

Removal of Copper Ions from Water of Boilers by a Modified Natural Based, Corncobs

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ABSTRACT: The objective of this study is to demonstrate the feasibility of using esterified derivatives of corncobs to clean back condensates from high-pressure industrial boilers. Copper ions were retained by these modified natural polymers based within working pH and temperature conditions even at very low concentrations as 10^{-12} mol/L. Acrylamide polymers or derivatives were not successful for such applications. The influence of granulometry of crude corncobs and temperature on

copper retention was first studied using UV spectroscopic and voltametry techniques. Then esterified derivatives were considered and succinic anhydride derivatives of corncobs are demonstrated to be more efficient than the maleic anhydride derivatives. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4637–4645, 2006

Key words: corncobs; modification; water treatment; copper ions

INTRODUCTION

The operating of a boiler is complex. There are many types, which may be used at low, average, or high pressure and reach spectacular heights (up to 40 m). Hence, it is important to have regard for some parameters to obtain a good care of boilers associated with an optimal yield. The advantage of a high-pressure boiler is that it can store a large energy and it may be compared to an energy accumulator. A high-pressure industrial boiler may be simplified as a parallelepiped in which each face was covered by series of tubes through which water flows, finished by a receiving balloon. Burners are found at the center of the boiler. Raw materials of the boiler are combustibles (gas, fuel, or black liquor) and water as vapor supplier. This water may be provided from drilling well available on the production site or city. It will be dealt with all attentions because all problems met inside a boiler come from water, and more precisely from the dissolved ions (Na^+ , Ca^{2+} , Cu^{2+} , Fe^{3+} , Al^{3+} , . . .). Boiler water may in addition contain pollutants coming from back condensates, and among them, copper ions are the origin of major problems. They consist in the apparition of corrosion phenomena from the formation of bimetallic battery first,

and second from the formation of deposits on inner face of tubes. Irreversible damage as cracking due to pit corrosion may be the consequence of such problems. It is then necessary to develop methods for cleaning boilers.

Recovery of metals from industrial effluents may be performed according to different processes.^{1–4} Besides mechanical treatments of waste water (sedimentation) or biological ones (activated muds), some chemical treatments are used to eliminate these metals. Most current processes are the precipitation by hydroxides or sulfides,⁵ the oxidation–reduction,⁶ ion exchange, liquid–solid separation by decanting–flotation, and the separation using membranes.⁷ But, the major drawback of these treatments is the formation of muds, which have to be subjected to confining. Adsorption on active coal was widely studied,⁸ and more economical alternative processes based on the use of material polymers have been developed.⁹ These processes have a serious fundamental support, because many studies have been carried out on interactions between polyelectrolytes and metallic ions and the selective trapping of ionic species of opposite charge.^{10–12} When elimination of multivalent cations is concerned, synthetic or natural polycarboxylates are good candidates because carboxylate groups strongly interact with these ionic species. The binding or complexation of Na^+ , Ca^{2+} , Cu^{2+} , Fe^{3+} , Al^{3+} ions by polyacrylic acid, acrylamide/acrylic acid copolymers (HPAM), and polymethacrylic acid (PMA) is well documented,^{13–19} and this property is very often used in depollution treatments. New

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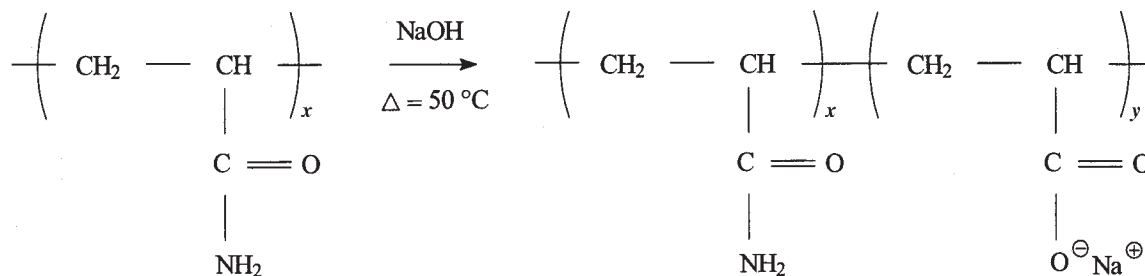
adsorbents were considered to find more efficient and less expensive materials. Thus, the adsorption by living organisms (bacteria, fungi, seaweeds, etc.) or chemicals extracted from these organisms was studied.^{20,21} Moreover, polymers considered as biomass wastes may also be very efficient, considering specific interactions between ionic species and polar groups present within these polymeric chains.²²⁻²⁵

In a previous work, the complexation of copper by crude corncobs and corncobs modified by grafting additional carboxylate groups at their surfaces was studied.²⁵ It was found that the capacity of copper binding by the modified materials is equivalent to that found for polymeric resins. In this study, we compare complexation of copper by synthetic polymers of the HPAM type with that obtained using crude and modified corncobs. It is demonstrated that the corncob-based materials are the most efficient when applied on solutions simulating boiler water.

