the as-prepared cellulose bead dry mass, was calculated with the equation proposed by Ettenauer et al. (Ettenauer et al., 2011).

Copper content in the catalysts was determined by thermogravimetric analysis (TGA-SDTA) in a Mettler Toledo STAR instrument with a TGA/SDTA851e module. A 70 μL alumina pan containing 30–40 mg of sample was heated from 30°C to 600°C in air flow (50 mL/min). A $10^\circ\text{C min}^{-1}$ heating rate was fixed. The derivative form of TGA (DTG) was obtained using TGA differentials data. The residual weight after the experiment was related to CuO content in the sample. The TGA analyses of the supports without copper were also performed in order to verify the total combustion of the cellulosic material in the experimental conditions.

FTIR spectra of samples were obtained with a Shimadzu IR Prestige-21 spectrometer, in the 4000–400 cm^{-1} range, with a resolution of 4 cm^{-1} . The dried supports and catalysts were powdered and mixed with BrK, and pressed to form the corresponding wafers.

The surface morphology of the material was studied using scanning electron microscopy (SEM benchtop Phenom ProX) working at 5–15 kV. Measurements were performed in a holder with controlled cooling. The samples were cooled at -20°C and normal pressure. After that, they were introduced into the microscope measurement chamber where water was removed by sublimation at high vacuum.

The nature of the copper species on the surface catalyst was analyzed with a multi-technique system (SPECS) equipped with a dual Mg/Al X-ray source and a PHOIBOS150 hemispherical analyzer, operating in the fixed analyzer transmission mode (FAT). The spectra were obtained with a passing energy of 30 eV and the AlK α X-ray source was operated at 100 W. The analysis chamber pressure was less than 2×10^{-9} kPa. The XPS spectra of Cu 2p and C 1s were recorded and all the binding energies were referenced to the C 1s peak surface at 284.6 eV. The kinetic energy (KE) in the region of the Cu LMM Auger transition was also measured. The analysis of the peaks was performed with the CasaXPS software, using a weighted sum of the Lorentzian and Gaussian components after Shirley background subtraction. For the quantification of the elements, sensitivity factors provided by the manufacturer were used.

2.5 Catalytic Activity Of The Synthesized Catalysts

Catalytic wet peroxide oxidation (CWPO) of phenol was used as a reaction test to analyse the catalytic performance of the copper containing beads. The experiments were performed in a batch reactor equipped with magnetic stirring. The final catalyst system contained 50 mg of Cu in 50 mL of 1000 ppm phenol (Cicarelli 99 %) solution. As soon as the phenol solution reached 70°C, the catalyst was added and, finally 5 mL of 8.8 M H₂O₂ (Cicarelli Pro-analysis) were incorporated. That moment was considered as the initial reaction time. During the total time reaction (2 h) several aliquots of the reactive solution were taken in order to analyse the phenol and total organic carbon (TOC) conversion. The phenol concentration was analysed using a colorimetric method according to assay 5530-D (Clesceri, Greenberg, & Eaton, 2012). Additionally, at the final reaction TOC was determined according to ISO-8245 (1999) using a TOC Analyzer (Elementar, Vario TOC Cube/Trace). For TOC conversion calculation, the original phenol solution was assumed as the initial organic carbon source.

3 Results And Discussion

3.1 Material Characterization

The properties of the regenerated bead-shaped products prepared from cellulose direct dissolution (RC/D), cellulose carbamate solution (RC/C) and viscose solution (RC/V), are shown in Table 1. It could be observed that in all the bead types, the average diameter and the total porosity resulted similarly. The coefficients of variation (CV %) were below 10 % indicating a homogeneous diameter distribution in all cases.

Table 1
Characterization of the synthesized RC material.

Support	Dissolution method	Diameter (mm)	CV (%)	Total porosity (%)
RC/D	Direct	2.73 ± 0.03	5.57	93.80
RC/C	Carbamate	2.77 ± 0.02	3.87	92.70
RC/V	Viscose	2.57 ± 0.04	5.82	94.30

During the incorporation of copper nanoparticles into the supports, several reaction steps were observed. The different paths are shown in the Supplementary Data.

Table 2 shows the copper content in the prepared catalysts measured by TGA, and the copper addition yield referred to the initial concentration of the precursor solution (5 wt.%). The efficiency of Cu incorporation on RC/C and RC/V resulted higher when the reaction temperature was 25°C, when the temperature was 80°C, the yield decreased 60 % and 35 % respectively. However, the temperature did not greatly affect the incorporation of copper on RC/D beads.

