

Crude and Modified Corncobs as Complexing Agents for Water Decontamination

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Received 15 May 2002; accepted 15 June 2003

ABSTRACT: The ability of corncobs to retain copper ions was studied with respect to the origin of the materials (inner or outer parts of the cobs), the granulometry, the pH, and chemical modifications with maleic anhydride (MA) and succinic anhydride (SA). Esterification, characterized by Fourier transform infrared and X-ray photoelectron spectroscopy, led to a large increase in copper retention in comparison with unmodified corncobs. The retention capacity was improved up to 6 times with SA-modified corncobs at

pH 5. The adsorption behavior of MA- and SA-grafted samples, with respect to copper, appeared to be different at pH 4 and pH 5, and this was attributed to a difference in the pK_a values of the grafted carboxylic functions. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 820–826, 2004

Key words: biomaterials; corncobs; modification; complexation; decontamination

INTRODUCTION

Modern society is increasingly concerned by environmental issues related to industrial activity, and polluting industries need to conform to more and more rigid environmental regulations. In particular, heavy metals in wastewater need to be recovered^{1,2} with conventional methods based on precipitation, electrochemistry, ion-exchange resins, and solvent extraction. These methods are generally expensive and often fail to attain the residual concentrations imposed by new regulations. Therefore, efficient and cost-effective alternatives have to be developed.

Some current synthetic materials, such as poly(sodium acrylate), which are extensively used as hygienic products and are, consequently, low-cost, have been employed with success to retain multivalent ionic species.^{3–6} This success is related to the strong electrostatic interactions between carboxylate groups and cations. Nevertheless, the elimination of these nonbiodegradable materials after use remains a problem.

In this context, lignocellulosic materials, such as wood, bark, and plant fibers, and other natural substances are currently considered potential candidates for water decontamination. Although the adsorptive properties of these natural products have been reported elsewhere,^{7–9} their low cost, biodegradability,

and renewability permit researchers to envision the development of a new kind of biofilter, both inexpensive and natural.

The ion-exchange capacity of a wide variety of lignocellulosic materials has been widely investigated,^{10–15} but their binding capacity appears to be insufficient to really compete with synthetic ion-exchange polymers. Hence, chemical modification has been proposed to increase this binding capacity.^{14,16–18} In particular, the chemical reaction of succinic anhydride (SA) with wood has been reported to increase the efficiency of the adsorbent with respect to cadmium(II).¹⁹

In this study, we considered corncobs as a new candidate for water decontamination. First, the ability of corncobs to retain copper was assessed with crude samples. Second, we examined the modification of corncobs through esterification reactions with maleic anhydride (MA) and SA and studied the efficiency of the modified materials with respect to copper retention.

EXPERIMENTAL

Materials

Grinded corncob samples were provided by Eurama (Maubourguet, France). Two types of products, Eu-Feeds and Eu-Grits, were obtained from the low-density inner part and high-density outer part, respectively, of the cobs (≈ 250 and 500 kg m^{-3} , respectively). Two sets of Eu-Feeds samples with different granulometries were used: Eu-Feeds 1 ($100\text{-}\mu\text{m}$ average size) and Eu-Feeds 2 ($1500\text{-}\mu\text{m}$ average size). Eu-Grits

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was used in the form of 1500- μm particles only. The chemical compositions of both sample types consisted mainly of cellulose, hemicelluloses, and lignine.^{11,20} At room temperature and atmospheric pressure, they contained a fraction of adsorbed water, which was eliminated by oven drying before they were weighed.

MA and SA were used as received from Aldrich (Saint Quentin, France).