EXPERIMENTAL

Materials

Grinded corncob samples were provided by Eurocob (Maubourguet, France). Two types of products, Eu-



The polymer was recovered by precipitation in acetone (for an acetone volume 5–10 times larger than the solution volume). Purified polymer was obtained after dialysis of the polymer (dissolved in thrice-distilled water) against pure water and then freeze-drying.²⁹

The degree of hydrolysis y is a function of time,²⁸ and the values of y (measured by ¹³C-NMR) were 0.10, 0.25, and 0.40, for the three samples, respectively, considered in this work.

Corncob esterification

Esterification reactions by succinic acid were conducted with Eu-Feeds only. Indeed, in a previous study,²⁵ we have demonstrated the higher capacity of ionic retention of Eu-Feeds. Before the reaction, the samples were subjected to Soxhlet extraction with a mixture of toluene, acetone, and methanol (4 : 1 : 1 v/v/v)

Feeds and Eu-Grits, are extracted from the low-density inner part and high-density outer part of the cobs. The chemical compositions of both sample types consisted mainly of cellulose, hemicellulose, and lignin,^{26,27} as given in Table I. At room temperature and atmospheric pressure, they contained a fraction of absorbed water, which was eliminated by oven-drying under vacuum at 105°C during 15 h before they were weighed. The characteristics of the different samples used are given in Table II.

Succinic and maleic anhydrides were used as received from Aldrich. Acrylamide from Aldrich was used without purification or distillation.

KBr (IR grade) from Acros Organics was used without purification being kept in a desiccator.

Preparation of polymers

Preparation of acrylic acid/acrylamide copolymers

Acrylamide/sodium acrylate copolymers (HPAM) were obtained from polyacrylamide precursor (synthesized by free radical polymerization) by basic hydrolysis ([NaOH] = 0.25 mol/L) at a temperature of 50°C to reach the sodium acrylate salt, as already described.²⁸

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 succinic anhydride, in 100 mL of *N,N*-dimethylformamide (DMF), at 80°C and for various periods of time. After the reaction, DMF and unreacted

TABLE I
Composition of the Crude Corncob Samples

	Eu-Grits (%)	Eu-Feeds (%)
Cellulose	47.1	35.7
Hemicellulose	37.3	37
Lignin	6.8	5.4

TABLE II
Granulometry and Density of Crude Corncob Samples

	Radius size S (μm)		Density (kg/m^3)		Cu ²⁺ adsorption (10^5 mol/g)
	Eurocob	Measured (average)	Eurocob	Measured	
Eu-Grits 6/8	2000–4500	2900	440	450	1.5
Eu-Grits 8/10	2000–3100	2300	430	435	3.5
Eu-Grits 30/60	250–700	500	500	500	4.9
Eu-Grits-200	<180	150			5.4
Eu-Grits-100	<100	–			5.4
Eu-Feeds1	<100	–	260	245	

The average sizes were measured by optical microscopy and the density by a flotation method.

anhydride were eliminated by Soxhlet extraction with acetone for 15 h, and the modified corncob was oven-dried at 105°C for a least 12 h. The weight percent gain (WPG) obtained after esterification was then measured by weighing the samples before and after chemical modification. 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 WPG of the sample prepared in this work is 30%, and it is designed by Eu-Feeds SA30.

Analysis of copper and characterization of polymers

Measurement of copper by UV spectrometry

A Shimadzu UV-visible spectrometer was used for the determination of residual copper, with cells 1 cm thick. *Corncoobs*. All corncob samples (crude and modified) were dried at 100°C for a least 2 h before they were weighed. Solutions of copper chloride (CuCl_2) at a concentration of 269 mg/L (2×10^{-3} mol/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 to 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 solution samples were filtered on glass-fiber filters (Wathman GF/C), and ethylene diaminetetraacetic acid (EDTA) was added in excess. The amount of residual copper was determined by UV spectroscopy. A calibration curve, corresponding to the absorbance at 740 nm of the Cu-EDTA complex (A_{740}) as a function of the copper concentration, was previously established with CuCl_2 solutions (concentration = 20–200 mg/L; $A_{740} = 87.135 [\text{Cu}^{2+}]$, $[\text{Cu}^{2+}]$ in mol/L). Then, the value of A_{740} obtained with the supernatant solution was directly correlated to the concentration of residual copper, using the calibration curve.

Synthetic polymers. Since no precipitation of HPAM occurs when copper ions are adsorbed, EDTA in excess was simply added in the solutions without filtration. This means that the amount of free copper determined by this way is overestimated or the fraction of copper bound to the polymer underestimated. In fact, one should take into account the complexation competition between polymer and EDTA.

Polymer solutions of HPAM at $C_p = 0.5$ and 1% (w/w) were studied in the presence of 2×10^{-3} mol/L of CuCl_2 .

