

Research Article

EPR Spectroscopy Investigation of Cu^{2+} Ions Adsorbed in Tannin-Formaldehyde Resins of Mimosa (*Acacia mearnsii*) Bark Extracts

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The chemical environment of Cu^{2+} ions adsorbed in tannin-formaldehyde resins of *Acacia mearnsii* bark extracts, prepared from polybutene, is investigated by EPR spectroscopy at 300 K. The spectrum is simulated considering two isolated axial Cu(II) species (Species 1: $A_{\parallel} = 16.50(5)$ mT, $A_{\perp} = 1.20(10)$ mT, $g_{\parallel} = 2.28(1)$, and $g_{\perp} = 2.08(1)$; Species 2: $A_{\parallel} = 15.00(5)$ mT, $A_{\perp} = 1.50(10)$ mT, $g_{\parallel} = 2.32(1)$, and $g_{\perp} = 2.05(2)$), superposed to a broad line ($g_{\text{iso}} = 2.14(1)$; linewidth = 30.0(5) mT) assigned to Cu(II) aggregates. Measurements at 77 K did not improve spectral resolution. Heating at 413 K changes the hyperfine parameters of Species 2 ($A_{\parallel} = 14.20(5)$ mT, $A_{\perp} = 1.20(10)$ mT, $g_{\parallel} = 2.33(1)$, and $g_{\perp} = 2.07(2)$) and slightly modifies the parameters of the broad line ($g_{\text{iso}} = 2.11(2)$; linewidth = 40.00(50) mT) but does not change Species 1, assigned to Cu(II) species immobilized into resin pores in catecholate-type coordination sites. Species 2 is assigned to Cu(II) species immobilized at the outer resin surface. Upon extended heating, a reversible formation of semiquinone-type paramagnetic radicals ($g_{\text{iso}} = 2.0037(1)$) is observed, assigned to the partial collapse of the resin polymeric network.

1. Introduction

Tannin substances are potential ion-adsorbers due to the high number of hydroxyl groups present in their structures. As a drawback they are highly water soluble, precluding their practical utilisation *in natura* [1]. Nevertheless, some efforts have been made in order to modify tanning substances aiming at the synthesis of insoluble materials that might be used as ion-adsorbers. As an example, resins can be prepared by condensation of tannin with formaldehyde, taking into account that tannins are good natural resources for replacing petroleum-derived phenolic compounds [2].

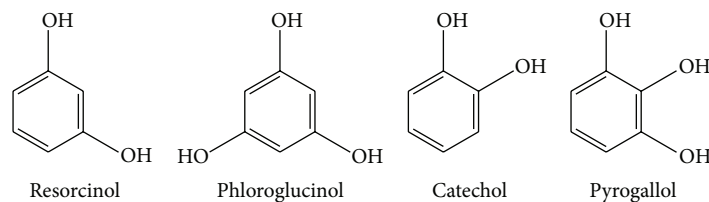
The properties and technological uses of tannin-formaldehyde resins have been reviewed by Raquez et al. [3]. According to them, tannin compounds extracted from wood, bark, leaves, and galls of plants are now considered as raw renewable materials in the design of phenolic resins.

Formaldehyde reacts with tanning substances inducing polymerisation through methylenic bridging, which after drying or curing processes gives a three-dimensional insoluble network.

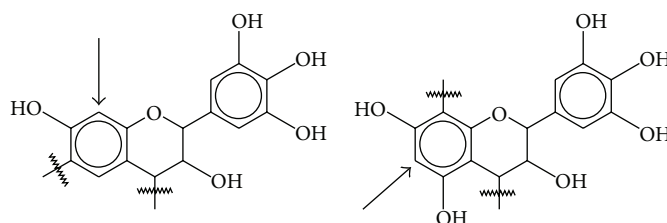
Also, in order to further enhance the mechanical properties of these resins making them suitable for utilisation in columns, it is usual to add a synthetic polymer to the reactive mixture [4].

Tanning substances present in *Acacia mearnsii* bark extracts include the four possible combinations of resorcinol and phloroglucinol with catechol and pyrogallol, shown in Scheme 1.