Esterification

Esterification reactions were conducted with Eu-Feeds 1 only. Before the reaction, the samples were subjected to Soxhlet extraction with a mixture of toluene, acetone, and methanol (4:1:1 v/v/v) for 12 h (for the removal of extractives), oven-dried at 105°C for 15 h, and cooled to the ambient temperature in a desiccator containing phosphorous pentoxide. All chemical modifications were performed in a round-bottom flask equipped with a condenser and a calcium chloride drying tube under a standard set of conditions: 10 g of dried and extracted corncob was stirred with 10 g of MA or SA, in 100 mL of *N,N*-dimethylformamide (DMF), at 80°C and for various periods of time. After the reaction, DMF and unreacted anhydride were eliminated by Soxhlet extraction with acetone for 15 h, and the modified corncob was oven-dried at 105°C for at least 12 h. The weight percent gain (WPG) obtained after esterification was then calculated. In addition, a control sample subjected to the same treatment conditions (i.e., temperature, DMF, and Soxhlet extractions) was prepared and used as a reference (Eu-Feeds R). The nomenclature of the esterified samples is as follows: Eu-Feeds XXxx, where XX is MA or SA and xx indicates the WPG.

Interactions with copper ions

All corncob samples (crude and modified) were dried at 100°C for at least 2 h before they were weighed. Solutions of copper chloride (CuCl_2) at a concentration of 200 mg/L were prepared ahead of time, and various amounts of corncob per liter of solution were added (between 8 and 20 g/L). The pH of the solution was adjusted at a constant value by the addition of aliquots of acetic acid or NaOH during the experiments, and the mixtures were stirred with a magnetic stirrer. Periodically, 10 mL of the solution was sampled. These supernatant solutions were filtered on glass-fiber filters (Wathman GF/C), and ethylene diamine tetraacetic acid (EDTA) was added in excess. The amount of residual copper was determined with an ultraviolet spectrometer by the following method. First, a calibration curve, corresponding to the absorption at 740 nm of the Cu-EDTA complex (A_{740}) as a function of the copper concentration, was established ahead of time with CuCl_2 solutions (concentration

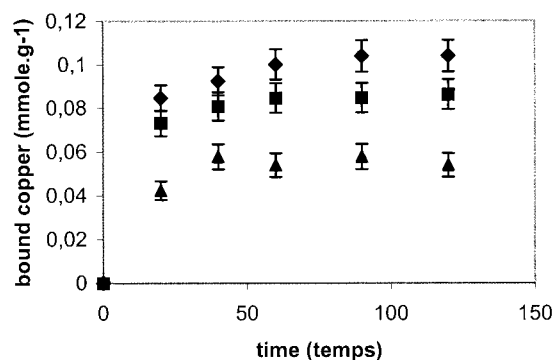


Figure 1 Kinetics of copper binding on crude Eu-Feeds 1 at (▲) pH 2.5, (◆) pH 4, and (■) pH 6.

= 20–200 mg/L; $A_{740} = 0.0011[\text{CuCl}_2]$). Second, the value of A_{740} obtained with the supernatant solution was directly correlated to the concentration of residual copper.

Infrared spectroscopy

Infrared absorption spectra of crude and modified corncobs were obtained with the KBr technique with a Bruker IFS 66/S Fourier transform infrared (FTIR) spectrometer (Wisssembourg, France) at a resolution of 4 cm^{-1} .

X-ray photoelectron spectroscopy (XPS)

XPS measurements were performed with a Surface Science Instrument model 301 spectrometer (San Francisco, CA) with focused monochromatic Al $K\alpha$ radiation ($h\nu = 1486.6$ eV). The diameter of the irradiated area was 600 μm , and the residual pressure inside the analysis chamber was approximately 10^{-8} Pa. The calibration was made with respect to the C_{13} peak of aliphatic carbon (284.6 eV).

Charging effects were minimized with a low-energy electron flood gun in conjunction with a transmitting fine-mesh proximity screen. The XPS signals were analyzed with a peak synthesis program, in which a nonlinear background was assumed, and the theoretical peak fitting was defined by a combination of Gaussian (80%) and Lorentzian (20%) functions.

Ultraviolet–visible (UV–vis)

A Shimadzu UV–vis spectrometer was used for the determination of residual copper, with cells 1 cm thick.