Measurement of copper by voltametry

Differential pulse anodic stripping voltametry (DPASV) is a titration method derived from polarography, but more sensitive, and applying only to traces of metals amalgamating with mercury (Sb, Sn, Ag, Cu, Pb, Cd, Zn. . .). Electrodes are similar, but working electrode was a pending mercury drop electrode, or a vitrous carbon electrode overlaid with mercury film. In this work, a pending drop electrode was used. The operation proceeds along three steps (the preelectrolysis, the equilibration, the anodic redissolution). The obtained peak during the third step was proportional to the solution concentration of metallic ion in solution.

Applying DPASV, it is possible to titrate traces down to 10^{-11} mol/L for metals soluble in mercury leading to stable amalgams and belonging to quick voltammetric systems.

For all these determinations, reproducibility and reliability were considered by performing a series of measurements, and average values were given.

Characterization of polymers by NMR and IR

NMR spectroscopy

¹H and ¹³C spectra were recorded, at 400 MHz for ¹H-NMR, on a Bruker Advance AM400 spectrometer in D₂O. Experiments were carried out at 25°C using polymer concentrations of 10 mg/mL for ¹H spectra and

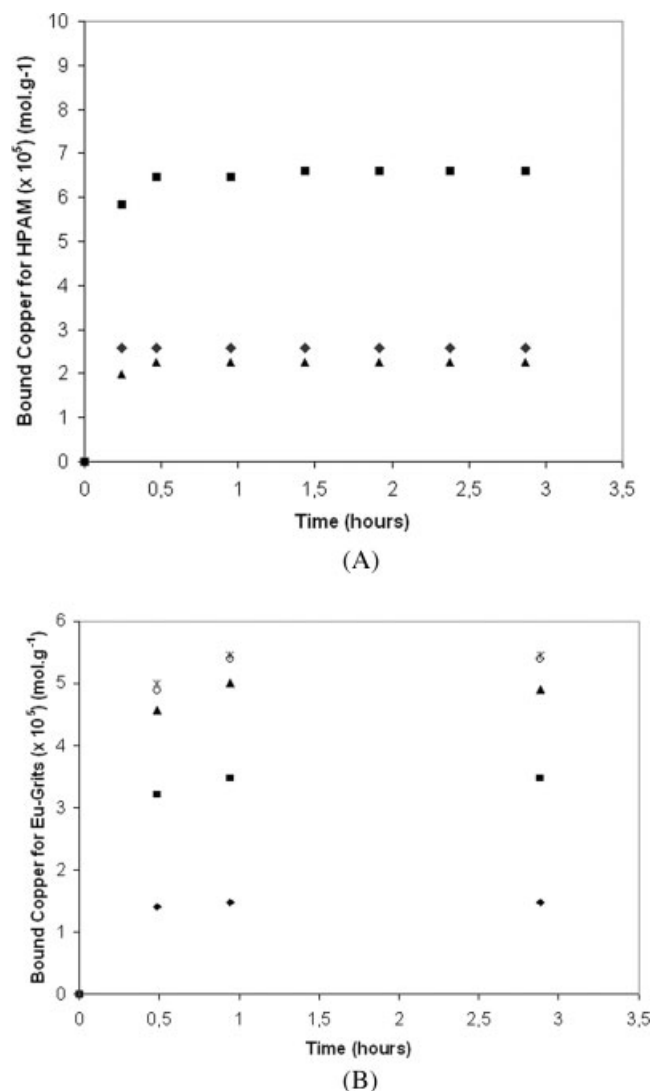


Figure 1 (A) Retention of copper as a function of time (determined from UV experiments) for HPAM samples at 10 g/L: $y = 0.10$ (▲); $y = 0.25$ (◆); $y = 0.40$ (■) (the hydrolysis contents are 10%, 25%, or 40%). (B) Retention of copper as a function of time (determined from UV experiments) for Eu-Grits samples of different granulometries (see Table II) at 20 g/L (pH 5): 6/8 (◆); 8/10 (■); 30/60 (▲); -200 (○); -100 (*).

30 mg/mL for ¹³C spectra. The chemical shifts (δ) in ppm are referred to internal Me₄Si.

Infra red spectroscopy

IR spectroscopy was carried out on original Eu-Feeds SA30 and on filtrate residue under KBr tablet. They

were done using an IR spectrometer IFS 66/S from Brüker.

Determination of the nature of dissolved residues

To determine the nature of chemicals responsible for yellowish color after copper complexation by Eu-Feeds SA30 at high temperature, the following experiment was performed: Eu-Feeds SA30 was mixed at a concentration of 2% in water, at pH 6.2, and a temperature equal to 60°C. Suspension was stirred during 1 h and then filtrated on Büchner. The filtrate was freeze-dried and analyzed using IR, ¹H, and ¹³C-NMR spectroscopy.

RESULTS AND DISCUSSION

The conditions of back condensates from an industrial boiler are $T \approx 100^\circ\text{C}$, pH around 6, and cation concentrations around 10^{-6} mol/L as traces.

