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Synthesis, Characterization, and Catalytic Properties of Cationic Hydrogels Containing Copper(II) and Cobalt(II) Ions

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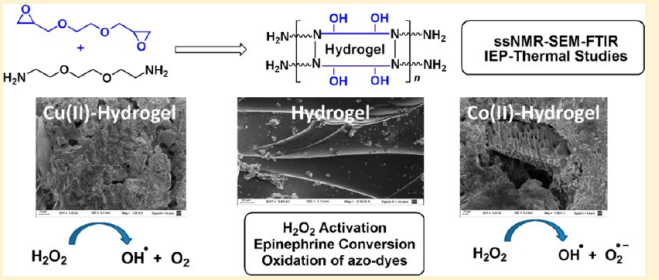
Supporting Information

ABSTRACT: Here, we report the synthesis and characterization of a hydrogel based on ethylene glycol diglycidyl ether (EGDE) and 1,8-diamino-3,6-dioxaoctane (DA). Chemically stable Co(II) and Cu(II) coordination complexes were prepared with this nonsoluble polyelectrolyte, *poly*(EGDE-DA), and studied by *ss*-NMR, FT-IR, thermogravimetry, and microscopy. Mesopores were found in all the samples, the thermal stability of the polymer matrix was highly affected by the presence of metal ions, and the ^{13}C CP-MAS spectrum for the Cu(II)-complex evidenced a significant increase in the reticulation degree by Cu(II) ions. The catalytic activity of these materials on H_2O_2 activation was studied by electron spin resonance (ESR). The Co(II)-*poly*(EGDE-DA)/H_2O_2 heterogeneous system produced O_2, an anion superoxide ($O_2^{\bullet-}$), and a hydroxyl radical ($OH^{\bullet}$), which diffused into the solution at the time that a decrease in pH was detected. In the same way, the Cu(II)-*poly*(EGDE-DA)/H_2O_2 heterogeneous system produced O_2 and $OH^{\bullet}$. H_2O_2 activation by the *poly*(EGDE-DA) complexes with Co(II) and Cu(II) were applied on the decolorization of solutions of the azo-dye methyl orange (MO). In the presence of 63 mM H_2O_2, 87% of MO was removed in 10 min with Cu(II)-*poly*(EGDE-DA) and in 110 min with Co(II)-*poly*(EGDE-DA). In addition, the pharmaceutical product epinephrine was partially oxidized to adrenochrome by the $O_2^{\bullet-}$ released from the Co(II)-*poly*(EGDE-DA)/H_2O_2 heterogeneous system.



1. INTRODUCTION

The coordination of a polymeric ligand by a transition metal ion is an efficient way to obtain processable materials with unique and valuable properties. Polymer networks offer new possibilities to scientists for the creation of artificial materials. In recent years, hydrogels with chelating ligands attracted the attention for industrial applications.[1] In particular, polyelectrolyte and polyampholyte hydrogels have become of great interest in the macromolecular chemistry area due to their versatility as excellent adsorbents of chemical compounds.[2] Stimuli-sensitive hydrogels are used in a variety of novel applications, including controlled drug delivery, immobilized enzyme systems, separation processes, fuel cells, and sensor development.[3,4]

We have previously demonstrated that nonsoluble polymers can be prepared from ethylene glycol diglycidyl ether (EGDE) using methacrylic acid (MAA) and/or *N*-heterocycles. The synthetic process involves the opening of the epoxy groups from EGDE by the reaction with MAA, and a peroxide-initiated radical polymerization of MAA segments covalently bound to EGDE to give a polyelectrolyte [*poly*(EGDE-MAA)]. When imidazole (IM) is added to the reaction mixture, the epoxy groups are opened up by both the carboxylic acid of the MAA and the pyridine-type nitrogen of the *N*-heterocycle, yielding a polyampholyte [*poly*(EGDE-MAA-IM)].[5−7] When EGDE and IM are mixed in the absence of the radical polymerization initiator [*poly*(EGDE-IM)], a polyelectrolyte is also synthesized. The respective polyampholytes and polyelectrolytes were derived from a variety of *N*-heterocycles such as 2-methylimidazole (2MI), pyrazole (PYR), and triazole (TRZ).[8,9]

These materials offer the versatility to complex different metal ions due to the presence of the imidazole ligand,

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carboxylic, and hydroxyl groups in the structure. In Cu(II)-*poly*(EGDE-MAA-IM) and Cu(II)-*poly*(EGDE-MAA-2MI) complexes, the imidazole ring has been found to be the main group involved in metal ion uptake and the carboxylic group appears to have a coordinating role only at high concentrations of the metal ion.[10,11] A similar behavior has been reported for the complexation of copolymers from unsaturated carboxylic acids and vinylimidazole with Cu(II)[10] and for Cu(II) coordination to some peptides.[11]

Functional materials are often made by the synergistic combination of organic and inorganic components. Cu(II) and Co(II) complexes with these hydrophilic, nonsoluble matrices have been demonstrated to activate hydrogen peroxide (H_2O_2) to produce free radicals and dioxygen.[12,13] When Cu(II) and Co(II) complexes are used as heterogeneous catalysts, the formation of hydroxyl radical ($OH^{\bullet}$) and anion superoxide ($O_2^{\bullet-}$), respectively, is evidenced by electron spin resonance (ESR). Both reactive species have been proven to oxidize the azo-dye methyl orange (MO), and $O_2^{\bullet-}$ effectively converts epinephrine into a partially oxidized product named adrenochrome.[12,13]

Herein, we report a synthetic strategy to prepare polyelectrolytes based on a diepoxy monomer and a bifunctional primary amine, using EGDE and DA as reactants. Because it is well-established that the coordination compounds of nonsoluble polymers with Co(II) and Cu(II) play a key role in H_2O_2 activation, we explored performance of the new complexes as heterogeneous catalysts. Although H_2O_2 is an attractive reagent of low environmental impact because water is the only byproduct, it is a rather slow oxidizing agent in the absence of activators.[14] Nowadays, the advanced oxidation processes by means of hydroxyl radicals are widely recognized as highly efficient treatments for recalcitrant wastewater.[15] At the same time, H_2O_2 is being applied in eco-friendly technologies dealing with the synthesis of value-added chemical products, which involve oxidations under mild conditions.[16] To explore the environmental and industrial applications of the novel complexes on H_2O_2 activation, we used two different organic substrates: MO (a synthetic dye found in wastewater) and epinephrine (a model compound of pharmaceutical precursors).

2. EXPERIMENTAL SECTION

2.1. Materials and Reagents. Ethylene glycol diglycidyl ether (EGDE; 50 wt % in ethylene glycol dimethyl ether) was from TCI America. 1,8-Diamino-3,6-dioxaoctane (DA), epinephrine bitartrate, and 5,5-dimethyl-1-pyrroline-N oxide (DMPO) were purchased from Sigma–Aldrich. Superoxide dismutase (SOD) was from Biosidus (Buenos Aires, Argentina). Acetonitrile from Baxter was of HPLC grade.

$CoSO_4$ and cobalt acetate were purchased from Mallinckrodt. $CuSO_4{\cdot}2H_2O$, Na_2SO_4, and H_2O_2 (30 wt %) were acquired from Merck (Darmstadt, Germany). Methyl Orange (MO) was from Santa Cruz Biotechnology, Inc. Soybean peroxidase (SBP) was extracted from soybean seed coat with water.

Water was distilled with a FIGMAY glass apparatus (Córdoba, Argentina). All other reagents were of analytical grade.