RESULTS AND DISCUSSION

Interactions of copper with crude corncobs

All measurements were performed below the solubility limit of copper hydroxide. Figures 1 and 2 summa-

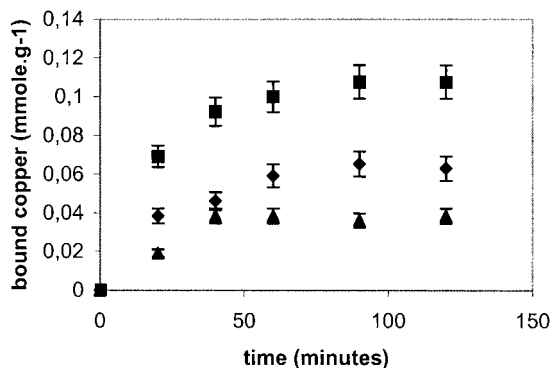
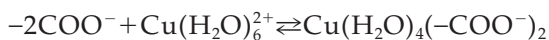


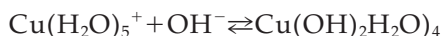
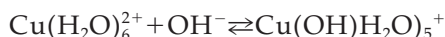
Figure 2 Kinetics of copper binding on crude (■) Eu-Feeds 1, (◆) Eu-Feeds 2, and (▲) Eu-Grits.

ribe the results obtained with different crude corncob samples. Copper adsorption was studied at three different pHs with Eu-Feeds 1 (Fig. 1). The variations of the adsorption observed with the pH suggest an interaction of copper ions with ionized carboxylate functions. This result is not surprising because hemicelluloses contain carboxylic acid groups, and hemicelluloses are among the major constituents of corncob¹¹ (up to 40% of corncob). These groups have already been proposed as potential binding sites for copper in wood. Even if the interaction of copper and corncob hydroxyl groups is not excluded, it is expected at a much higher pH. Corncobs adsorb the maximum amount of copper at an optimum pH of approximately 4. Such an optimum has already been observed with synthetic poly(carboxylic acid)s, such as poly(acrylic acid), partially hydrolyzed polyacrylamide, and poly(methacrylic acid).^{21–23} Copper/carboxylate complexes have been shown to be ruled mainly by electrostatic interactions (with a constant K_{c2}):



This equilibrium assumes that two carboxylate functions are bound to one copper ion. One cannot neglect the formation of monocomplex $\text{Cu}(\text{H}_2\text{O})_5(-\text{COO}^-)^+$.

At low pHs (2–3), copper exists mainly in the form of the divalent cation $\text{Cu}(\text{H}_2\text{O})_6^{2+}$, but the fraction of ionized carboxylate groups ($[\text{COO}^-]/[\text{COOH}]$) calculated from the acid–base equilibrium $[(\text{COO}^-][\text{H}^+])/[\text{COOH}] = K_a$ is very low. The fraction of carboxylate groups complexed by Cu^{2+} depends on the values of K_{c2} and K_a but is generally found to be rather low. With increasing pH, the ionization of carboxylic functions and the hydrolysis of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ take place:



At a pH close to neutrality, a certain amount of uncharged copper hydroxide is present in solution (when the concentration is below the solubility limit) that does not interact with COO^- species, and the fraction of complexes is low. Consequently, the optimum pH is found in an intermediate range (pH 4–5), within which the fractions of both ionized carboxylates and divalent copper cations are simultaneously present in solution. Experience shows that this pH value is around 4, depending on the charge density and concentration of the polymer, because pK_a of weak polyacids is strongly dependent on pH. Experimental results obtained with crude corncobs, in qualitative agreement with those obtained with soluble synthetic polyelectrolytes, stressed the strong influence of carboxylate groups in the process and led us to consider the modification of corncobs to increase the number of carboxyl sites.

The influence of the particle size is shown in Figure 2. Eu-Feeds 1 and Eu-Feeds 2 are compared, and 1.6 times more copper appears to be bound to the smaller particles, that is, those with a higher specific area (Eu-Feeds 1). This result indicates that the binding occurs mainly at the surface of the corncob rather than within the corncob. Besides, for a given particle size (1500 μm), low-density Eu-Feeds particles are much more efficient than high-density Eu-Grits; this emphasizes the impact of material porosity on copper adsorption.

In the view of the results obtained in this preliminary study, an optimum copper retention capacity of 0.11 mmol g^{-1} was found at pH 4. This value compares favorably with the retention capacities displayed by other lignocellulosic materials^{7,11,14,17,24,25} but is still insufficient for corncobs to really compete with synthetic ion-exchange resins. The chemical grafting of carboxylic acid groups onto corncobs was, therefore, considered. The Eu-Feeds 1 sample, having a higher porosity and a smaller size, was chosen for this modification.