The thermal degradation of the pure supports and catalysts were or was tested by TGA and DTG analysis (Fig. 1). The TGA thermograms showed the complete weight loss of the supports at 600°C, and no char residue was observed. However, in the presence of copper a residual weight was observed in all cases. This residual weight associated with copper oxide formed during the organic support combustion revealed the Cu content in the cellulosic matrix (Table 2). During the heating treatment in flowing air, three steps could be observed: (1) 50–100°C corresponding to the evaporation of adsorbed water, (2) 200–400°C because of the main degradation of cellulosic support and (3) 400–600°C final combustion of organic material (J. Wu, Zhao, Zhang, & Xu, 2012).

In all cases, the initial temperature of the second step decreased after the copper addition in the cellulosic matrix. On the other hand, the highest weight loss temperature decreased after the incorporation of the metal. The shifts of the degradation temperatures compared with that of bare beads depend on the support nature and on the Cu content. The higher Cu content, the lower temperature shifts (Table 2). As a result, the inclusion of the metallic NPs reduced the catalyst thermostability of the catalysts. That effect is lower on the samples prepared with the RC/D support.

Table 2
Thermogravimetric results.

Sample	Cu (wt.%) ¹	Yield (%) ²	T _{max} DTG (°C)	ΔT (°C) ³
RC/D	-	-	334	-
Cu-25/D	0.80	16.0	331	3
Cu-80/D	0.92	18.4	332	2
RC/C	-	-	342	-
Cu-25/C	1.09	21.8	332	10
Cu-80/C	0.44	0.44	334	8
RC/V	-	-	329	-
Cu-25/V	1.40	1.40	319	10
Cu-80/V	0.69	0.96	324	5

(¹) Catalyst copper content determined by TGA, (²) Copper addition yield related to the initial precursor concentration. (³) Difference between the observed maximum DTG temperature in the pure support and the corresponding T_{max} observed in the catalyst.

The chemical state of the copper species supported on the surface of the RC beads was analysed by XPS. After scanning a wide spectra region, the Na 1s signal was slightly detected in the beads with lower Cu content (Cu-25/D and Cu-80/C), whereas in the samples with higher Cu content, Na signal was not observed. This is in agreement with Li et al. who reported that the Na 1s signal corresponding to Na-counterions on the structural carboxylates, disappeared after the CuNPs addition (Li, Messele, Boluk, & El-Din, 2019). This phenomenon could contribute to copper stabilization on the cellulosic matrix through coordination with -COO terminals, giving rise to more stable chemical links.

The Cu 2p XPS region presents two main peaks at around 932 eV and 952 eV, which correspond to Cu 2p_{3/2} and Cu 2p_{1/2} respectively. The shakeup located at 10 eV, which is higher than the Cu 2p_{3/2} signal, suggests the presence of Cu²⁺. In order to differentiate Cu⁰ entities from Cu⁺ species, X-ray excited Auger electron spectroscopy was measured. The Auger parameter is defined as the sum of the Cu 2p_{3/2} binding energy (BE) and the kinetic energy (KE) of the Auger Cu LMM signal (Devard, Brussino, Marchesini, & Ulla, 2019; Wagner & Joshi, 1988). The integration results are shown in Table 3, while Figure S2 in the Supplementary data displays the spectra used for such integrations and calculations. It could be seen that all spectra presented two components in the Cu 2p_{3/2} region. The lowest BEs 932.4 to 933.7 eV (Fig. S2. A) are related to both Cu⁰ and Cu⁺ species (Dai, Sun, Deng, Wu, & Sun, 2001; Ling, Li, & Wang, 2012), while the signals observed at 934.8 to 935.7 eV are assigned to Cu²⁺ entities linked to the support (Baoquan Jia & Li Cheng, Jinping Zhou, 2012). In all samples, the modified Auger parameter (α')

resulted between 1848.3 and 1848.9 eV, confirming the presence of Cu⁺ (Biesinger, 2017; Biesinger, Lau, Gerson, & Smart, 2010; Dai et al., 2001).

As a result, it could be concluded that there were no significant differences between the atomic ratio of Cu²⁺/ (Cu⁺+Cu⁰) in the RC/D and RC/C samples. However, the Cu-80/V sample displayed the biggest quantity of the reduced component, showing the lowest atomic ratio. This observation suggests that some chemical groups which are present in the viscose support surface promote Cu⁰ formation.

Table 3
Catalyst XPS results.

Sample	BE Cu _{2p 3/2} (eV)	KE Cu LMM (eV)	α* (eV)	Cu ²⁺ / (Cu ⁺ +Cu ⁰)
Cu-80/D	933.2	915.1	1848.3	2.9
	935.5			
Cu-25/C	933.3	914.9	1848.2	2.4
	935.5			
Cu-80/C	933.7	915.2	1848.9	2.8
	935.7			
Cu-80/V	932.4	915.9	1848.3	1.6
	934.8			
*Auger parameter.				