As the objective of this study was to establish comparison between corncobs and synthetic polymers, we have in a first time considered conditions of moderate copper concentration (2×10^{-3} mol/L) when the determination of the free copper ions is easily performed by UV-spectroscopy.

When copper salts are dissolved in water, according to pH and initial metal concentration, different ionic or nonionic species have to be considered. From the hydrolysis constants, it is possible to calculate the molar fraction of each species; at pH 5, 100% of copper is under the form of the mononuclear divalent form $\text{Cu}(\text{OH})_6^{2+}$, and at pH 6, one finds 85% of $\text{Cu}(\text{OH})_6^{2+}$ and 15% of the dimeric divalent ions $\text{Cu}_2(\text{OH})_2(\text{H}_2\text{O})_{10}^{2+}$.³⁰ Precipitates of $\text{Cu}(\text{OH})_2$ start to be formed above pH 9. Because of these considerations, all our experiments were performed in the range $5 < \text{pH} < 6$.

Interactions of HPAM with copper ions

HPAM are weak polyacids and their complexation with copper ions has been studied as a function of pH.³¹ For a degree of hydrolysis y or molar fraction of acrylic units lower than 0.35 and at $\text{pH} < 6$, HPAM form only mononuclear complexes ($-\text{COO}_2\text{Cu}$), and the complexation constant was found to be $K_{\text{Cu}} = 2 \times 10^6$ (concentrations being expressed in mol/L).

Time to time samplings were made and EDTA added in excess. Figure 1(A) shows the variation of amount of copper apparently bound by carboxylate

TABLE III
Copper Retention by Synthetic HPAM Copolymers

	HPAM (10%)		HPAM (25%)		HPAM (40%)	
Polymer concentration (%)	0.5	1	0.5	1	0.5	1
Trapped copper (10^{-4} mol/L)	1.3	2.2	2.4	2.6	4.3	6.4
Trapped copper (%)	6.5	11.2	11.9	13	12.5	32.0

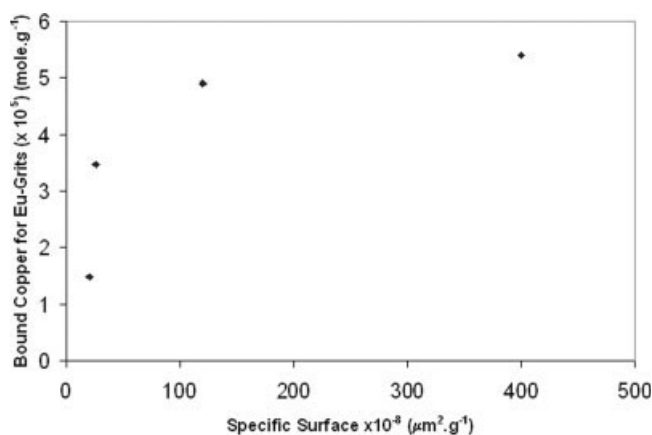


Figure 2 Variation of the copper retention versus specific surface of the Eu-Grits (determined from UV experiments).

groups of HPAM as a function of time, for $C_p = 1\%$ (w/w). At first, no precipitation was observed under these conditions. This is not surprising, since it has been demonstrated that for sodium poly(acrylate) ($y = 1$), phase separation occurs for a molar ratio $R = [\text{divalent cation}]/[\text{carboxylate}] \leq 1/2$,¹³ while for lower values of y , this critical ratio is higher than 1.³² This behavior was explained by considering that the monomer units complexed with copper ions are insoluble in water, and the polyelectrolytes in the presence of multivalent cations can be considered as copolymers constituted of uncomplexed soluble monomer units and complexed insoluble ones.¹⁸ In our experimental conditions, the ratio R varies between 0.568 for $y = 0.1$ and $C_p = 0.5\%$ (w/w) and 0.071 for $y = 0.4$ and $C_p = 1\%$, which is much below the critical ratios. If we consider the practical conditions of boilers (concentration of divalent cations of the order of 10^{-6} mol/L), phase separation is expected for C_p lower than 10^{-8} g/g, amount which is very difficult to recover even under the form of precipitates.

The variation of apparent bound moles of copper per gram of polymer is reported as a function of time in Figure 1(A) for $C_p = 1\%$ (w/w). One observes that the content of free copper able to form complexes with EDTA is lower than in the absence of polymer. This means that the complexation constant of copper with these polymers, even for low values of y , is higher than that of the complexation of copper with EDTA. This is consistent with the high value of the complexation constant previously found for an HPAM of $y = 0.27$.³¹ The amount of "apparent" trapped copper is given in Table III for two polymer concentrations of 5 and 10 g/L. As expected, HPAM ($y = 40\%$) is the most efficient polymer or that which leads to the lower amount of copper free for complexation with EDTA. One can find from the value of K_{Cu} that almost the totality of copper should be in fact complexed by the polymer in the absence of EDTA, but in the presence of a strong com-

plexing molecule such as EDTA, a part of the bound cations are released from the polymer.