Esterification reaction

Because corncobs are natural products consisting primarily of cellulose, hemicelluloses, and lignin,^{11,20}

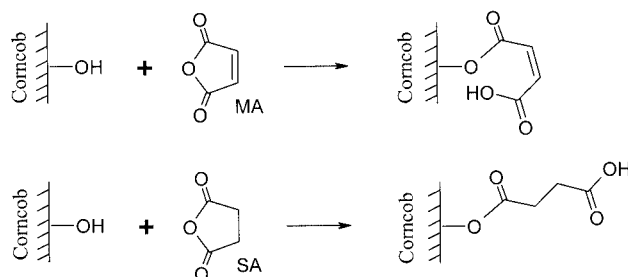


Figure 3 Reactions between the corncob and cyclic anhydrides MA and SA.

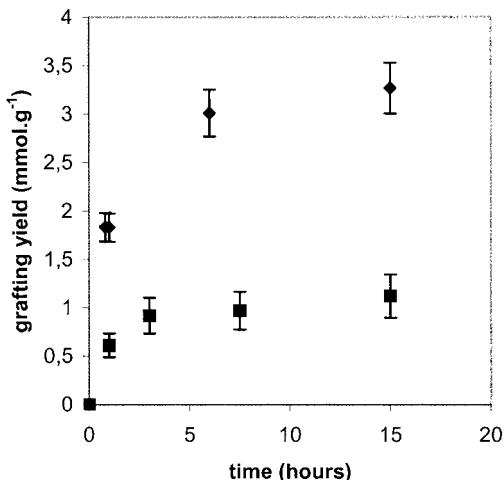


Figure 4 Kinetics of corn cob esterification (Eu-Feeds 1) with (■) MA and (◆) SA.

many reactive hydroxyl sites are available to form covalent bonding with various chemical reagents. Therefore, it is possible to introduce carboxylic acid groups to corncobs via esterification with cyclic anhydrides such as MA and SA. Such reactions have been reported with wood^{26–28} and proceed as follows: the hydroxyl groups of corncobs react with MA or SA by the ring opening of the anhydrides and generate esterified corncobs bearing carboxylic acid groups (Fig. 3). Depending on the anhydride used, the spatial po-

sition of the grafted groups will differ because, in the case of MA (and unlike in the case of SA), the presence of the C=C bond prevents any free rotation between the two carbons.

The mechanism shown in Figure 3 is generally acknowledged for wood, but we should keep in mind that the addition of cyclic anhydrides in the diester form cannot be totally ruled out;^{19,26} that is, the total number of grafted carboxylic acid groups may be lower than predicted from the WPG.

The kinetics of esterification reactions were studied by measurements over time; the WPGs were obtained with MA and SA (Fig. 4). Grafting proceeds rapidly in the initial stage of reaction and then more gradually as the WPG increases. The reaction in this initial stage is faster with SA than with MA, and the maximum WPG obtained after 15 h is three times higher with SA, although the molecular weights are close (MA molecular weight = 98 g/mol and SA molecular weight = 100 g/mol). Such a difference in reactivity has been observed with wood²⁶ and can probably be explained by the existence of a conjugated system in the case of MA (O=C–C=C–C=O), which reduces the electrophilic character of the carbonyl groups. The difference in the spatial conformations of the maleated and succinated esters may also be involved.

Infrared spectra (500–4000 cm⁻¹) of unreacted and esterified corn cob samples are presented in Figure 5.