2.2. Instruments. High-resolution ^{13}C solid-state spectra for the polymers were recorded using the ramp $\{^1H\}\rightarrow\{^{13}C\}$ CP-MAS (cross-polarization and magic angle spinning) sequence with proton decoupling during acquisition. All the *solid-state* nuclear magnetic resonance (*ss*-NMR) experiments were performed at room temperature in a Bruker Avance II-300 spectrometer equipped with a 4 mm MAS probe. The operating frequencies for protons and carbons were 300.13 and 75.46 MHz, respectively.[12,17]

The FT-IR spectra of the polymers and their copper complexes were recorded on a Nicolet 380 spectrometer using KBr pellets. SEM imaging and EDS were carried out with a scanning electron microscope field emission SEM (Zeiss Gemini DSM 982) operated at a 0.3 kV acceleration voltage and an INCA Energy (Oxford Instrument), respectively. Elemental analysis was performed with a Carlo Erba EA 1108 device. A nitrogen adsorption isotherm was collected at 77 K on a Micromeritics Gemini 2360 system. Specific surface area was calculated using the BET (Brunauer–Emmett–Teller) equation. The electron spin resonance (ESR) spectra were obtained at 20 °C using an X-band ESR Spectrometer Bruker EMX plus (Bruker Instruments, Inc., Berlin, Germany). Partial pressure of O_2 was measured with an Orbisphere A1100-Oxygen Sensor. UV–visible spectrophotometric measurements were made on a Hewlett-Packard instrument, HP 8452A model with diode array.

The isoelectric point (IEP) value was obtained by diffusion potential determination as described elsewhere.[18] Electromotive force (EMF) measurements were carried out with a Keithley 616 digital electrometer instrument with Metrohm calomel electrodes. Potentiometric titration of the polyelectrolyte was performed with a HANNA Instrument pH meter as elsewhere.[5,6]

2.3. Synthesis of *Poly*(EGDE–DA). An aliquot of 176 μL (1.2 mmol) of 1,8-diamino-3,6-dioxaoctane (DA) and 0.4 mL (1.28 mmol) of ethylene glycol diglycidyl ether (EGDE; 50 wt % in ethylene glycol dimethyl ether) was mixed with 0.4 mL of acetonitrile. The solution was placed in a tube glass and thermostatted at 60 °C for 24 h. The product was placed at 20 °C, milled, washed three times with distilled water, and dried at 60 °C during 24 h. The polyelectrolyte was used without further purification.

2.4. Swelling Equilibrium. Equilibrium swelling measurements were performed in triplicate at pH 3.00 with an ionic strength (I) of 0.50 and <0.001 and at pH 9.80 with I = 0.50.

An amount of the polyelectrolyte was immersed in a measured volume of the corresponding aqueous solution and kept for 2 days to reach equilibrium. Swollen material was separated by filtration, weighed, and dried at 90 °C until constant weight. The dried material was cooled at 20 °C in a desiccator and weighed again. The swelling degree and water content were calculated as elsewhere.[5,6]

2.5. Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG). The glass transition temperature (T_g) values of the polyelectrolyte and its copper and cobalt complexes were measured on a Shimadzu 60 type differential scanning calorimeter (DSC) at a rate of 15 °C min^{-1} during the second heating trace in the calorimeter under a nitrogen purge.

Thermogravimetric measurements were carried out with a TA Instrument SDT Q600, under nitrogen flux over a temperature range from 30 to 400 °C, with a heating rate of 10 °C min^{-1}. The average sample size was 10 mg.

2.6. Cobalt Uptake. Cobalt binding studies were performed with 0.0500 g of polyelectrolyte and 4.0 mL of $CoSO_4$ solution in a 5.0–40 mM concentration range. The samples were centrifuged and filtered after 48 h of contact time at 24 °C. Free Co(II) concentration at the equilibrium in each supernatant solution could be determined spectrophotometrically since Co^{2+} forms a coordination compound with SCN^- in the presence of HCl and acetone, which absorbs radiation at 622 nm.[19]

2.7. Copper Uptake. Copper binding studies were performed with 0.0250 g of polyelectrolyte and 4.0 mL of $CuSO_4$ solution in a 4.0–70 mM concentration range. The samples were centrifuged and filtered after 48 h of contact time at 24 °C. Free Cu(II) concentration in each supernatant solution could be determined spectrophotometrically since $Cu(NH_3)_4^{2+}$ (formed by ammonium hydroxide addition) absorbs radiation at 640 nm. The isotherm and kinetic parameter sets were determined by nonlinear regression. The algorithm based on the Gauss–Newton method was used. The error function employed to evaluate the fit was the second order corrected Akaike criterion (AIC_C).[20,21]

2.8. Preparation of Co(II)-*poly*(EGDE-DA) and Cu(II)-*poly*(-EGDE-DA). The complexes were prepared mixing 0.5000 g of polymer powder and 40 mL of 70 mM $CoSO_4$ solution for Co(II)-*poly*(EGDE-

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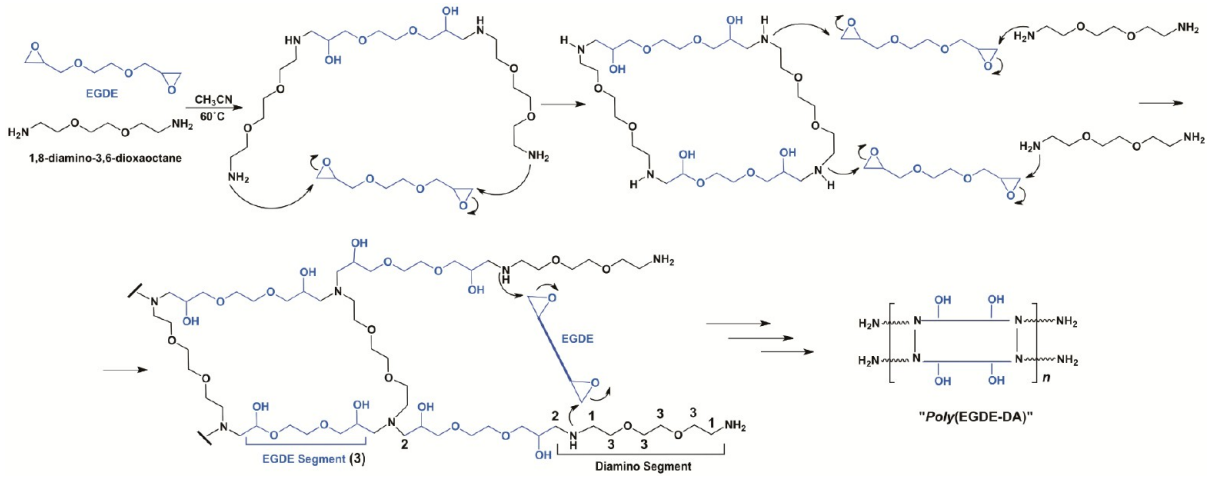
Scheme 1. Synthesis of *Poly*(EGDE-DA) and the Representative Structure of the Product



DA) and of 140 mM $CuSO_4$ solution for Cu(II)-*poly*(EGDE-DA), in distilled water at 24 °C for 48 h.

The samples were then centrifuged, washed with three 20 mL portions of distilled water to remove the cation weakly adsorbed on the particles, filtered, dried at 60 °C, and milled in a mortar. The last portion of water from the wash step did not present detectable amounts of free cation in solution, when each one was tested by the colorimetric methods described in Cobalt Uptake and Copper Uptake. The loading capacity for each cation under the mentioned conditions was 15.2 mg Co(II) g^{-1} and 170 mg Cu(II) g^{-1} (0.258 mmol Co(II) g^{-1} and 2.67 mmol Cu(II) g^{-1}, respectively).