The main disadvantage of these polymers is their great solubility and the fact that phase separation requires a high amount of copper ions or other multivalent cations. In conclusion, and taking into account the application to boiler back condensates, even if polymers are able to trap the cations, recovery of the formed complexes will not be easy. Moreover, it will be very difficult to perform experiments in application conditions (copper concentration as low as 10^{-6} mol/L).

As a consequence, experiments must be performed on solids able to interact with copper ions. This will make easier the recovery of active matter by sedimentation or filtration.

Interaction of copper with corncobs

Crude corncobs

The results of copper retention experiments performed at pH = 5 and 25°C with series of Eu-Grits samples were reported in Figure 1(B). This retention is due to presence of carboxylic groups within hemicelluloses, which are among the major constituents of corncob (up to 40% of corncob, see Table I). 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.

The retention capacity was improved using sample with lowest particle size. The Eu-Grits-100 sample (with the lowest particle size, see Table II) was able to retain more than 50% of original copper, but this retention was still partial at this copper concentration. More copper appears to be bound to the smaller particles,

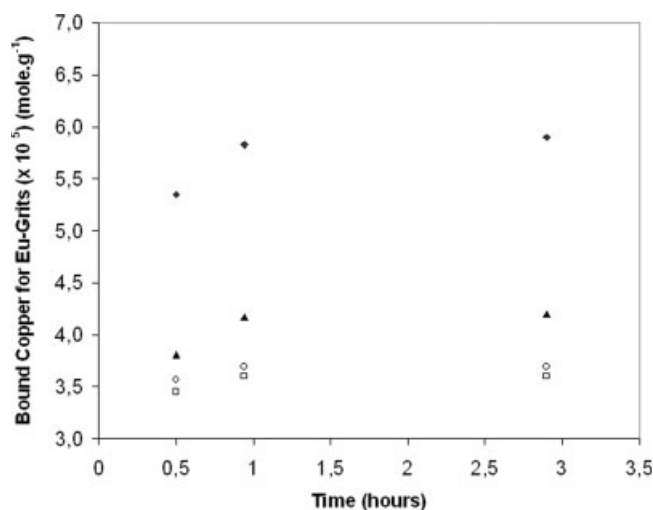


Figure 3 Retention of copper by Eu-Grits-100 (20 g/L) as a function of time (pH 5) at various temperatures 25°C (◆); 40°C (▲); 60°C (○); 80°C (□) (determined from UV experiments).

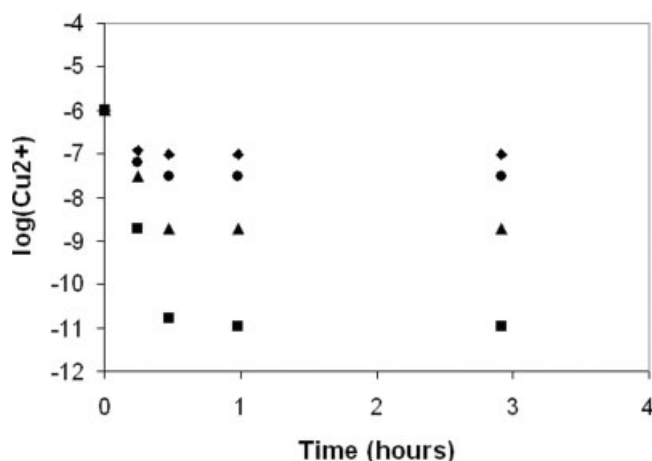


Figure 4 Residual copper versus time for Eu Feeds SA30 (low copper concentration (10^{-6} mol/L), $T = 25^{\circ}\text{C}$, determined from voltametry experiments) at various material concentrations: 1 g/L (◆); 5 g/L (●); 10 g/L (▲); 20 g/L (■) (Cu^{2+} concentration in mol/L).

that is, those with a higher specific area. The plots of the copper retention (in mol/g) as a function of the specific surface ($\mu\text{m}^2/\text{g}$) calculated from the data of Table II are not linear as expected from the hypothesis of a simple surface mechanism (Fig. 2). This is due to the interaction of copper with carboxylate groups present on the surface inside particles, which is not surprising if one considers the alveolar structure of corncobs and the low density of these materials, associated to existence of pores. Probably, a part of the inner carboxylate groups are accessible to copper ions.