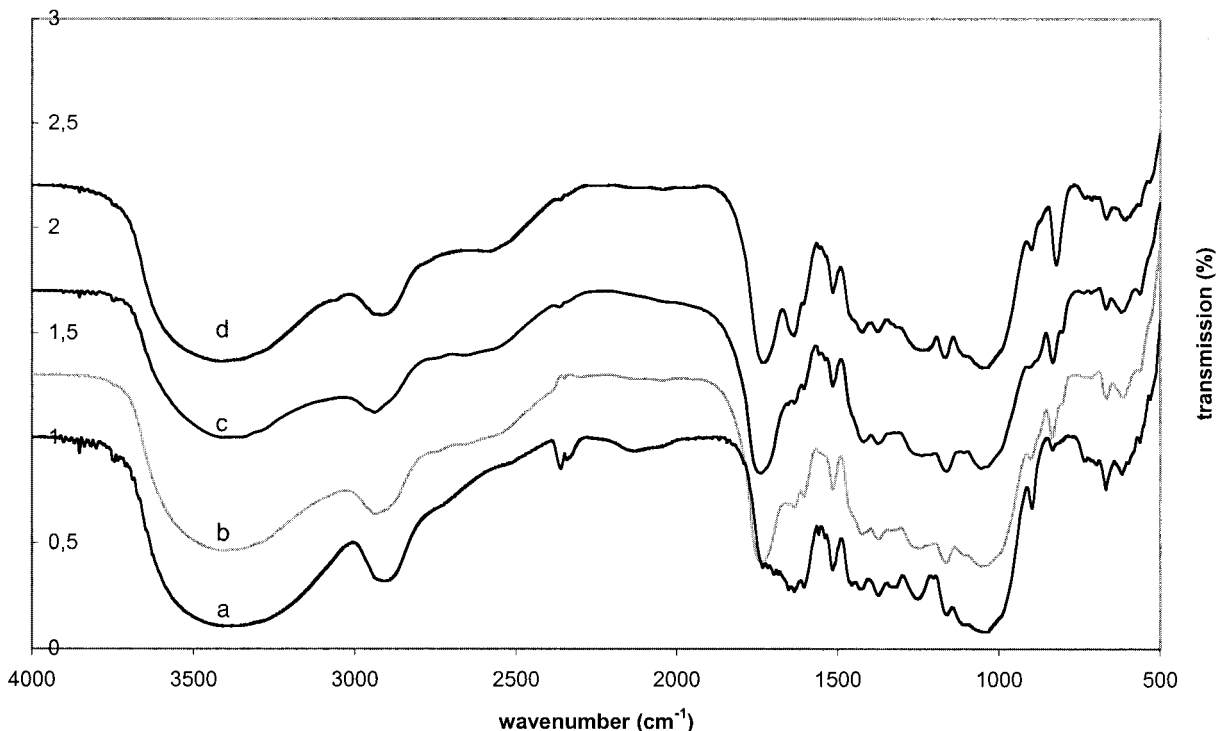


Figure 5 FTIR spectra of (a) Eu-Feeds R, (b) Eu-Feeds SA 18, (c) Eu-Feeds SA 30, and (d) Eu-Feeds MA 10.