2.9. Measurement of H_2O_2 Concentration. This peroxide reacts with phenol and 4-aminoantipyrine in the presence of soybean peroxidase (SBP), giving a product that absorbs radiation at 505 nm.[12,22] An amount of 0.0500 g of each complex was suspended in 50 mL of 42 mM H_2O_2. The concentration of H_2O_2 was monitored as a function of time from 20 μL samples of the reaction.[12,22]

2.10. Measurement of Free Radicals by ESR. The initial H_2O_2 concentration was set close to 60 mM. Higher concentration levels of H_2O_2 were expected to be less efficient in oxidative processes due to possible deleterious effects on the polymeric catalysts.[12,13] An amount of 0.0500 g of each complex was suspended in 50 mL of 63 mM H_2O_2 solution and the production of free radicals was followed by ESR. The experiment was also performed in the presence of SOD with an activity of 200 units mL^{-1} added to the system before H_2O_2.

Aliquots of 32 μL taken at different times of reaction were mixed with 16 μL of 3 M DMPO (spin trap), and the continuous wave (CW) ESR spectra of the DMPO spin adducts were recorded at 20 °C, 3 min after the end of incubation, in an X-band ESR Spectrometer Bruker EMX Plus (Bruker Biospin GmbH, Germany). The spectrometer settings and simulations conditions were reported previously by Lombardo Lupano et al.[12]

In parallel, the measurements of O_2 partial pressure were made in triplicate with a O_2 sensor, at 10 min of reaction.

2.11. Methyl Orange Decolorization. An amount of 0.1000 g of Co(II)-*poly*(EGDE-DA) or Cu(II)-*poly*(EGDE-DA) was suspended in 100 mL of 42 μM MO and 63 mM H_2O_2 solution. The medium of reaction was distilled water. The absorbance of the solution was monitored as a function of time at 464 nm. For turbidity correction, the absorbance was measured at 700 nm and subtracted to the absorbance at 464 nm. The control of MO adsorption on the catalyst was made in the absence of H_2O_2.

For the evaluation of the chemical stability of the catalysts on reutilization, the experiment with MO was repeated three times with the same recycled catalyst and new aliquots of solution.

The experiments conducted to study the MO degradation by soluble free radicals were made with 0.1000 g of Co(II)-*poly*(EGDE-DA) or Cu(II)-*poly*(EGDE-DA) suspended in 80 mL of 79 mM H_2O_2 solution. Here, the H_2O_2 solution was activated during 10 min with the solid particles of each complex. Then, the suspension was filtered, the supernatant was recovered and mixed with 20 mL of 210 μM MO solution, and the MO concentration in the resulting solution was monitored as a function of time.

For the detection of cobalt or copper intermediate species catalytically active, 0.1000 g of Co(II)-*poly*(EGDE-DA) or Cu(II)-*poly*(EGDE-DA) were put in contact with 100 mL of 63 mM H_2O_2 solution for 10 min. The suspension was centrifuged, the supernatant was discarded, the particles were washed with three portions of distilled water, and they were not dried. The activated particles of the catalyst were put in contact with 100 mL of 42 μM MO solution, and the MO concentration was monitored as a function of time by visible spectrophotometry.

Additional controls and tests were made by changing the chemical composition of the medium of reaction or the mass of catalyst (g) to volume of solution (L) ratio. A 0.1 M Na_2SO_4 solution was used as an alternative medium.

For the experiments with equimolar amounts of catalytic sites (0.644 mmol of sites L^{-1}), 0.2500 g of Co(II)-*poly*(EGDE-DA) were suspended in 100 mL of 42 μM MO, and 0.0241 g of Cu(II)-*poly*(EGDE-DA) were suspended in 100 mL of 42 μM MO. H_2O_2 was added to initiate the catalytic reaction, and it was absent in the adsorption control.

2.12. Epinephrine Oxidation. An amount of 0.0400 g of Co(II)-*poly*(EGDE-DA) was suspended in 20 mL of 2 mM epinephrine and 46 mM H_2O_2 solution (higher concentrations of H_2O_2 were proved to be less effective). The absorbance of the solution was monitored as a function of time at 480 nm. For turbidity correction, the absorbance was measured at 700 nm and subtracted to the absorbance at 480 nm.

A control experiment of epinephrine oxidation in the homogeneous system was made with a solution of 2 mM epinephrine and 46 mM H_2O_2. Another control experiment was made with 0.0400 g of Co(II)-*poly*(EGDE-DA) suspended in 20 mL of 2 mM epinephrine in absence of H_2O_2. This experiment was repeated with previous and continuous bubbling of argon in the solution to displace the dissolved O_2.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of the Polyelectrolyte. The novel hydrogel *poly*(EGDE-DA) was synthesized in a one-step batch synthetic strategy using ethylene glycol diglycidyl ether (EGDE) and 1,8-diamino-3,6-dioxaoctane (DA). Initially, the nitrogen atom of DA caused the opening of the epoxy group present in the EGDE molecule with the concomitant proton transfer and the generation of a hydroxyl group and a secondary amine (Scheme 1). Then, the pendant amino groups may react with other oxirane rings to give rise to a hydrogel system with hydroxyl groups together with different

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primary, secondary, and tertiary amines, which may adopt a positive charge in acidic medium. The presence of linear polyamines is only possible as short pendant chains at the end of the cross-linked network. In this sense, the nonsoluble behavior of the poly(EGDE-DA) in strong acidic medium indicated that the cross-linked structure is more significant than the linear polyamine segment.

This makes this system an interesting polyelectrolyte material and also an attractive coordination hydrogel against metal ions through the nitrogen and/or oxygen ligands. Scheme 1 exhibits the most representative chemical structure of this product.

The dried and milled polymer rendered 95%, with an elemental composition of N, 5.1%; C, 52.1%; H, 9.2%. From this result, it can be concluded that 1.82 mmol of DA residues were bound to the EGDE segment per gram of polymer. The number of titrable basic sites (represented as $-R_2N$, where R can be either H or organic chain) was 0.978 mmol g^{-1}, determined by potentiometry. The titration curve and the acid–base properties of *poly*(EGDE-DA) are presented in Figure S1 and the Discussion of Figure S1 of the Supporting Information.

The diffusion potential determination gave an IEP of 10.5, indicating that the particles were positively charged up to that pH value (Figure S2 of the Supporting Information).

3.2. Characterization by FT-IR and *ss*-NMR. The polymer material was characterized using FT-IR and *ss*-NMR spectroscopy, and the results are shown in Figure S3 of the Supporting Information and in Figure 1, respectively. The FT-IR spectrum of *poly*(EGDE-DA) indicated a lack of good resolution with the presence of amorphous particles of the gel. However, some bands were observed at 1112 cm^{-1} (due to the stretching of the C–O ether groups), 1460 and 1650 cm^{-1} (deformation motion of $-O-CH_2-$ and –N–H, respectively), 2930 cm^{-1} (stretching of C–H), and ~3400 cm^{-1} (stretching of the N–H/O–H groups).

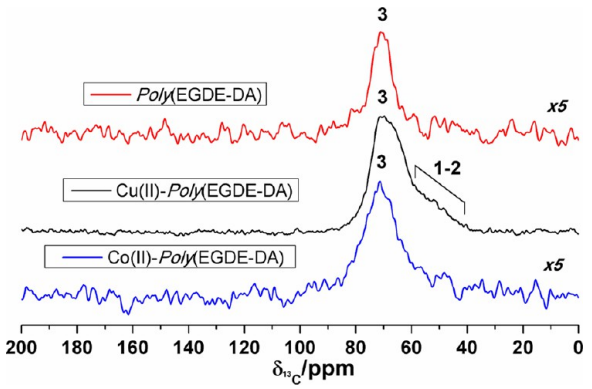

Figure 1. ^{13}C CP-MAS spectra for *poly*(EGDE-DA) and for its Cu(II)- and Co(II) complexes containing 125.0 and 12.5 mg of metal ion per gram of polymer, respectively. The assignments correspond to those in Scheme 1.