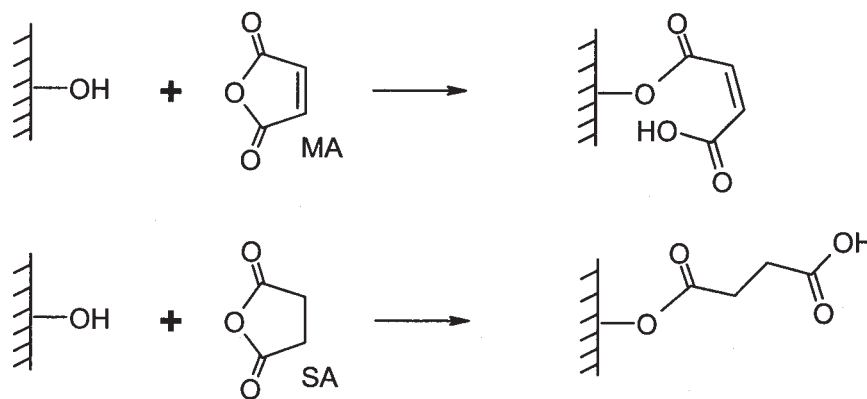
Copper solution was mixed with corncobs under stirring in a thermostated cell. Used temperatures were 40, 60, and 80°C , pH being equal to 5. This pH value was controlled and kept constant using a 0.1M sodium

hydroxide solution. Results were gathered in Figure 3. Increasing temperature decreases copper retention from 25 to 80°C , and the retention loss was around 20% (from 54% to 35% of retained copper). This may be due to damage at relatively high temperature (80°C) of Eu-Grits, but it has to be confirmed.

These results are consistent with a previous comparison of Eu-feeds samples with two different granulometries. Besides, it was shown that for the same granulometry, copper retention was higher with the low density Eu-Feeds than with the higher density Eu-Grits. The effect of porosity of the material is then well confirmed. At equilibrium, the retention of copper by Eu-Feeds 100 in the same experimental conditions as those of Figure 1, is 1.1×10^{-4} mol/g. This probably corresponds to that best efficiency one can expect from crude materials. Then the depollution of 1 L of water containing copper at concentration of about 10^{-6} mol/g requires at least 10^{-2} g of crude corncob which corresponds to 10 g/m^3 . But, if one considers the legislation in terms of minimum acceptable content of copper in water, it is not possible to use simple proportionality laws and to minimize the amount of depolluting materials, one has to check (i) more efficient materials such as obtained by chemical modification of crude corncobs (ii) to work under true practical conditions (very low content of copper) and measure residual copper traces.

Modified corncob

It was demonstrated that corncobs modified by introducing carboxylic groups improve copper retention compared with original corncob.²⁵ Esterification reaction of corncob with cyclic anhydrides (maleic anhydride, MA, and succinic anhydride, SA) proceeds as follows:



Use of succinic anhydride leads to better copper retention at $\text{pH} = 5$, and it was explained by the possible conformations of the grafts.²⁵ The carboxylic function would be closer to the corncob matrix in the case of MA, leading to an electrostatic influence of the nega-

tively charged groups present mainly on hemicellulose and cellulose, which may favor then deprotonation and lead to a lower pK_a value. Hence, the optimal pH appeared to be different according to the anhydride used.

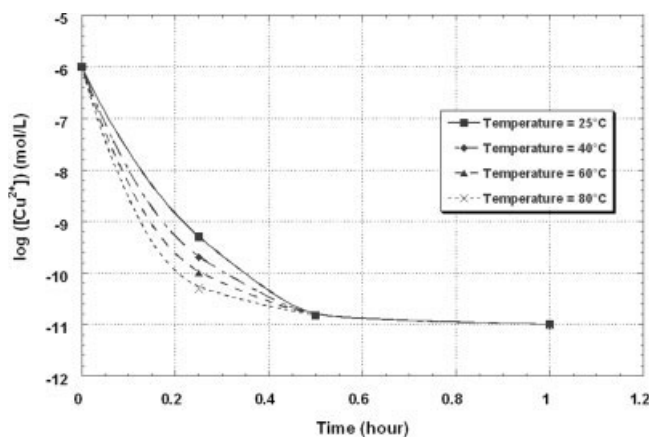


Figure 5 Residual copper versus time for Eu Feeds SA30 (low copper concentration (10^{-6} mol/L), determined from voltametry experiments) at various temperatures (polymer concentration: 20 g/L, pH = 6.2).

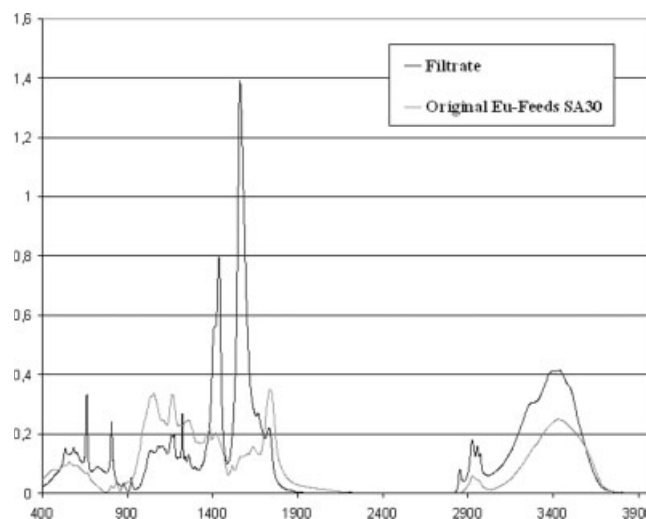


Figure 6 Infra Red spectra of filtrate residues after copper complexation at 80°C and original Eu-Feeds SA30.