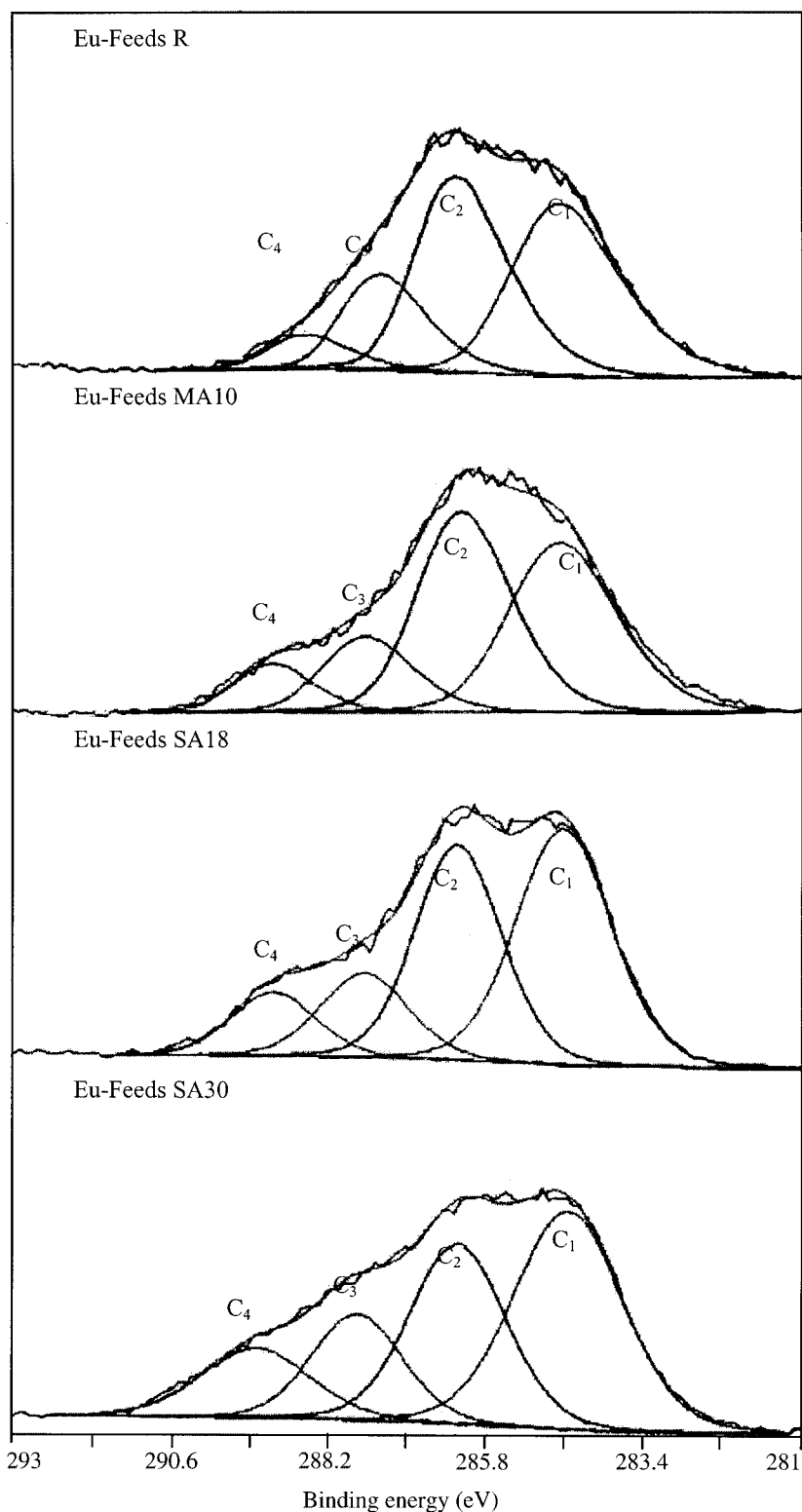


Figure 6 XPS C1s spectra of Eu-Feeds R, Eu-Feeds MA 10, Eu-Feeds SA 18, and Eu-Feeds SA 30.

In all cases, esterification leads to an increase in the carbonyl stretching vibration $\nu(\text{C}=\text{O})$ in the region of 1740 cm^{-1} , which is due to ester bond formation and pendent carboxylic acid groups.

The band at 2600 cm^{-1} is assigned to the O—H stretching vibration of the grafted carboxylic acid groups [$\nu(\text{COO—H})$]. In addition, two vibrations characteristic of the maleated ester have been identified (spectrum d): the band at

TABLE I
Relative Composition of C_1 , C_2 , C_3 , and C_4 in the
High-Resolution Spectra of Carbon

Sample	Relative percentages (%)			
	C_1	C_2	C_3	C_4
Eu-Feeds R	38.9	39.9	17.1	6.1
Eu-Feeds SA 18	41.8	34.2	13.9	10.1
Eu-Feeds SA 30	40.7	29.5	16.6	13.2
Eu-Feeds MA 10	38.2	37.5	14.3	8.0

1637 cm^{-1} is assigned to the $\text{C}=\text{C}$ stretching vibration (ν), and the band at 820 cm^{-1} is assigned to out-of-plane $\text{C}=\text{H}$ bending (δ). These assignments agree with the results reported for wood.^{26,27}