Figure 2 shows FTIR normalized spectra of the regenerated cellulose (RC) supports and the corresponding catalysts. The spectra of all samples showed the characteristic bands of the cellulosic matrix. The bands at c.a. 3448 cm⁻¹ and c.a 2910 cm⁻¹ are assigned to O-H and C-H stretching vibrations respectively. While the signal at c.a. 1640 cm⁻¹ corresponds to the O-H bending due to the strong water molecules absorption in the cellulose structure. The C-H bending vibration and C-O stretching mode appear at c.a. 1371 cm⁻¹ and 1070 cm⁻¹ respectively (Teow, Kam, & Mohammad, 2018).

FTIR spectra of the supports prepared via viscose (RC/V) and direct dissolution (RC/D) presented identical bands. However, the cellulose carbamate beads (RC/C) showed a band at ca. 1723 cm⁻¹ which corresponds to the carbonyl stretching in the bases of urethanes formed during the synthesis of cellulose derivatization (Fu et al., 2015; Yin et al., 2007).

The intensity of the band at c.a. 1640 cm⁻¹ remained stable after copper addition in all cases, regardless of the synthesis temperature. Nevertheless, some differences on the signals could be remarked when comparing the catalyst spectra with their corresponding bare supports. These differences suggest that

copper entities were successfully joined on the cellulose chains. In the spectra of Cu-RC/V and Cu-RC/D catalysts, the band at c.a. 1723 cm^{-1} assigned to carbonyl groups added to the cellulose structure due to the presence of ascorbic acid. In all cases, the synthesis temperature increment led to 1723 cm^{-1} lower intensity signal, suggesting the loss of C=O terminals. The appearance of a slight peak at 612 cm^{-1} could also confirm the presence of copper nanoparticles on the cellulose matrix (Prenesti & Berto, 2002). After copper addition, the C-OH band decreased, in agreement with Dong et al. who proposed that these groups could immobilize the copper nanoparticles through electrostatic interactions (Dong & Hinestroza, 2009).

The optical images of supports and catalysts are shown in Figs. 3A and 3B. Figure 3C presents the copper impregnated beads after the cryo-congelation performed previously on the SEM observations. It could be seen that the beads preserved their shape and surface morphology. As a result, the morphological data obtained from SEM observations could be considered for the no cryo-treated beads.

SEM micrographs of the three types of regenerated cellulose and catalysts are shown in Figs. 4 and 5. RC/C support (Fig. 4A) showed a non-homogeneous pore structure with different shapes and sizes in a smooth surface. The RC/D sample (Fig. 4B) presented a surface with wavy cavities and big pores. In contrast, in the RC/V support (Fig. 4C) a highly porous smoothly wavy surface could be observed.

The presence of copper is evidenced in the surface of all the prepared supports (Fig. 5). The distribution of the copper particles was greatly influenced by the RC morphology; however, the metallic phase addition did not modify the initial support structure. It could be also suggested that the greater the material porosity, the more possibility of metallic entities deposition on the surface of the pores. The metal particles on the RC/C support appeared to be supported as platelet arrangement (Fig. 4). This conformation is present in all supports but, in the RC/C samples, in which the surface seems to be softer and more closed the particles are notably bigger (Sone, Diallo, Fuku, Gurib-Fakim, & Maaza, 2020). This could be observed by comparison of Fig. 5A to D. On the other hand, it could be seen that the higher the synthesis temperature the more aggregation of copper particles. The EDS results confirmed the presence of copper in all the prepared catalysts.

3.2 Catalytic tests

In order to prove the activity and efficiency for ECs elimination of the synthesized Cu/RC catalysts, the catalytic degradation of phenol with H_2O_2 was used as a reaction test.

Several supports were studied for the proposed catalytic reaction with copper as the active site (Table S1). Devard et al. reported the catalytic activity of Al_2O_3 supported catalysts containing 5 wt. % of copper as active phase (Devard et al., 2019). This catalyst presented 100 % phenol conversion after 10 min under reaction and high mineralization (TOC = 85%) at 70°C . Meanwhile, Lozano et al. (Lozano, Devard, Ulla, & Zamaro, 2020) studied Cu (5–10 wt.%) supported on MOF materials (Cu/UiO-66) under comparable reaction conditions. These authors also reported good results of these materials for the phenol CWPO reaction. On the other hand, Devard's preliminary experiments (not reported, Table S1) showed that the

synthesis of Cu/SiO₂ and Cu/Al₂O₃ catalysts starting from pre-formed copper nanoparticles with controlled particle size (Gioria et al., 2019) with lower Cu loadings (lower than 1.0 wt.%) converted 100 % of phenol with a more than 50 % of mineralization (Table S1). As a result, cellulose was proposed as an interesting biodegradable low-cost organic material for the same reaction.

Firstly, in order to analyse the cellulosic support (RC/D, RC/C and RC/V) activity for phenol degradation, blank experiments were performed using the supports without metal active phase. The experiments were carried out under the same experimental conditions of temperature, time, and peroxide concentrations. As a result, phenol conversion was not detected.