The ^{13}C CP-MAS spectrum of the material gave only information related to the methylene groups bound directly to the oxygen atom at 70 ppm ($-CH_2-O-$). These carbons are both present in the "EGDE" and "diamino" segments (Figure 1), but no information regarding the carbons bound to nitrogen was obtained.

3.3. Swelling Degree. The water content of polyelectrolytes is related to charge solvation. The repulsive forces among fixed charges and the osmotic pressure due to counterions induce network expansion.[23,24] The results for this new material are summarized in Table S1 of the Supporting Information. At pH 3.0, the basic groups of polymeric units are protonated (Figure S1 of the Supporting Information), acquiring a positive charge and forcing the segments to stretch out. This creates more room for solvent between the cross-links and allows the hydrogel to swell.

The results at pH 3.0 show the dependence of the swelling degree on *I*.[25] At low *I*, the counterions (responsible for the osmotic effect) are assumed to remain in the matrix, making the electrostatic repulsion between chains the dominant effect on expansion. At higher *I*, the Donnan effect caused a decrease in swelling because of the additional shielding of the fixed charges on the chain by the additional diffusible counterions. At pH 9.8, the swelling degree did not change significantly, finding about 50% of the basic residues protonated due to the low apparent acid dissociation constant of the $-R_2NH^+$ (discussion of Figure S1 of the Supporting Information).

3.4. Adsorption of Cu(II) and Co(II). The mechanism of copper uptake was explored by analyzing the results of the adsorption isotherm for the polyampholyte at 20 °C. Four isotherm models (Temkin, Langmuir, Dubinin–Radushkevich (D–R), and Freundlich) were used to fit the experimental adsorption data by nonlinear regression (Table 1).

The best fit of experimental adsorption data was obtained with Temkin, Langmuir, and D–R isotherms (Figure S4 of the Supporting Information), according with the evidence ratio based on the Akaike criterion.[20] The Freundlich model had no statistical support due to its significantly larger residual sum of squares.

The negative change in free energy ($\Delta G°$) derived from K_L^{-1} in the Langmuir model indicated the spontaneous nature of the adsorption (Table 1).

The Temkin model assumes that the heat of adsorption of all molecules in the layer will decrease linearly rather than logarithmically with coverage due to adsorbate/adsorbate interactions.[26]

$$q_e = \frac{RT}{b_T}\ln(K_T C_e) \quad (1)$$

Table 1. Isotherm Parameters for Cu(II) Adsorption on *Poly*(EGDE-DA). Regression coefficients, values of AICc Criterium and Evidence Ratio for Temkin, Langmuir, Dubinin–Radushkevich (D–R), and Freundlich Models[a]

model	parameters			R^2	AIC_C	evidence ratio
Temkin	K_T: 1.37 ± 0.46 L mg^{-1}	b: 0.1300 ± 0.0069 kJ mol^{-1}		0.9676	61.35	1
Langmuir	q_m: 151.4 ± 3.6 mg g^{-1}	K_L: 41.1 ± 5.5 mg L^{-1}	$\Delta G°$: −17.880 ± 0.058 kJ mol^{-1}	0.9574	62.78	2.03
D–R	q_m: 225 ± 11 mg g^{-1}	B_D: 1.80 × 10^{-3} ± 0.10 × 10^{-3} mol^2 kJ^{-2}	E: 16.67 ± 0.46 kJ mol^{-1}	0.9500	66.96	16.42
Freundlich	K_F: 42.2 ± 5.1	n: 6.05 ± 0.61		0.9175	73.74	489.50

[a] q_e (mg g^{-1}) vs C_e (mg L^{-1}) except for in the D–R model, in which C_e is in g g^{-1}.

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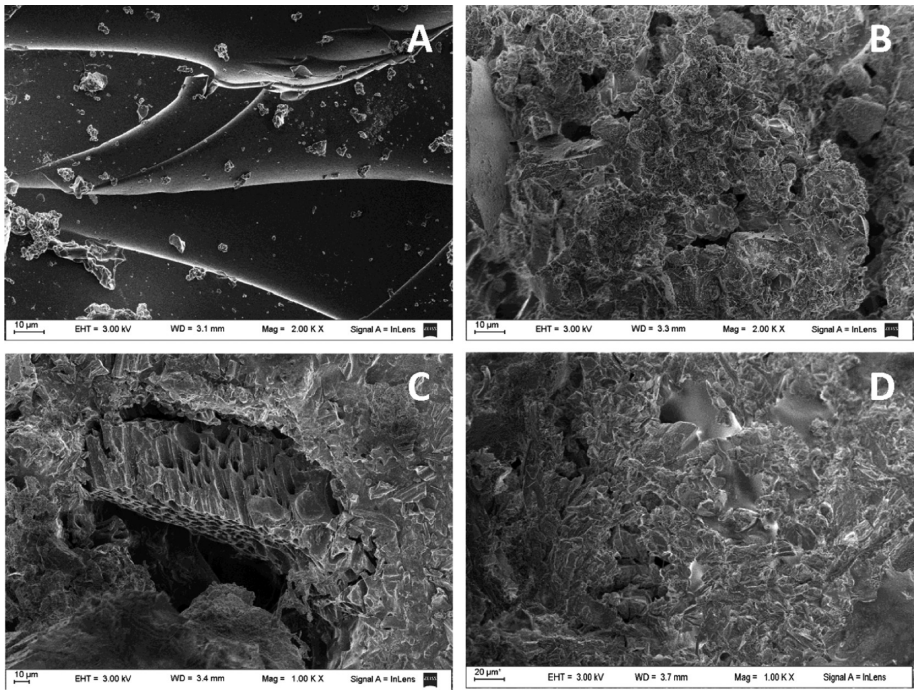

Figure 2. SEM images of (A) *poly*(EGDE-DA), (B and C) Co(II)-*poly*(EGDE-DA), and (D) Cu(II)-*poly*(EGDE-DA).

where q_e is the adsorption capacity in equilibrium with the corresponding C_e, which is the concentration of metal ion.

The D−R isotherm is a semiempirical equation which was originally developed for subcritical vapors in microporous solids, where the adsorption process follows a pore-filling mechanism:

$$q_e = q_m e^{-B_D \varepsilon^2} \quad (2)$$

where q_m is the maximum amount of adsorbate that can be adsorbed in micropores, B_D is a constant related to the energy, and ε is the Polanyi potential.[12,27]

The value estimated for q_m was 225 mg of Cu(II) per gram of polymer (3.54 mmol g^{-1}), significantly higher than that predicted by Langmuir model (151.4 mg g^{-1}) (Table 1).

Equation 2 is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. The approach is usually applied to distinguish the physical and chemical adsorption of metal ions by means of eq 3

$$E = \frac{1}{\sqrt{2B_D}} \quad (3)$$

where E is the mean free energy of sorption,[28] whose magnitude is a way to estimate the type of sorption process.[29] The E value observed was higher than 16 kJ mol^{-1} K^{-1}, suggesting the coordination of Cu(II) with the primary, secondary, and/or tertiary amine-type groups, −OH residues, and/or O atoms of the polymer. The green color of the particles of Cu(II)-*poly*(EGDE-DA) is another evidence of coordination (Figure S5 of the Supporting Information). In addition, the ESR spectra of Cu(II)-*poly*(EGDE-DA) also suggested that different coordination modes could coexist in this material, being the N atoms more significant than O atoms in the uptake of Cu(II) (Figure S6 and Discussion of Figure S6 in the Supporting Information).[9]

The loading capacity for Co(II) was estimated in 15.2 ± 2.9 mg g^{-1} (0.258 ± 0.049 mmol g^{-1}). When the Co(II) uptake equilibrium was studied, the material was saturated in all the range of concentrations tested, giving a brown product (Figure S5 of the Supporting Information).