In tannin extracts from *Acacia mearnsii* bark the mono-flavonoid units flavan-3-ol are repeated and linked mainly in the 4 and 6 ring positions, as shown in Scheme 2 [5]. When these monoflavonoid units react with formaldehyde



SCHEME 1: Combinations of resorcinol and phloroglucinol with catechol and pyrogallol afford the tanning substances present in *Acacia mearnsii* bark extracts.



SCHEME 2: Monoflavonoid units flavan-3-ol react with formaldehyde to polymerise through methylenic bridges in the reactive ring positions indicated by arrows.

they polymerise through methylenic bridges in the reactive ring positions indicated by arrows in Scheme 2.

These polymeric units arrange themselves into a disordered network, forming a porous material suitable to ion adsorption. Removal of heavy metal ions from water and effluent water by renewable biomaterials usually proceeds by sorption processes involving functional groups associated with proteins, polysaccharides, lignin, and other cell-containing biopolymers [1, 2, 6]. For example, Huang et al. have reported the sorption of Hg(II) ions by bayberry tannin-immobilized collagen fiber [7], Erdem et al. have investigated the sorption of boron by tannic acid resin [8], Zhanhua et al. studied the adsorption of Cr(VI) by larch tannin resin [9], and Gurung et al. reported the recovery of Au(III) by low cost adsorbent prepared from persimmon tannin extract [10].

The basic precipitation of Cu^{2+} ions from effluent water is an industrial process carried out to reduce the ion concentration. Although ion exchange is an efficient process in the removal of copper ions from effluents, synthetic ion-exchange resins are rather expensive when compared to the abundant and less costly biopolymers. Moreover, it is desirable to achieve an understanding at the molecular level of the changes that occur in the ion-absorber resins upon ion sorption. In connection with structural studies concerning the changes in the resins themselves, it is also interesting to study the environment of the sorbed ion.

Electron paramagnetic resonance (EPR) spectroscopy is a powerful tool for investigating the immediate environment of a paramagnetic ion. For the Cu(II), the EPR spectral parameters are sensitive to changes in the symmetry of that environment and usually allow the study of the ion state in a resin or matrix as a function of the degree of hydration, temperature of the resin, and structural arrangement of a functional group. However, to our knowledge, the existing EPR studies are concentrated on different kinds of synthetic ion-exchange resins [11, 12] and modified polymers [13–15]; there

is a lack of similar studies concerning tanning-formaldehyde resins obtained from vegetable resources, although we have used EPR to characterize the Cu(II) biosorption by *Sargassum filipendula* algae [16].

In this work we present and discuss the results of the EPR investigation of Cu^{2+} ions adsorbed tannin-formaldehyde resins prepared from polybutene.

2. Materials and Methods

The tannin-formaldehyde resins were prepared from polybutene following the experimental procedure described by Yamaguchi et al. [4]. Briefly, in a typical batch, to an aqueous solution of tannin extract (TANAC S/A, Brazil) from *Acacia mearnsii* bark at 50% a solution of formaldehyde at 37% (Merck, grade reagent) was added in 1:1 molar ratio. The mixture was added to 200 mL of polybutene (Polibutenos S/A, Brazil, M.W. ~ 400 g/mol) heated at 353 K and stirred for 30 minutes. After that, the resin was washed with toluene and methanol (grade reagent, 5 times each), filtered under reduced pressure, and dried at room temperature. For the adsorption tests 0.6 g of the resin was stirred with 200 mL of a solution of 50 mg/L of Cu^{2+} for 60 minutes at constant pH = 5. The EPR measurements were performed in a Bruker ESP 380E spectrometer operating in X-band equipped with a rectangular dielectric cavity with 100 kHz field modulation, 0.5 mT modulation amplitude, 10 dB attenuation, and 2×10^4 gain. Spectra of the as-prepared and postheating resin were measured at room temperature and at 77 K, using a nitrogen finger. The heating treatment consisted in heating the resin at 413 K for 1 hour in a home-made electric circular furnace, outside of the resonator, either in an open tube or under vacuum. Cooling down the resins did not improve spectral resolution, so only the room temperature spectra were simulated, using the Bruker SimFonia shareware program. The simulations were done by considering the two