Then the cellulosic supported catalysts were tested for the phenol CWPO reaction. Figure 6 shows the catalytic results of phenol conversion during 2 h reaction time. It could be observed that the catalysts prepared at 80°C presented more than 90% of phenol conversion. Whereas the catalyst synthesized at 25°C on RC/D and RC/V supports presented lower conversions. In contrast, the conversion of phenol with cellulose carbamate-based catalysts (Cu-RC/C) did not present differences in the catalytic activity (Fig. 6C).

The mineralization process (TOC) measured after 120 min reaction time (Fig. 6) suggested that the phenol was not totally degraded to CO₂, resulting in a colourless organic by-product mixture. It could be observed, that: (i) in Cu-RC/D and Cu-RC/V solids, the higher phenol conversion the higher the mineralization process and (ii) that the catalysts prepared at 80°C showed similar TOC conversions and high phenol conversion after 120 min.

Clearly, it is not possible to establish a direct relationship between the solid catalytic performances with their total copper content. However, the XPS results could help drawing some relevant hypotheses. In fact, RC/D and RC/C catalysts contain a higher proportion of surface Cu²⁺ (Table 3), while the Cu²⁺/(Cu⁺+Cu⁰) ratio calculated in RC/V was lower than the other catalysts, suggesting a higher proportion of copper remained as reduced species.

It is well known that the organic contaminant present in the reaction medium could reduce the Cu⁺² site deposited on the catalyst surface to Cu⁺ cation (Santos, Yustos, Quintanilla, Ruiz, & García-Ochoa, 2005). Then the obtained reduced species are again oxidized by the generated oxygen from H₂O₂, and then, the CE oxidation cycle restarts.

Catalyst morphology (surface area and porosity) plays an important role in catalytic activity together with the active site size and its distribution into the support. The combination of these catalyst properties could give rise to different availability and accessibility of the active sites into the catalytic matrix. As a result, it is difficult to establish a direct relationship between the catalytic results and the physicochemical characteristics of the catalysts due to the observed disparate morphological characteristics of the RC supports. Even so, to the best of our knowledge, the use of copper-based catalysts on this eco-friendly organic matrix has not been reported, at least for CEs degradation in water.

For this reaction, some advantages of the Cu-cellulosic beads could be remarked. In comparison to Cu-based catalysts prepared on large specific area commonly used supports: (i) in the low specific area cellulosic material lower content of copper conduces to similar catalytic yield, (ii) the synthesis of cellulosic supports is more economic and simpler than the synthesis of other more complex materials, (iii) the protocol for the catalytic site incorporation on the cellulose matrix resulted facile and suitable, (iii) facile recovery of the catalyst from the reaction vessel.

4 Conclusions

Looking for "greener" synthesis routes of catalysts, a protocol was developed to obtain Cu/cellulose hybrid materials for wastewater treatment. As a result, different supports based on regenerated cellulose showed good properties to anchor copper nanoparticles. Applying these bead shaped catalysts for liquid phase heterogeneous catalytic reactions allowed the easy separation of the solid/liquid media after the reaction processes.

The characterization by FTIR, TGA, SEM and XPS of the synthesized materials confirmed the successful incorporation of copper on the supports prepared by the direct dissolution and from both solutions of viscose and carbamate. TGA analysis showed that copper incorporation affects the support thermal stability, being this effect more evident in the catalysts prepared at 25°C. Morphology observations showed that the synthesis protocols of the supports conducted to particular surface properties and consequently to different Cu particles size on the cellulosic material.

Among the prepared materials the Cu-80/D solid showed a slightly better catalytic performance: conversion 96.7 % and mineralization 31.7 %. This behaviour could be attributed to the bigger Cu particles size compared with the observed on the other catalysts. Based on these results, it could be asserted that it is necessary to improve the metallic phase NPs incorporation on the biodegradable support in order to obtain an optimal particle size. Even though all the catalysts presented activity for the removal phenol, further insights are needed so as to enhance the catalytic behaviour.

In view of these promising results, several future studies have been proposed in order to improve the use of cellulosic materials. Among them, the optimization of the active site addition protocol to produce well dispersed Cu nanoparticles, and the use of cellulosic fibers and/or nanocellulose for the subsequent incorporation of metallic catalytic sites for low temperature aqueous reactions.