3.5. Characterization of the Complexes by FT-IR and *ss*-NMR. The resulting Co(II)- and Cu(II)-complexes were spectroscopically characterized through FT-IR and *ss*-NMR experiments (Figure S3 of the Supporting Information and Figure 1, respectively). First, the FT-IR spectra presented a better resolution than with the initial material without metal ions. In particular, the copper complex showed a better spectral resolution, when one considers that this material is more rigid than the original unloaded hydrogel and could be easily milled in small particles, being more appropriate for spectroscopic determinations. In addition, the effects of the cross-linking induced by metal ions was more evident in the case of copper because *poly*(EGDE-DA) presented a higher amount of Cu(II) per gram of polymer than the Co(II) complex, which reinforced the interactions between the polymer chains and the metal ion. For the Cu(II)-complex, a new band was observed at 603 cm^{-1}, associated with the stretching of the S−O bond from SO_4^{2-} arising as a counterion of copper. The wagging of the N−H bond at 880 cm^{-1} and also the stretching band of the N−H bond at 3566−3600 cm^{-1} were well-resolved. In the case of the Co(II) complex, the FT-IR spectrum showed bands similar to those of the Cu(II)-complex, but the signals were vanished because the low amount of cobalt ion uptake was not the optimal to mill in small particles as in the case of copper.

The ^{13}C CP-MAS spectrum for the Cu(II)-complex shows the missing methylene carbons in the *poly*(EGDE-DA) bound to nitrogen as a shoulder of the principal signal at around 50 ppm ($C_{1,2}$, Figure 1), as a consequence of the cross-linking of the system by the copper ions. In general, the signal-to-noise radio was improved. However, even when the copper ion induced the reticulation of the system, the paramagnetic ion

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also enhanced the relaxation behavior on the carbons in the proximity of the metal ion ($-CH_2-NH_2$---Cu). For that reason, the signal of the mentioned methylene at around 50 ppm was not completely resolved. Finally, in the case of the Co(II) complex, the ^{13}C CP-MAS spectrum was similar to that of the unloaded material, without a significant increase in the reticulation degree as in the *poly*(EGDE-DA).

3.6. DSC and TG Analyses. The thermal behavior of the complexes and the hydrogel was studied by DSC and TG analyses. The glass transition temperature (T_g) was determined by DSC curves during the second scan over the temperature range of 20−160 °C (Figure S7 of the Supporting Information). The T_g value obtained for the polyelectrolyte was 120.0 °C, while that for the Cu(II)-complex containing 131 mg of Cu(II) per gram of polymer was 169.5 °C. This shift to higher temperature values was due to the stabilization of the *d*-electron of the copper ion on coordination, as expected,[30−34] and it was also another fact of the cross-link between the polymer chains and the copper ion. For the Co(II) complex, the T_g value was 134.1 °C, and it was lower than in the case of copper, in concordance with the low amount of cobalt ions adsorbed to the polymer material, reducing the cross-linking between the polymer chains and cobalt ions.

In addition, the thermogravimetric analysis (TG-DTG) showed an initial loss of weight due to the evaporation of water in all the cases, coincident with an endothermic peak in the first DSC scan. *Poly*(EGDE-DA) initiated its thermal decomposition at ∼300 °C with a maximal loss of weight at 377 °C. The Cu(II)-complex presented a lower decomposition temperature than the unloaded polymer (∼200 °C). The presence of the paramagnetic Cu(II) ion center caused changes in the electronic density in the proximity of the metal ion which weakened the chemical bonds and decreased the thermal stability of the polymer backbone at high temperatures, regardless of the concentration of Cu^{2+} adsorbed, as it is shown in the TG profile for the Cu(II) complexes containing 50 or 131 mg of the metal ion per gram of material (Figure S8 of the Supporting Information).[30−34] Moreover, the Co(II) complex showed a TG profile similar to that of any of the copper complexes, indicating that the thermal stability of the polymer matrix is highly affected by the presence of a metal ion even at a low concentration. The fact that all the polymers doped with Cu(II) or Co(II) have lower decomposition temperature than the undoped materials indicated that the metal ion acted as a catalyst, accelerating and reducing the thermal degradation of the polymer matrix.

3.7. SEM and EDS Analysis. SEM images were obtained without surface modifications. The complexes with Cu(II) and Co(II) were characterized using SEM to evidence the surface morphological changes when compared with the polyelectrolyte. The SEM image of *poly*(EGDE-DA) depicted in Figure 2 is regular in contrast with the surfaces of the complexes, which exhibit a significant difference in homogeneity degree. On the other hand, the magnification of Co(II)-*poly*(EGDE-DA) shows a regular arrangement of 5 to 10 μm diameter macropores, not evident in the other samples (Figure 2C).

The identities of copper and cobalt were manifested in EDS spectra (Figure S9 of the Supporting Information). In agreement with the FT-IR results, the presence of sulfur in the samples was detected because $CoSO_4$ and $CuSO_4$ were used to obtain the respective complexes. The presence of SO_4^{2-} evidenced the existence of fixed positive charges on the surface of the particles, coming from Co(II), Cu(II), and/or $-R_2NH^+$. This SO_4^{2-} could eventually be exchanged by other anions.

The BET surface area for each material is presented in Table S2 of the Supporting Information.

The specific surface area determined by N_2 adsorption was very low in all the cases due to the hydrophilic nature of the polymer. This accessible area increased with the number of cations adsorbed, probably as a consequence of the network expansion due to electrostatic repulsion. *Poly*(EGDE-DA) can be classified as a mesoporous material, with an adsorption average pore width at the lower limit for this category.[35] The significantly larger mesopores in its complex with Cu(II) would also arise from the expansion of the chains.

3.8. H_2O_2 Activation by the Metal Complexes. We have previously demonstrated that the complexes of EGDE-based polymers with Cu(II) and Co(II) have catalytic activity on H_2O_2 activation.[12,13] In the present study, the Co(II)-*poly*(EGDE-DA) and Cu(II)-*poly*(EGDE-DA) were tested as catalysts for the activation of this peroxide. Both complexes were put in contact with 42 mM H_2O_2, and the concentration of H_2O_2 was monitored as a function of time. In each case, the reaction followed pseudo-first order kinetics (Figure S10 of the Supporting Information).

$$[H_2O_2]_t = [H_2O_2]_{deg} \times e^{-kt} \quad (4)$$

For Co(II)-*poly*(EGDE-DA), the estimated parameters and their standard deviations (S.D.) were 41.86 mM $[H_2O_2]_{deg}$ (S.D.: 0.31) and 3.7×10^{-3} min^{-1} k (S.D.: 0.2×10^{-3}), with R^2 = 0.9735. For Cu(II)-*poly*(EGDE-DA), the estimated parameters were 41.82 mM $[H_2O_2]_{deg}$ (S.D.: 0.19) and 9.0×10^{-4} min^{-1} k (S.D.: 0.6×10^{-4}), with R^2 = 0.9597. The H_2O_2 concentration decay was slow but evident. The evolution of gas bubbles from the surface of the particles of Co(II)-*poly*(EGDE-DA) with the addition of H_2O_2 and only in the presence of immobilized Co(II) was indicative of the formation of O_2, which coincided with the decrease in pH of one unit at 10 min of reaction (Table S3 of the Supporting Information).