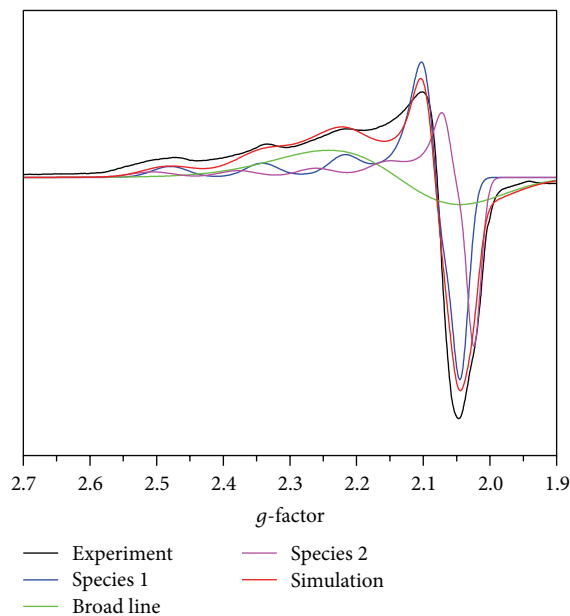


FIGURE 1: Room temperature EPR spectra of the as-prepared tannin-formaldehyde resins loaded with copper and computational simulations.

copper isotopes (^{63}Cu and ^{65}Cu), but the results indicated that the contribution of the ^{65}Cu isotope to the spectra is marginal, so the values listed in Table 1 are for the ^{63}Cu isotope only.

3. Results and Discussion

Figure 1 shows the room temperature EPR spectrum of as-prepared resins loaded with copper. This spectrum reveals the anisotropic shape characteristic of Cu^{2+} ions in axial symmetry, such as tetragonal distorted coordination, indicating that copper ions are immobilised by resin functional groups. The spectrum was simulated by considering two isolated $\text{Cu}(\text{II})$ species (Table 1). A broad isotropic line was also used, accounting for $\text{Cu}(\text{II})$ aggregates.

Heating the copper-loaded resin at 413 K for 1 hour into an open tube or under vacuum leads to broadening of the EPR spectra, indicating that the immediate environment of copper ions is modified by the heat treatment. In order to grasp on the structural changes of the $\text{Cu}(\text{II})$ coordination upon heating the EPR spectra taken after the heating process were also simulated (Figure 2). The simulated EPR parameters are listed in Table 1.

Table 1 lists the spectral parameters obtained by simulation of the room temperature EPR spectra of the as-prepared (Cu-RTF), heated (Cu-RTF-A), and heated under vacuum (Cu-RTF-AV) resins.

The relative changes in the hyperfine parameters showed in Table 1 are indications of different $\text{Cu}(\text{II})$ coordination that results from resin structural changes. In fact, after heating the resin, Species 2 presents hyperfine parameters consistent with a harder chemical environment in comparison to the as-prepared resin.

TABLE 1: Spectral parameters obtained by simulation of the room temperature EPR spectra of the resins.

Sample		A_{\parallel} [mT]	g_{\parallel}	A_{\perp} [mT]	g_{\perp}
Cu-RTF	S1	16.50(5)	2.28(1)	1.20(10)	2.08(1)
	S2	15.00(2)	2.32(1)	1.50(10)	2.05(2)
Cu-RTF-A	S1	16.50(5)	2.28(1)	1.30(10)	2.07(1)
Cu-RTF-AV	S2	14.20(2)	2.33(1)	1.20(10)	2.07(1)
$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ^(a)		12.78(5)	2.40(1)	1.26(10)	2.09(2)

Cu-RTF: as-prepared copper-loaded resin; Cu-RTF-A: heated resin and Cu-RTF-AV: heated under vacuum resin. Uncertainties are in parenthesis. S1 and S2 refer to Species 1 and Species 2, respectively. Values are for the ^{63}Cu isotope. The linewidths used in the simulations were 7.0(10) mT for the parallel lines and 3.0(5) mT for the perpendicular lines. ^(a)Taken from [17].

The EPR technique has been used to get a deeper insight into the microscopic environment of transition metal ions adsorbed in various polymeric materials, both natural and synthetic. The most accurate parameters of an axial divalent copper EPR spectrum are usually those measured in the parallel region, where the hyperfine splitting is usually better resolved. The magnitudes of A_{\parallel} and g_{\parallel} are correlated to the nature of the ligands, that is, to the degree of covalence in the complex. In this way, these values can be used to assign structure [18].