5. Declarations

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6. References

1. Baoquan Jia YM, Li Cheng J, Zhou, and L. Z (2012) Preparation of copper nanoparticles coated cellulose films with.pdf. American Chemical Society Applied Materials Interfaces 4:2897–2902
2. Biesinger MC (2017) Advanced analysis of copper X-ray photoelectron spectra. Surf Interface Anal 49(13):1325–1334. <https://doi.org/10.1002/sia.6239>
3. Biesinger MC, Lau LWM, Gerson AR, Smart RSC (2010) Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Sc, Ti, V, Cu and Zn. Appl Surf Sci 257(3):887–898. <https://doi.org/10.1016/j.apsusc.2010.07.086>
4. Chiron S, Fernandez-Alba A, Rodriguez A, Garcia-Calvo E (2000) Pesticide chemical oxidation: State-of-the-art. Water Res 34(2):366–377. [https://doi.org/10.1016/S0043-1354\(99\)00173-6](https://doi.org/10.1016/S0043-1354(99)00173-6)
5. Clesceri S, Greenberg AE, Eaton AD (2012) *Standard Methods for the Examination of Water and Wastewater. Standard Methods*. <https://doi.org/ISBN 9780875532356>
6. Dai WL, Sun Q, Deng JF, Wu D, Sun YH (2001) XPS studies of Cu/ZnO/Al₂O₃ ultra-fine catalysts derived by a novel gel oxalate co-precipitation for methanol synthesis by CO₂ + H₂. Appl Surf Sci 177(3):172–179. [https://doi.org/10.1016/S0169-4332\(01\)00229-X](https://doi.org/10.1016/S0169-4332(01)00229-X)
7. Devard A, Brussino P, Marchesini FA, Ulla MA (2019) Cu(5%)/Al₂O₃ catalytic performance on the phenol wet oxidation with H₂O₂: Influence of the calcination temperature. Journal of Environmental Chemical Engineering, 7(4). <https://doi.org/10.1016/j.jece.2019.103201>
8. Dong BH, Hinstroza JP (2009) Metal nanoparticles on natural cellulose fibers: Electrostatic assembly and in situ synthesis. ACS Applied Materials Interfaces 1(4):797–803. <https://doi.org/10.1021/am800225j>
9. Egal M, Budtova T, Navard P (2008) The dissolution of microcrystalline cellulose in sodium hydroxide-urea aqueous solutions. Cellulose 15(3):361–370. <https://doi.org/10.1007/s10570-007-9185-1>
10. El Seoud OA, Heinze T (2005) Organic Esters of Cellulose: New Perspectives for Old Polymers. Advanced Polymer Science 186:103–149. <https://doi.org/10.1007/b136818>
11. Ettenauer M, Loth F, Thümmeler K, Fischer S, Weber V, Falkenhagen D (2011) Characterization and functionalization of cellulose microbeads for extracorporeal blood purification. Cellulose 18(5):1257–1263. <https://doi.org/10.1007/s10570-011-9567-2>
12. Eyley S, Thielemans W (2014) Surface modification of cellulose nanocrystals. Nanoscale 6(14):7764–7779. <https://doi.org/10.1039/c4nr01756k>
13. Fink HP, Ganster J, Lehmann A (2014) Progress in cellulose shaping: 20 years' industrial case studies at Fraunhofer IAP. Cellulose 21(1):31–51. <https://doi.org/10.1007/s10570-013-0137-7>

14. Fu F, Guo Y, Wang Y, Tan Q, Zhou J, Zhang L (2014) Structure and properties of the regenerated cellulose membranes prepared from cellulose carbamate in NaOH/ZnO aqueous solution. *Cellulose* 21(4):2819–2830. <https://doi.org/10.1007/s10570-014-0297-0>
15. Fu F, Xu M, Wang H, Wang Y, Ge H, Zhou J (2015) Improved Synthesis of Cellulose Carbamates with Minimum Urea Based on an Easy Scale-up Method. *ACS Sustainable Chemistry Engineering* 3(7):1510–1517. <https://doi.org/10.1021/acssuschemeng.5b00219>
16. Fu F, Yang Q, Zhou J, Hu H, Jia B, Zhang L (2014) Structure and properties of regenerated cellulose filaments prepared from cellulose carbamate-NaOH/ZnO aqueous solution. *ACS Sustainable Chemistry Engineering* 2(11):2604–2612. <https://doi.org/10.1021/sc500559g>
17. Gautam P, Kumar S, Lokhandwala S (2019) Advanced oxidation processes for treatment of leachate from hazardous waste landfill: A critical review. *J Clean Prod* 237:117639. <https://doi.org/10.1016/j.jclepro.2019.117639>
18. Gericke M, Trygg J, Fardim P (2013) Functional Cellulose Beads: Preparation, Characterization, and Applications. *Chem Rev* 113(7):4812–4836. <https://doi.org/https://doi.org/dx.doi.org/10.1021/am3007609>
19. Gioria E, Marchesini FA, Soldati A, Giorello A, Hueso J, Gutierrez LB (2019) Green Synthesis of a Cu/SiO₂ Catalyst for Efficient H₂-SCR of NO. *Applied Sciences* 9(19):4075. <https://doi.org/10.3390/app9194075>
20. Giwa A, Yusuf A, Balogun HA, Sambudi NS, Bilad MR, Adeyemi I, Curcio S (2021) Recent advances in advanced oxidation processes for removal of contaminants from water: A comprehensive review. *Process Saf Environ Prot* 146:220–256. <https://doi.org/10.1016/j.psep.2020.08.015>
21. Grönqvist S, Kamppuri T, Maloney T, Vehviläinen M, Liitiä T, Suurnäkki A (2015) Enhanced pre-treatment of cellulose pulp prior to dissolution into NaOH/ZnO. *Cellulose* 22(6):3981–3990. <https://doi.org/10.1007/s10570-015-0742-8>
22. Guo Y, Zhou J, Song Y, Zhang L (2009) An efficient and environmentally friendly method for the synthesis of cellulose carbamate by microwave heating. *Macromol Rapid Commun* 30(17):1504–1508. <https://doi.org/10.1002/marc.200900238>
23. Guo Y, Zhou J, Wang Y, Zhang L, Lin X (2010) An efficient transformation of cellulose into cellulose carbamates assisted by microwave irradiation. *Cellulose* 17(6):1115–1125. <https://doi.org/10.1007/s10570-010-9446-2>
24. Hachemaoui M, Molina CB, Belver C, Bedia J, Mokhtar A, Hamacha R, Boukoussa B (2021) Metal-loaded mesoporous mcm-41 for the catalytic wet peroxide oxidation (Cwpo) of acetaminophen. *Catalysts* 11(2):1–17. <https://doi.org/10.3390/catal11020219>
25. Hamzavi SF, Gerivani S, Saeedi S, Naghdipari K, Shahverdizadeh G (2020) Preparation and characterization of a novel spherical cellulose–copper (II) oxide composite particles: as a heterogeneous catalyst for the click reaction. *Mol Diversity* 24(1):201–209. <https://doi.org/10.1007/s11030-019-09942-7>