The Co(II)-*poly*(EGDE-DA)/H_2O_2 heterogeneous system also produced free radicals that diffused to the solution and were detected by spin trapping experiments with DMPO (Figure 3A).

The simulation and fits of the experimental spectrum allowed establishing the presence of two species: DMPO/OOH and DMPO/OH adducts from anion superoxide ($O_2^{\bullet-}$) and hydroxyl radical ($OH^{\bullet}$), respectively (Figure S11A of the Supporting Information).[36]

The addition of the enzyme superoxide dismutase (SOD) to the medium of reaction gave rise to a spectrum with the characteristic shape of DMPO/OH (Figure S12 of the Supporting Information).

On the basis of this experimental evidence, we propose a reaction of H_2O_2 activation catalyzed by immobilized Co(II), with the production of O_2, $O_2^{\bullet-}$, and H^+:[37]

$$Co^{2+} + 2H_2O_2 \rightleftharpoons Co^{3+} + 2H_2O + O_2^{\bullet-}$$

$$2Co^{3+} + H_2O_2 \rightleftharpoons 2Co^{2+} + O_2 + 2H^+$$

where $OH^{\bullet}$ is an intermediate in $O_2^{\bullet-}$ formation.

The presence of $OH^{\bullet}$ as a minor product of the reaction and as the main product after the addition of SOD, could be explained by splitting the first step as follows:

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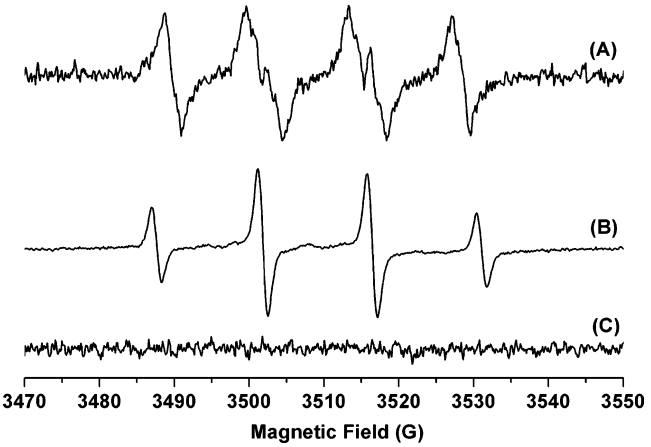

Figure 3. Experimental CW ESR in band X spectra from spin trapping experiments with DMPO 10 min after the addition of H_2O_2. Heterogeneous systems: (A) Co(II)-*poly*(EGDE-DA)/63 mM H_2O_2; (B) Heterogeneous system: Cu(II)-*poly*(EGDE-DA)/63 mM H_2O_2. The ESR spectrum of DMPO is depicted as C.

$$Co^{2+} + H_2O_2 \rightleftharpoons Co^{3+} + OH^- + OH^\bullet$$

$$OH^\bullet + H_2O_2 \rightleftharpoons HO_2^\bullet + H_2O$$

$$HO_2^\bullet \rightleftharpoons O_2^{\bullet -} + H^+$$

$$H^+ + OH^- \rightleftharpoons H_2O$$

The stage of $OH^\bullet$ degradation must be the slowest in the presence of SOD, which would explain the observation of the DMPO/OH signal.

When Co(II)-based homogeneous catalysts are oxidized by H_2O_2, they can eventually form cobalt intermediate species ([(HOO)L-Co(III)]) with catalytic activity. There are several reports with spectroscopic evidence about intermediate formation.[38,39] In our heterogeneous system, both the [(HOO)L-Co(III)] intermediate and the radicals could eventually react with organic substrates.

In the same way, the Cu(II)-*poly*(EGDE-DA)/H_2O_2 heterogeneous system produced gas bubbles and free radicals detected by spin trapping experiments with DMPO (Figure 3B). The pH did not vary significantly at the time that the partial pressure of O_2 increased together with the concentration of free radicals (Table S3 of the Supporting Information). The simulation and fits of the experimental spectrum allowed for the establishment of the presence of the DMPO/OH adduct from $OH^\bullet$ (Figure S11B of the Supporting Information).[36]

On the basis of previous studies on H_2O_2 activation catalyzed by copper complexes of EGDE-derived polymers,[13,40,41] a possible reaction could be

$$3H_2O_2 \rightleftharpoons O_2 + 2OH^\bullet + 2H_2O$$

where the steps should be:

$$Cu^+ + H_2O_2 \rightleftharpoons Cu^{2+} + OH^- + OH^\bullet$$

$$Cu^{2+} + H_2O_2 \rightleftharpoons Cu^{+\bullet}O_2H + H^+$$

$$Cu^{+\bullet}O_2H + H_2O_2 \rightleftharpoons Cu^+ + O_2 + OH^\bullet + H_2O$$

$$H^+ + OH^- \rightleftharpoons H_2O$$

The Cu(I)-superoxide complex ($Cu^{+\bullet}O_2H$) should be in equilibrium with the $Cu^{2+}(O_2H)^-$ complex by the reversible exchange of an electron. The occurrence of such transient complexes has been proposed and discussed before.[41,42] Masarwa et al. determined that, in the mechanism of "Fenton-like" reactions, the cation forms a transient complex with H_2O_2 of the type $(H_2O)_{m-1}Cu^{+\bullet}O_2H^-$, which can be decomposed into $Cu(H_2O)_m^{2+} + OH^\bullet$ or can react with an organic substrate such as alcohol (ethanol, 2-propanol, or 2-butanol).

3.9. Decolorization of Methyl Orange (MO). H_2O_2 activation by the *poly*(EGDE-DA) complexes with Co(II) and Cu(II) was applied on the decolorization of MO solutions (Scheme S1 of the Supporting Information).[13]

Without the nonsoluble polymer acting as a ligand, the Co(II)/H_2O_2 and the Cu(II)/H_2O_2 systems only oxidized less than 10% of the dye in 1 h.[12,13]

In the presence of Co(II)-*poly*(EGDE-DA) or Cu(II)-*poly*(EGDE-DA) and H_2O_2, the dye removal from the solution was a consequence of two parallel processes: surface adsorption on the catalyst and oxidative degradation, both of them following pseudo-first-order kinetics.[12,13] MO degradation is expected to be slower than the adsorption process which only involves mass transport and noncovalent bond formation.[12] In agreement with this, we propose an empirical model where each process is described by a pseudo-first order kinetic term, assigning the term with the highest kinetic constant (k) to the adsorption (Table 2):

$$[MO]_t = [MO]_{ads} \times e^{-k_{ads}t} + [MO]_{deg} \times e^{-k_{deg}t} + [MO]_\infty \quad (5)$$

where $[MO]_\infty$ represents the permanent free MO, $[MO]_{ads}$ is the total amount of MO per liter of solution that would be removed by adsorption, and $[MO]_{deg}$ is the total amount of MO per liter of solution that would be removed by degradation.