The surface chemistry of corncobs was investigated with the XPS technique. High-resolution XPS spectra were recorded in the carbon region. Figure 6 shows the $\text{C}1\text{s}$ spectra of Eu-Feeds R and its modified samples (Eu-Feeds MA 10, Eu-Feeds SA 18, and Eu-Feeds SA 30). In each case, the carbon peak consists of four component peaks: C_1 , C_2 , C_3 , and C_4 at approximately 284.6, 286.2, 287.6, and 289 eV, respectively. These values agree with those reported in the literature for wood,^{28–30} where C_1 is assigned to carbon atoms bound to carbon or hydrogen ($\text{C}-\text{C}$ and/or $\text{C}=\text{C}$ and/or $\text{C}-\text{H}$), C_2 is assigned to carbon singly bonded to a single oxygen ($\text{C}-\text{OR}$ and/or $\text{C}-\text{OH}$), C_3 is assigned to carbon singly bonded to two oxygen atoms or double-bonded to a single oxygen ($\text{O}-\text{C}-\text{O}$ and/or $\text{C}=\text{O}$), and C_4 is assigned to carbon of carboxylic acids and esters ($\text{O}-\text{C}=\text{O}$). The C_1 component arises mainly from lignin, and C_2 arises from both carbohydrates and lignin. C_3 can be assigned to an acetal linkage and reducing end groups of carbohydrates, with a small contribution possibly coming from carbonyl groups of lignin. Finally, C_4 arises mainly from the carboxylic acid or acetyl groups of hemicelluloses. Table I summarizes the relative compositions of C_1 , C_2 , C_3 , and C_4 . The C_3 and C_4 atomic ratios of unmodified corncobs appear to be substantial in comparison with what is usually observed at the surface of wood.²⁸ This result is consistent with the higher hemicellulose content usually found in non-woody lignocellulosic materials such as corncobs.^{14,30}

Esterification led to an increase in the C_4 atomic ratio commensurate with the WPG, confirming the introduction of new ester and carboxylic acid groups at the surface of the modified corncobs. With SA, a decrease in the C_2 atomic ratio was observed with increasing grafting and could be attributed to the grafted groups that screened, to some extent, the underlying C_2 . This trend was not observed with MA, but in that case, the WPG may have been too small to be critical.

The changeable behavior observed for the C_3 atomic ratio has not been explained.

Interactions of copper with modified corncobs

The results of the copper retention experiments, performed at pH 4, are reported in Figure 7. The retention capacities of Eu-Feeds 1 (crude sample), Eu-Feeds R, Eu-Feeds MA 10, Eu-Feeds SA 18, and Eu-Feeds SA 30 are then compared.

First, the retention capacity of Eu-Feeds R is improved with respect to that of the crude sample (Eu-Feeds 1). This can be explained by the fact that extractive compounds have been eliminated in Eu-Feeds R because of extensive extraction with a mixture of toluene, acetone, and methanol. The noninvolvement of these extractives in the retention process will naturally lead to an increase in the retention capacity per mass unit, after extraction.

The effect of chemical modification must be discussed with respect to Eu-Feeds R. At pH 4, corncobs modified by MA (ca. 1 mmol of grafted carboxylic group/g, as predicted from the WPG) lead to higher copper retention than Eu-Feeds R, as expected from the presence of a larger number of carboxylic acid groups. Surprisingly, with SA (Eu-Feeds SA 18), the grafting of a larger number of carboxylic acid groups (ca. 1.8 mmol g^{-1} predicted from the WPG) does not enhance adsorption with respect to Eu-Feeds R. Besides, only a slight improvement is observed with increasing grafting (Eu-Feeds SA 30). This behavior can be attributed to the formation of a large amount of diester in the case of modification with SA, but the contrasting results observed at pH 5 (Fig. 8) have led us to propose another interpretation. Because copper binding involves an ionic interaction, the lower efficiency of Eu-Feeds SA compared with that of Eu-Feeds MA can be attributed to a difference in the $\text{p}K_a$ values of the grafted acidic functions, which may be higher for Eu-Feeds SA. An increase in the retention capacity of Eu-Feeds SA will then be expected at higher pH values.