Taking into account the Eu-Feeds SA30 sample one can calculate that for particles of average 100 μm diameter, the WPG value of 30% corresponds to 2×10^{14} SA molecules per particle with an average area per molecule of 0.016 \AA^2 if one considers a grafting only at the surface of the particles. As the Eu-Feeds are very

porous, a major part of the SA molecules are also grafted inside the particles with an average distance between SA molecules favorable to copper binding.

The copper ion concentration being equal to 10^{-6} mol/L, close to that expected in practical conditions,

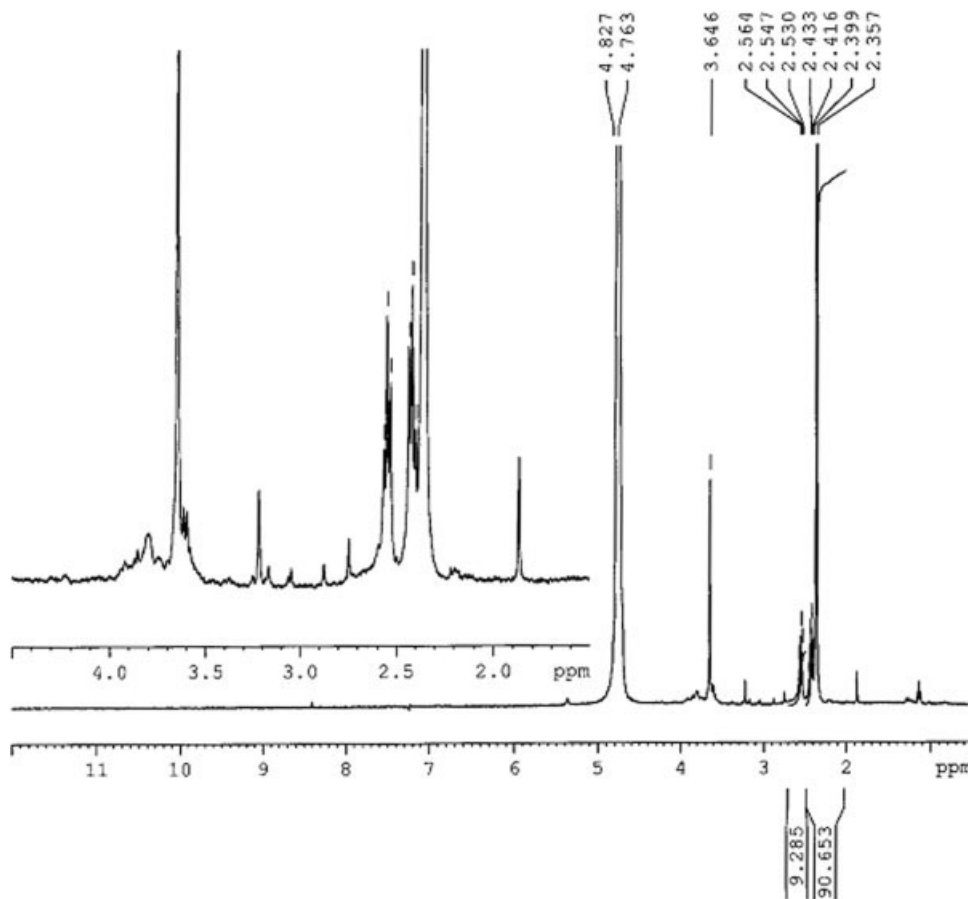
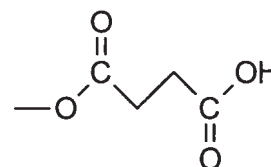


Figure 7 $^1\text{H-NMR}$ spectrum of filtrate.

the influence of the concentration of Eu-Feeds SA30 was studied at 25°C, the pH being kept constant to 5–6 as previously described. As metal concentration was very small, anodic stripping voltammeter (ASV) was used to determine copper concentration in solution. Results are given in Figure 4. Eu-Feeds SA30 is very efficient, since for 20 g/L the residual copper concentration reaches values as low as 10^{-11} mol/L.

Complementary measurements were made with Eu-Feeds SA30 at variable temperature and no difference was observed for $25^{\circ}\text{C} < T < 80^{\circ}\text{C}$ on the final copper retention, but it seems that the binding process is faster for the higher temperatures (Fig. 5). This behavior was different from that of nonmodified corncobs as already demonstrated.²⁵ This confirms the influence, and the interest, of the chemical modification of such materials on the complexation of metallic ions. However, a slight modification of the color of filtrates was observed when temperature was increased. To determine the nature of chemicals responsible for yellowish color, specific experiments were carried out and the filtrate was analyzed through spectroscopic techniques. IR spectra (Fig. 6) demonstrate a better peak definition in case of the filtrate residue compared with original feeds. This assumes that molecules which were solubilized were simpler than those present in feeds. Moreover, the apparition of a band at 1733.5 cm^{-1} , characteristic of car-

boxylic groups, is more intense in Eu-Feeds SA30 related with a lower quantity of compound which was dissolved. The $^1\text{H-NMR}$ spectrum of the filtrate displays one singlet (2.357 ppm) and two triplets (2.416 and 2.547 ppm) as given in Figure 7. The singlet is dedicated to CH_2 groups from succinic anhydride, which has not reacted during chemical modification and was kept trapped within the material. The triplets were dedicated to a molecule formed from the succinic anhydride grafted on Eu-Feeds after scission of a C-C bond of the corncob material, such as