Table 2. Estimated Parameters and Standard Deviation of the Pseudo-First Order Kinetic Model for the Decolorization of MO Solutions by Activation of H_2O_2 with Co(II)-*poly*(EGDE-DA) or Cu(II)-*poly*(EGDE-DA)[a]

parameters	first catalytic cycle of Co(II)-*poly*(EGDE-DA) $[H_2O_2]_0$: 63 mM	adsorption on Co(II)-*poly*(EGDE-DA) in absence of H_2O_2	first catalytic cycle of Cu(II)-*poly*(EGDE-DA) $[H_2O_2]_0$: 63 mM	adsorption on Cu(II)-*poly*(EGDE-DA) in absence of H_2O_2
$[MO]_{ads}$ (μM)	23.87 ± 0.30	28.23 ± 0.60	12.3 ± 1.4	19.46 ± 0.71
k_{ads} (min^{-1})	0.2867 ± 0.0077	0.234 ± 0.012	2.9 ± 1.4	0.81 ± 0.06
$[MO]_{deg}$ (μM)	15.58 ± 0.25		29.7 ± 1.3	
k_{deg} (min^{-1})	0.0102 ± 0.0006		0.175 ± 0.011	
$[MO]_\infty$ (μM)		15.50 ± 0.44		21.37 ± 0.18
R^2	0.9972	0.9893	0.9957	0.9706

[a]Initial MO concentration: 42 μM.

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When Cu(II)-*poly*(EGDE-DA) was used, $[MO]_\infty$ represented the free MO that was decomposed with a very low kinetic constant since complete removal was observed after 24 h of reaction.

The first studies of interaction were performed in the absence of H_2O_2, for a mass of complex (g) to volume of solution (L) ratio equal to 1.0 and an initial MO concentration of 42 μM. About 64.6% of the dye adsorbed on Co(II)-*poly*(EGDE-DA) and 47.7% on Cu(II)-*poly*(EGDE-DA) (Table 2).

The most probable binding sites of these negatively charged dye molecules are the $-R_2NH^+$ residues from DA and the adsorbed cations.

In the presence of 63 mM H_2O_2, the amount of MO adsorbed was lower in both systems. The fraction of degraded MO by activated H_2O_2 was 40% with Co(II)-*poly*(EGDE-DA) and 71% with Cu(II)-*poly*(EGDE-DA). The parameter k_{deg} related to MO oxidation was 17.2 times higher for Cu(II)-*poly*(EGDE-DA) than for Co(II)-*poly*(EGDE-DA). Figure 4 shows that 87% of MO was removed in 10 min with Cu(II)-*poly*(EGDE-DA); instead, it would take 110 min with Co(II)-*poly*(EGDE-DA).

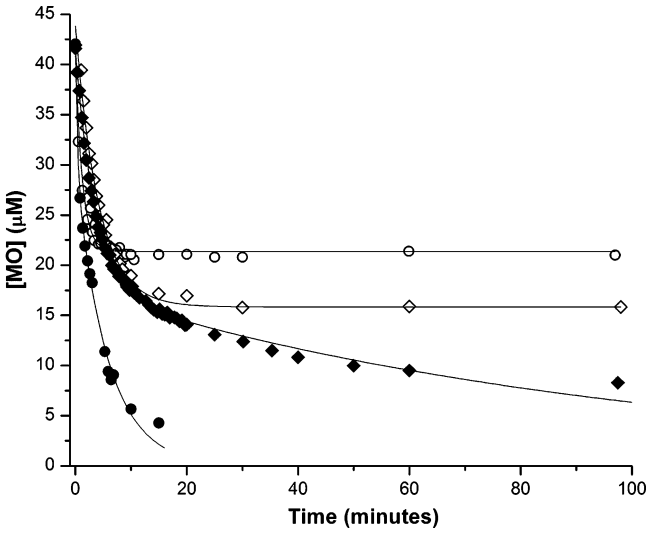

Figure 4. MO concentration profile in the heterogeneous system, which consisted of 100 mL of 42 μM MO solution in contact with 0.1000 g of the Co(II)-*poly*(EGDE-DA) and 63 mM H_2O_2 (♦), 0.1000 g of the Co(II)-*poly*(EGDE-DA) (◊), 0.1000 g of the Cu(II)-*poly*(EGDE-DA) and 63 mM H_2O_2 (●), and 0.1000 g of the Cu(II)-*poly*(EGDE-DA) (○).

When the catalysts were recycled, the adsorption sites for MO remained occupied by the molecules bound on the first stage, at the time that $[MO]_\infty$ increased on the two successive cycles.

The UV−visible spectra of the MO solutions are presented in Figure S13 and Discussion of Figure S13 in the Supporting Information.

MO concentration was also monitored in the presence of *poly*(EGDE-DA) (Figure S14 of the Supporting Information). The amount of MO removed by adsorption on the positive surface of the polyelectrolyte was significantly higher than that adsorbed on the particles of the complexes. The addition of H_2O_2 produced the release of O_2 (Table S3 of the Supporting Information) and the decolorization of the solution by adsorption (mostly), together with an alternative reaction which would involve the functional groups of the polyelectrolyte (−OH, $-R_2N$, and −O−), and contributed only with 8.41% of MO removal.

The normalized efficiency of Co(II)-*poly*(EGDE-DA) and Cu(II)-*poly*(EGDE-DA) was also compared. When we used equimolar amounts of catalytic sites in the medium of the reaction (0.644 mmol of sites per liter of MO solution), 40.9% of initial MO was decolorized by action of H_2O_2 with Co(II)-*poly*(EGDE-DA) against 77.9% with Cu(II)-*poly*(EGDE-DA), and the k_{deg} was 1.66 times higher with the latter catalyst (Figure S15 of the Supporting Information). The control experiment in the absence of H_2O_2 showed 67.3% of MO adsorption on Co(II)-*poly*(EGDE-DA) against 39.5% on Cu(II)-*poly*(EGDE-DA), consistent with the larger mass of complex with Co(II) and the lower mass of complex with Cu(II) needed to obtain equimolar number of sites per volume of solution (Figure S15 of the Supporting Information).

At the light of these results, the catalyst with Cu(II) was clearly more efficient in terms of kinetics, and its lower ability to bind MO helped to minimize passivation of the active surface.

To improve the performance of Co(II)-*poly*(EGDE-DA) and evaluate the influence of additional solutes, the decolorization of MO was tested in two different reaction media: distilled water and 0.1 M Na_2SO_4. The amount of decolorized MO by degradation increased 50% in the presence of inorganic salts, but k_{deg} was 3.39 times higher in distilled water. Even if the inorganic ions contributed to minimizing the adsorption, they exhibited some inhibitory effect on the chemical oxidation. Moreover, the chemical stability of Co(II)-*poly*(EGDE-DA) was affected in the presence of Na^+ and SO_4^{2-}, since a partial loss of complex was observed after the catalytic cycle.

The next experiments were conducted to evidence the mechanisms of MO degradation, the role of the solid matrix, and the potential participation of cobalt or copper intermediate species in the MO oxidative reaction (a possible metal-peroxo center).

We started with Co(II)-*poly*(EGDE-DA). First, the dye concentration in the H_2O_2-activated supernatant was monitored as a function of time, exhibiting a pseudo-first-order exponential decay with k_{deg} equal to $(3.50 \pm 0.04) \times 10^{-3}$ min^{-1} (Figure S16 of the Supporting Information). This parameter was significantly lower (34.4%) than the kinetic constant estimated for the degradation process (0.0102 ± 0.0006 min^{-1}) when the whole Co(II)-*poly*(EGDE-DA)/63 mM H_2O_2 heterogeneous system was used (Table 2).

The behavior of Co(II)-*poly*(EGDE-DA) as catalyst differed from that of Co(II)-*poly*(EGDE-MAA-2MI), the complex between Co(II) and the nonsoluble polyampholyte mentioned in Introduction.[12] In a previous work, we demonstrated that the free radicals from the H_2O_2 supernatant activated by Co(II)-*poly*(EGDE-MAA-2MI) were able to degrade MO with the same efficiency as the whole Co(II)-*poly*(EGDE-MAA-2MI)/63 mM H_2O_2 heterogeneous system.[12]

Here, the chemical oxidation of MO in solution by the activated supernatant with one single catalytic cycle did not represent the whole process of dye degradation. It is possible that more catalytic cycles are needed to reach the efficiency of the Co(II)-*poly*(EGDE-DA)/63 mM H_2O_2 system.