26. Han J, Liu Y, Singhal N, Wang L, Gao W (2012) Comparative photocatalytic degradation of estrone in water by ZnO and TiO₂ under artificial UVA and solar irradiation. *Chem Eng J* 213:150–162. <https://doi.org/10.1016/j.cej.2012.09.066>
27. Heinze T, Seoud OA, El, Koschella A (2018) *Cellulose Derivatives Synthesis, Structure, and Properties*, 1st edn. Springer Series, Switzerland. <https://doi.org/10.1007/978-3-319-73168-1>
28. Hokkanen S, Bhatnagar A, Sillanpää M (2016) A review on modification methods to cellulose-based adsorbents to improve adsorption capacity. *Water Res* 91:156–173. <https://doi.org/10.1016/j.watres.2016.01.008>
29. Hou M, Pu Y, Qi W, Kang, Tang Y, Wan P, Yang XJ, Fisher A (2018) Enhanced electrocatalytic reduction of aqueous nitrate by modified copper catalyst through electrochemical deposition and annealing treatment. *Chem Eng Commun*, 205(5). <https://doi.org/10.1080/00986445.2017.1413357>
30. Kotek R (2007) *Handbook of fiber chemistry (IV)*. (M. Lewin, Ed.) (3ra.). CRC Press / Taylor and Francis group
31. Lanieri DB (2017) *Obtención y caracterización de carbamato de celulosa como alternativa de disolución al proceso viscosa*. Universidad Nacional del Litoral, Santa Fe. Retrieved from <http://hdl.handle.net/11185/943>
32. Lanieri DB, Olmos GV, Alberini IC, Maximino MG (2014) Rapid estimation of gamma number of viscose by UV spectrophotometry. *O Papel* 75(2):60–65. ISSN 00311057
33. Levec J, Pintar A (2007) Catalytic wet-air oxidation processes: A review. *Catal Today* 124(x):172–184. <https://doi.org/10.1016/j.cattod.2007.03.035>
34. Li M, Messele SA, Boluk Y, El-Din GM (2019) Isolated cellulose nanofibers for Cu (II) and Zn (II) removal: performance and mechanisms. *Carbohydr Polym* 221(May):231–241. <https://doi.org/10.1016/j.carbpol.2019.05.078>
35. Ling P, Li D, Wang X (2012) Supported CuO/ γ -Al₂O₃ as heterogeneous catalyst for synthesis of diaryl ether under ligand-free conditions. *J Mol Catal A: Chem* 357:112–116. <https://doi.org/10.1016/j.molcata.2012.01.028>
36. Liu QM, Yasunami T, Kuruda K, Okido M (2012) Preparation of Cu nanoparticles with ascorbic acid by aqueous solution reduction method. *Transactions of Nonferrous Metals Society of China (English Edition)* 22(9):2198–2203. [https://doi.org/10.1016/S1003-6326\(11\)61449-0](https://doi.org/10.1016/S1003-6326(11)61449-0)
37. Lozano LA, Devard A, Ulla MA, Zamaro JM (2020) Cu/UiO-66: A novel nanocatalyst obtained by a microwave-assisted protocol in DMF-free media for the efficient phenol removal via catalytic wet peroxide oxidation. *Journal of Environmental Chemical Engineering* 8(5):104332. <https://doi.org/10.1016/j.jece.2020.104332>
38. Luo X, Zhang L (2010) Creation of regenerated cellulose microspheres with diameter ranging from micron to millimeter for chromatography applications. *J Chromatogr A* 1217(38):5922–5929. <https://doi.org/10.1016/j.chroma.2010.07.026>
39. Maduna K, Kumar N, Aho A, Wärnå J, Zrnčević S, Murzin DY (2018) Kinetics of Catalytic Wet Peroxide Oxidation of Phenolics in Olive Oil Mill Wastewaters over Copper Catalysts. *ACS Omega*