According to the tendency observed in the EPR parameters the immediate environment of copper ions in the resins is assigned as follows: in the as-prepared sample, the isolated copper ions assigned to Species 1 are surrounded by oxygen atoms in a square planar/tetragonal distorted octahedral environment, in catecholate-type coordination of $\text{Cu}(\text{II})$ complexes. These complexes may correspond to partially hydrated copper complexes interacting with oxygen atoms in adjacent deprotonated hydroxyl positions of the flavonoid unit and/or can be assigned to a similar environment with only one deprotonated resin hydroxyl. Considering the porous structure of the resin, Species 1 should be assigned to isolated $\text{Cu}(\text{II})$ species inside the resin pores. On the other hand, Species 2 is assigned to partially dehydrated $\text{Cu}(\text{II})$ species outside the resin pores. Other possibilities of coordination for the copper ions, mainly using hydroxyl groups of different flavonoid units, immobilised near each other in the resin matrix, cannot be discarded as the simulations required a broad line, indicating $\text{Cu}(\text{II})$ aggregates. However, the simple adsorption of hexaaquacopper(II) complex in the resin should be discarded, since the EPR parameters obtained by simulation are rather different for that complex and for Cu-RTF (see Table 1).

Analysis of simulated EPR data also indicates that in the heated resin there are two predominant environments for the copper ions. Species 1 should be considered the same observed in the as-prepared resin, but for Species 2 the value of A_{\parallel} is lower (14.20(5) mT) in comparison to the as-prepared resin (15.00(20) mT), indicating that in the heated resins Species 2 is surrounded by harder ligands, for example, water molecules [19]. Thus, the EPR results indicate that when the copper-loaded tanning-formaldehyde resin is heated at 413 K, there occurs a process in which copper(II) located outside

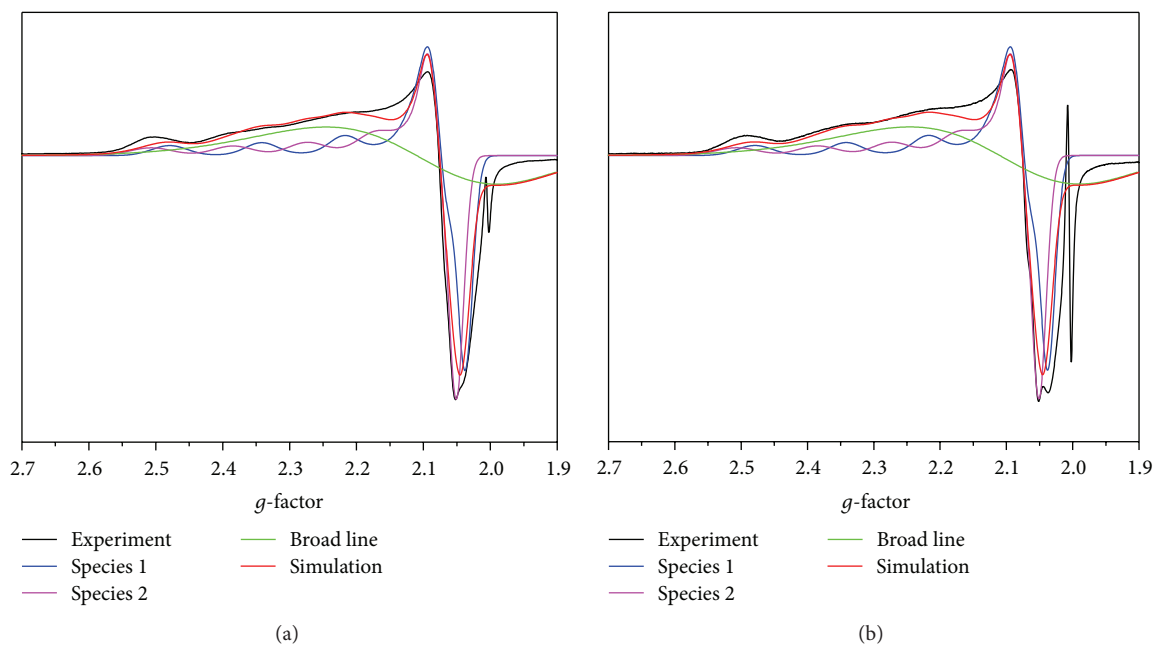


FIGURE 2: Room temperature EPR spectra of the heated tannin-formaldehyde resins loaded with copper in an open tube (a) and under vacuum (b).

the resin pores complexes with more water molecules and remained bonded to the resin surface. At the level of analysis of this work it was not possible to quantify either the isolated Cu(II) species or the Cu(II) aggregates.