The difference observed in the behavior of the catalysts is probably based on the nature of the ligand: *poly*(EGDE-MAA-2MI) is a polyampholyte combining positive and negative

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charges on the same network, whereas *poly*(EGDE-DA) is a positive polyelectrolyte that exchanged H^+ for Co(II) on the complex formation. So, species such as $O_2^{\bullet-}$ could be repelled out to the solution by the former and attracted by the latter on H_2O_2 activation.

Then, we looked for some evidence of Co(II) intermediate species formed on the catalyst surface by action of H_2O_2, acting as catalytic sites. The activated Co(II)-*poly*(EGDE-DA) particles were put in contact with the MO solution, which exhibited a decrease in MO concentration following an exponential decay. In this experiment, the kinetics of the decolorization was mostly ruled by MO adsorption (Figure S16 of the Supporting Information), giving no evidence of activity on the hypothetical first catalytic cycle.

Next, we explored the action of Cu(II)-*poly*(EGDE-DA). The dye concentration in the activated H_2O_2 supernatant exhibited a pseudo-first order exponential decay with k_{deg} equal to 0.0415 ± 0.0012 min^{-1} (Figure S17 of the Supporting Information), 23.7% of the kinetic constant estimated for the degradation process (0.175 ± 0.011 min^{-1}) with the heterogeneous Cu(II)-*poly*(EGDE-DA)/63 mM H_2O_2 system (Table 2).

On the other hand, the search for evidence of Cu(II) intermediate species on the surface of the particles led to a peculiar result: the amount of MO removed from the solution by the activated solid (37.1%) was lower than that removed by adsorption on the nonactivated catalyst (47.7%) (Figure S17 of the Supporting Information). This could be attributed to a decrease in the number of positive adsorption sites for the negatively charged MO as a result of the activation. Besides, this hypothetical Cu(II) intermediate seems to be inactive in contact with MO.

In the same way, the sum of the effects of the activated supernatant and the activated solid on MO concentration (corresponding to a first catalytic cycle) did not explain the whole process of MO decolorization using Cu(II)-*poly*(EGDE-DA).

3.10. Epinephrine Oxidation to Adrenochrome Using Co(II)-*Poly*(EGDE-DA)/H_2O_2.

Epinephrine is a catecholamine, susceptible to peroxide attack. It can be partially oxidized by superoxide to the industrial pink product adrenochrome (catecholamine *o*-quinone; Scheme S1 in the Supporting Information), a precursor of hemostatic drugs such as carbazochrome.[43]

Figure 5 presents the results of the epinephrine conversion in the presence of H_2O_2 and Co(II)-*poly*(EGDE-DA). About 77% of conversion was reached in 30 min, with a pseudo-first-order kinetic constant of 0.145 ± 0.019 min^{-1}.

In the absence of a catalyst, the oxidation of epinephrine by H_2O_2 was practically negligible.

A control experiment with epinephrine, H_2O_2, and Co(II)-*poly*(EGDE-DA), was made with previous bubbling of argon in the suspension of the complex to displace the dissolved O_2 and to saturate the atmosphere with the inert gas. Epinephrine conversion was found to be 11% lower than in the original reaction, meaning that H_2O_2 prevailed as oxidant and that the contribution of dissolved O_2 in epinephrine conversion was poor but evident.

Another control experiment performed with epinephrine and Co(II)-*poly*(EGDE-DA) in the absence of H_2O_2 exhibited some extent of catecholamine oxidation, being less efficient than the oxidation by H_2O_2. Then, the control experiment was repeated, this time with previous and continuous bubbling of argon. Here, the amount of adrenochrome released was negligible, confirming that the oxidation of epinephrine could also be achieved with atmospheric O_2 when it was activated in some way by Co(II)-*poly*(EGDE-DA).

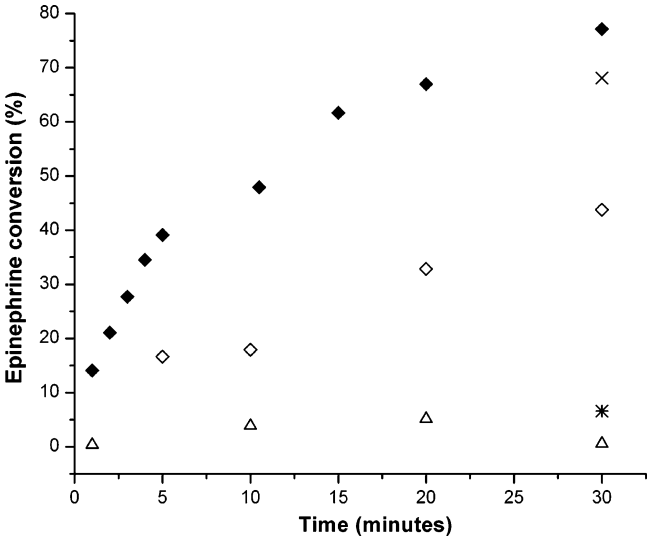

Figure 5. Epinephrine conversion: in the presence of Co(II)-*poly*(EGDE-DA) (◊), in the presence of Co(II)-*poly*(EGDE-DA) with argon bubbling (*), in the presence of Co(II)-*poly*(EGDE-DA) and 46 mM H_2O_2 (♦), in the presence of Co(II)-*poly*(EGDE-DA), and 46 mM H_2O_2 with argon bubbling (x), and in the presence of 46 mM H_2O_2 (Δ).

4. CONCLUSIONS

The novel hydrogel *poly*(EGDE-DA) was synthesized in a one-step batch synthetic strategy using a diepoxy monomer (EGDE) and a bifunctional primary amine (DA). The material swelled in a wide range of pH below 10.5. Around 27% of the N atoms were tritrable basic sites, which acted as ligands together with the hydroxyl groups on Co(II) and Cu(II) coordination. The uptake capacity for Cu(II) was 13.7 times higher than that for Co(II), giving a more rigid material with better spectral resolution in FT-IR and *ss*-NMR analysis.

The catalytic activity of these coordination compounds on H_2O_2 activation was deeply studied by ESR. We propose a mechanism of reaction for each complex, which involves the simultaneous production of free radicals and O_2.

The heterogeneous systems for H_2O_2 activation were tested on the oxidative degradation of the azo-dye MO. The complex with Cu(II) was more efficient on dye decolorization.

The experiments conducted to evidence the activation of the solid matrix by H_2O_2 and the role of the free radicals in MO oxidative reaction showed that one single reaction cycle did not represent the whole process of dye degradation, being a key indicator of the catalytic activity of these nonsoluble organo-metallic compounds.

The utility of $O_2^{\bullet-}$ on partial oxidation reactions was demonstrated when the Co(II)-*poly*(EGDE-DA)/H_2O_2 heterogeneous system was tested on the conversion of epinephrine to adrenochrome. In this case, we found that O_2 could also be activated by the complex.

Although the aim of this work was to prepare Co(II) and Cu(II) complexes of *poly*(EGDE-DA) that might be of interest in oxidation processes, there are many other possible uses of

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this polyelectrolyte in recovery processes of low environmental impact.

■ ASSOCIATED CONTENT

Supporting Information

Titration curve; Cu(II) adsorption isotherm; TG-DTG/DSC curves; FT-IR, EDS, and CW ESR spectra; H_2O_2 concentration profile; MO concentration profiles and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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