- 3(7):7247–7260. <https://doi.org/10.1021/acsomega.8b00948>
40. Mao Y, Zhou J, Cai J, Zhang L (2006) Effects of coagulants on porous structure of membranes prepared from cellulose in NaOH/urea aqueous solution. *J Membr Sci* 279(1–2):246–255. <https://doi.org/10.1016/j.memsci.2005.07.048>
 41. Medronho B, Lindman B (2014) Competing forces during cellulose dissolution: From solvents to mechanisms. *Current Opinion in Colloid Interface Science* 19(1):32–40. <https://doi.org/10.1016/j.cocis.2013.12.001>
 42. Miklos DB, Remy C, Jekel M, Linden KG, Drewes JE, Hübner U (2018) Evaluation of advanced oxidation processes for water and wastewater treatment – A critical review. *Water Res* 139:118–131. <https://doi.org/10.1016/j.watres.2018.03.042>
 43. Muthulakshmi L, Rajini N, Nellaiah H, Kathiresan T, Jawaaid M, Rajulu AV (2017) Preparation and properties of cellulose nanocomposite films with in situ generated copper nanoparticles using *Terminalia catappa* leaf extract. *Int J Biol Macromol* 95:1064–1071. <https://doi.org/10.1016/j.ijbiomac.2016.09.114>
 44. Navard P (2012) The European Polysaccharide Network of Excellence (EPNOE). Research initiatives and results. Springer Netherlands, Vienna. https://doi.org/10.1007/978-3-7091-0421-7_5
 45. Olmos GV (2016) *Alternativas de disolución de celulosa para la obtención de productos regenerados*. Universidad Nacional del Litoral. Retrieved from <http://hdl.handle.net/11185/945>
 46. Pinna F (1998) Supported metal catalysts preparation. *Catal Today* 41(1–3):129–137. [https://doi.org/10.1016/S0920-5861\(98\)00043-1](https://doi.org/10.1016/S0920-5861(98)00043-1)
 47. Prenesti E, Berto S (2002) Interaction of copper (II) with imidazole pyridine nitrogen-containing ligands in aqueous medium: A spectroscopic study. *J Inorg Biochem* 88(1):37–43. [https://doi.org/10.1016/S0162-0134\(01\)00325-7](https://doi.org/10.1016/S0162-0134(01)00325-7)
 48. Qi H (2017) *Nanocellulose-based functional materials*. *SpringerBriefs in Applied Sciences and Technology*. https://doi.org/10.1007/978-3-319-49592-7_5
 49. Qin X, Lu A, Cai J, Zhang L (2013) Stability of inclusion complex formed by cellulose in NaOH/urea aqueous solution at low temperature. *Carbohydr Polym* 92(2):1315–1320. <https://doi.org/10.1016/j.carbpol.2012.10.004>
 50. Rizzo L, Malato S, Antakyali D, Beretsou VG, Đolić MB, Gernjak W, Fatta-Kassinos D (2019) Consolidated vs new advanced treatment methods for the removal of contaminants of emerging concern from urban wastewater. *Science of the Total Environment*, 655(October 2018), 986–1008. <https://doi.org/10.1016/j.scitotenv.2018.11.265>
 51. Roy D, Semsarilar M, Guthrie JT, Perrier S (2009) Cellulose modification by polymer grafting: A review. *Chem Soc Rev* 38(7):2046–2064. <https://doi.org/10.1039/b808639g>
 52. Santos A, Yustos P, Quintanilla A, Ruiz G, García-Ochoa F (2005) Study of the copper leaching in the wet oxidation of phenol with CuO-based catalysts: Causes and effects, 61, 323–333. <https://doi.org/10.1016/j.apcatb.2005.06.006>