Structural modifications leading to heterogeneous structure of the polymeric matrix, due to a nonuniform distribution of pore sizes and regions with distinct immobilised ion concentrations, are observed in other polymeric systems, for example, polyvinyl alcohol [20]. Indeed, after heating the formation of paramagnetic radicals ($g_{\text{iso}} = 2.0037(1)$) is observed. The intensity of the radical signal is higher when the resin is heated under vacuum, and one could speculate on the participation of water in the mechanism. These radicals are assigned to oxygen-centred species, created by the partial breakdown of polymeric bonding among monoflavonoid units, following the work of Hoffmann et al. that used continuous wave and pulsed-EPR to reveal the formation of radicals in phenol-formaldehyde resins in various stages of curing [21]. Hoffmann et al. assign the observed EPR signal to semiquinone-type radicals having the unpaired electron mainly localised on the oxygen atoms, in a rather anisotropic environment, due to the rigidity of the resins they studied. In the system under study in this work, however, the line assigned to the paramagnetic radical is isotropic, suggesting a less rigid environment for the paramagnetic radical. Furthermore, the intensity of this line spontaneously decreases, vanishing after some days. We assign this line to radicals associated with the reversible depolymerisation by breaking the methylene bridges, following the heating treatment.

Concerning the adsorption of Cu^{2+} , Yamaguchi et al. [22] reported a very low (*ca.* 3.8×10^{-4} J/mol) heat of adsorption

of Cu^{2+} in tannin-formaldehyde resins, suggesting that the Cu^{2+} ions are physisorbed and that the rate-determining step of the adsorption is the diffusion of Cu^{2+} ions into the porous resin. The EPR measurements reported in this work reflect the first stages of sorption of Cu^{2+} ions in the tannin-formaldehyde resins. The data obtained from the heated resins support this proposal. Furthermore, the large EPR linewidths of the experimental spectra suggest a distribution of the spin Hamiltonian parameters, in the so-called g - and A -strain processes [18].

4. Conclusion

Tannin-formaldehyde resins of *Acacia mearnsii* bark extracts were prepared from polybutene and loaded with Cu^{2+} ions. The chemical environment of copper ions in the as-prepared resin was investigated by electron paramagnetic resonance at room temperature. Cooling down to 77 K did not improve the quality of the spectra. This procedure allowed the assignment of the molecular symmetry of the copper ions in the initial stages of sorption process. It was observed that in the as-prepared resin the copper ions are immobilised, as evidenced by the anisotropic EPR spectrum measured at room temperature. Simulation of the room temperature spectrum indicates two predominant isolated copper species and also copper aggregates. This result agrees with the low heat of adsorption previously reported in the literature and with the rate of adsorption being diffusion-limited.

Heating the resins at 413 K for one hour promotes modification of the copper ions environment, leading to further broadening of the EPR spectrum. The EPR parameters point to two Cu(II) species, one of them surrounded by

harder ligands after heating. Extended heating leads to the formation of semiquinone-type paramagnetic radicals ($g_{\text{iso}} = 2.0037(1)$), whose EPR signal intensity diminishes spontaneously after few days, suggesting that the collapse of the polymeric network is reversible.

Conflict of Interests

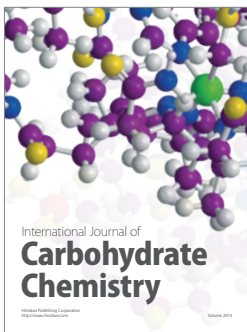
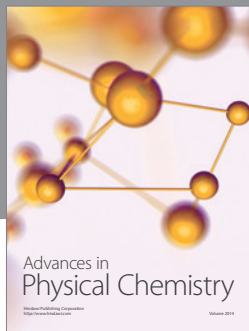
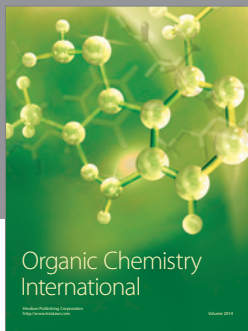
The authors declare that there is no conflict of interests regarding the publication of this paper.

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