The assumption was reinforced and confirmed by theoretical chemical displacements. From the areas of each of these signals and weight of material recovered after reaction, less than 1% of grafted units were solubilized at 60°C and pH 6.2. The $^{13}\text{C-NMR}$ spectrum (Fig. 8) confirms this assumption. Indeed, two distinct signals are observed for the two $-\text{CH}_2$ groups of the molecule issued from the grafts (32.31 and 34.38 ppm), one signal for $-\text{CH}_2$ groups from succinic anhydride

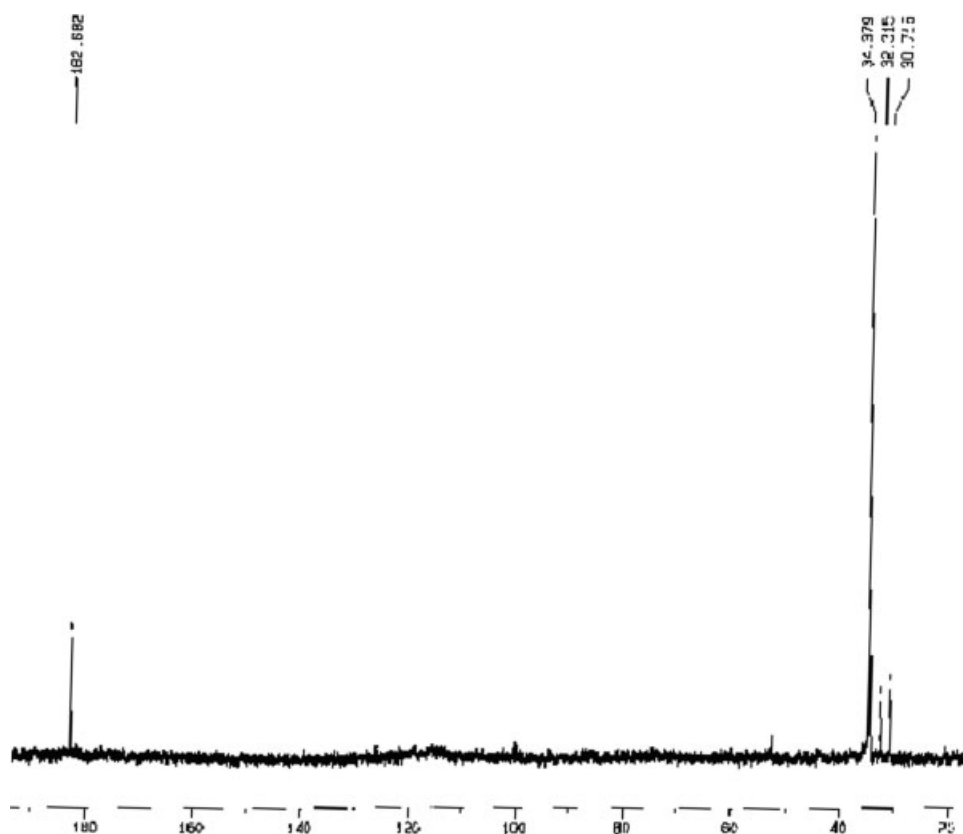


Figure 8 $^{13}\text{C-NMR}$ spectrum of filtrate.

(30.72 ppm) and a signal at 182.6 ppm, which is characteristic of C atom bearing O atom. Moreover, ^{13}C -NMR discloses the existence of a small signal around 51 ppm related to the presence of a quaternary C atom in solution. It is dedicated to carbon atom in α -position of ester function from grafted unit, which is unbound from material. It is assumed that the bond on the carbon in α -position with respect to the ester function is not stable, leading to a release in the supernatant after a too long time at high temperature.

CONCLUSIONS

We have demonstrated that water soluble polymers such as partially hydrolyzed polyacrylamides or poly(methacrylic acid) were not useable because of very low useable metal concentration and the inefficiency to be precipitated in presence of copper ions (which makes easier recovery of materials). By contrast, corncoobs modified with succinic anhydrides allow total copper retention in industrial conditions (traces of copper down to 10^{-12} mol/L, pH around 6, and high temperature). This property was kept in a wide temperature range (25–80°C), the binding process being faster at high temperature. Moreover, the use of such materials may be enlarged to wide conditions and use conditions (polymer concentration as an example) have to be optimized.

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