53. Schwarz JA, Contescu C, Contescu A (1995) Methods for Preparation of Catalytic Materials. *Chem Rev* 95(3):477–510. <https://doi.org/10.1021/cr00035a002>
54. Sone BT, Diallo A, Fuku XG, Gurib-Fakim A, Maaza M (2020) Biosynthesized CuO nano-platelets: Physical properties & enhanced thermal conductivity nanofluidics. *Arabian Journal of Chemistry* 13(1):160–170. <https://doi.org/10.1016/j.arabjc.2017.03.004>
55. Stuart M, Lapworth D, Crane E, Hart A (2012) Review of risk from potential emerging contaminants in UK groundwater. *Sci Total Environ* 416:1–21. <https://doi.org/10.1016/j.scitotenv.2011.11.072>
56. Teow YH, Kam LM, Mohammad AW (2018) Synthesis of cellulose hydrogel for copper (II) ions adsorption. *Journal of Environmental Chemical Engineering* 6(4):4588–4597. <https://doi.org/10.1016/j.jece.2018.07.010>
57. Trygg J, Fardim P, Gericke M, Mäkilä E, Salonen J (2013) Physicochemical design of the morphology and ultrastructure of cellulose beads. *Carbohydr Polym* 93(1):291–299. <https://doi.org/10.1016/j.carbpol.2012.03.085>
58. Valkaj K, Wittine O, Margeta K, Granato T, Katović A, Zrnčević S (2011) Phenol oxidation with hydrogen peroxide using Cu/ZSM5 and Cu/Y5 catalysts. *Polish Journal of Chemical Technology* 13(3):28–36. <https://doi.org/10.2478/v10026-011-0033-6>
59. Wagner CD, Joshi A (1988) The auger parameter, its utility and advantages: a review. *Journal of Electron Spectroscopy Related Phenomena* 47(C):283–313. [https://doi.org/10.1016/0368-2048\(88\)85018-7](https://doi.org/10.1016/0368-2048(88)85018-7)
60. Wang S, Lu A, Zhang L (2016) Recent advances in regenerated cellulose materials. *Prog Polym Sci* 53:169–206. <https://doi.org/10.1016/j.progpolymsci.2015.07.003>
61. Wu J, Zhao N, Zhang X, Xu J (2012) Cellulose/silver nanoparticles composite microspheres: Eco-friendly synthesis and catalytic application. *Cellulose* 19(4):1239–1249. <https://doi.org/10.1007/s10570-012-9731-3>
62. Wu Y, Zhang H, Yan Y (2020) Effect of copper ion-exchange on catalytic wet peroxide oxidation of phenol over ZSM-5 membrane. *J Environ Manage* 270(May):110907. <https://doi.org/10.1016/j.jenvman.2020.110907>
63. Xiong J, Wang Y, Xue Q, Wu X (2011) Synthesis of highly stable dispersions of nanosized copper particles using l-ascorbic acid. *Green Chem* 13(4):900–904. <https://doi.org/10.1039/c0gc00772b>
64. Yan Y, Wu X, Zhang H (2016) Catalytic wet peroxide oxidation of phenol over Fe₂O₃/MCM-41 in a fixed bed reactor. *Sep Purif Technol* 171:52–61. <https://doi.org/10.1016/j.seppur.2016.06.047>
65. Yin C, Li J, Xu Q, Peng Q, Liu Y, Shen X (2007) Chemical modification of cotton cellulose in supercritical carbon dioxide: Synthesis and characterization of cellulose carbamate. *Carbohydr Polym* 67(2):147–154. <https://doi.org/10.1016/j.carbpol.2006.05.010>
66. Yoosefi Booshehri A, Wang R, Xu R (2015) Simple method of deposition of CuO nanoparticles on a cellulose paper and its antibacterial activity. *Chem Eng J* 262:999–1008. <https://doi.org/10.1016/j.cej.2014.09.096>

Figures

Figure 1

TGA and DTG analyses of as-prepared supports and the corresponding catalysts. TGA: A, B and C. DTG: A1, B1 and C1. Inserted graph: remaining weight for the calculation of the copper content.

Figure 2

FTIR spectra of regenerated cellulose supports and the corresponding catalysts.

Figure 3

A y B: Optical images of as-prepared regenerated cellulose beads, and Cu supported beads: a) RC/C, b) RC/D, c) RC/V, d) Cu-80/V, e) Cu-80/D, f) Cu-25/C, g) Cu-80/C. C) d, e, f and g SEM of cryo-dried beads, according to figures A and B.

Figure 4

SEM images of the RC supports: A) RC/C, B) RC/D and C) RC/V.

Figure 5

SEM images of the RC based catalysts: A) Cu-25/C, B) Cu-80/C, C) Cu-80/D and D) Cu-80/V. Note: some Cu particles were circled on the micrographs.

Figure 6

Phenol conversion in CPWO reaction. A) Cu-RC/D, B) Cu-RC/V and C) Cu-RC/C catalysts. TOC conversions after 120 min under reaction are pointed out. Reaction conditions: see experimental.

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