Figure 8 presents the results obtained at pH 5. With respect to Eu-Feeds 1 alone, the curve reveals a lower

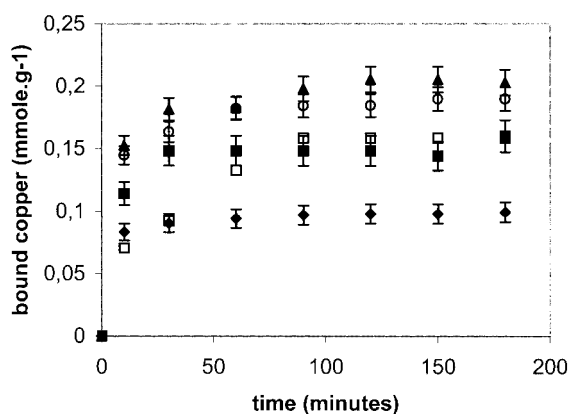


Figure 7 Kinetics of copper binding at pH 4: (\blacklozenge) crude Eu-Feeds 1, (\blacksquare) Eu-Feeds R, (\blacktriangle) Eu-Feeds MA 10, (\square) Eu-Feeds SA 18, and (\circ) Eu-Feeds SA 30.

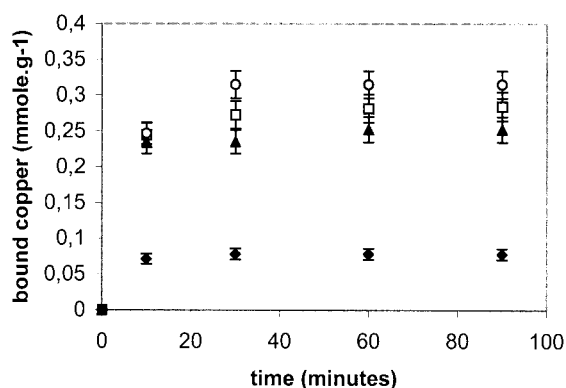


Figure 8 Kinetics of copper binding at pH 5: (◆) Eu-Feeds 1, (▲) Eu-Feeds MA 10, (□) Eu-Feeds SA 18, and (○) Eu-Feeds SA 30.

retention capacity at pH 5 than at pH 4, and this confirms the existence of an optimum value for crude corncobs below pH 5, as explained previously. However, the amount of copper adsorbed on Eu-Feeds SA increases drastically, and this is consistent with our previous hypothesis. Comparatively, this increase is less pronounced with Eu-Feeds MA 10, as expected.

The difference in behavior between MA- and SA-grafted corncobs may be explained with Figure 3, in which the possible conformations of the grafts are considered. We might expect that the carboxylic functions would be closer to the corncob matrix in the case of MA. They are subjected to the electrostatic influence of the negatively charged groups present mainly on hemicelluloses and cellulose, which may favor their deprotonation and lead to a lower pK_a value.

The maximum measured binding capacity is 0.64 mmol g^{-1} . This value has been obtained with Eu-Feeds SA 30 at pH 5 and is 6 times higher than that for unmodified corncobs.

Some additional XPS analysis has confirmed the adsorption of copper on corncobs. In agreement with the results of Figure 8, the quantitative data show that the amount of copper on the surface of Eu-Feeds SA 30 at pH 5 is higher than that obtained with Eu-Feeds MA 10 and Eu-Feeds SA 18.

CONCLUSIONS

This work emphasizes the ability of corncobs to bind pollutant divalent cations such as copper. The adsorptive capacity of crude corncobs is not excessively high, but the low cost of such subproducts can compensate for this moderate efficiency. Optimal conditions for their use as complexing agents have been determined: pH 4, small granulometry, and powders prepared from the low-density inner part. The adsorption properties demonstrated by corncobs can be explained by electrostatic interactions between the divalent cations and hemicellulose carboxylate groups.

Additional carboxyl sites were introduced to corncobs via a esterification reaction with MA and SA, this modification leading to a notable increase in copper retention. Under our experimental conditions, encouraging results were obtained because the ionic retention was multiplied by a factor of about 5 when SA was used at pH 5. However, the optimum pH appeared to be different according to the anhydride used, and this was explained by the assumption of a higher pK_a value for SA-grafted corncobs.

Finally, we have demonstrated that modified corncobs can reasonably compete with synthetic materials. This result may be confirmed with other metallic cations. However, the stability of the grafted carboxylate groups should be carefully investigated because recent unpublished results seem to indicate that less than 1% of the grafted functions may be cut through hydrolysis during copper adsorption experiments.

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