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Development of a heavy metal sorption system through the $P{=}S$ functionalization of coconut (*Cocos nucifera*) fibers

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ABSTRACT

Lignocellulosic residues are interesting materials for the production of heavy metal adsorbents for aquatic systems. Whole fibers taken from coconut (*Cocos nucifera*) husks were functionalized with the thiophosphoryl ($P{=}S$) group by means of the direct reaction with $Cl_3P{=}S$, $(CH_3O)_2ClP{=}S$ or $(CH_3CH_2O)_2ClP{=}S$ in order to obtain an adsorptive system for 'soft' metal ions, particularly Cd^{2+}. These functionalized fibers (FFs) were characterized by means of elemental analysis, infrared spectroscopy, thermal analysis and acid–base titration. Adsorption isotherms for Cd^{2+} fitted the Langmuir model, with binding capacities of 0.2–5 mmol g^{-1} of FF at 25 °C.

1. Introduction

Traditional methods for heavy metal removal from aqueous systems, such as ion exchange, reverse osmosis, charcoal adsorption and chemical precipitation are expensive and inefficient for the treatment of large amounts of water with low concentrations of toxic species (Min et al., 2004). Sorption systems developed from residues from agro-industrial activities are very attractive alternatives for environmental remediation.

Lignocellulosic polymers are the most abundant biopolymers in the biosphere. They are structural elements of wood and other plant materials. Coconut (*Cocos nucifera*) husk is attractive due to the high proportion of well-defined polymeric structures in its composition: the polysaccharides cellulose and hemicellulose, and lignin (*ca.* 28%, 38% and 32.8%, respectively (Pollard et al., 1992)). These polymers show affinity for metal complexation (Min et al., 2004; Marmiroli et al., 2005), and are involved in the metabolic mobilization of metals (Guillon et al., 2001; Dupont et al., 2004) and in the control of their oxidation states in the environment (Dupont et al., 2004). Coconut fibers offer cost-effective advantages as a toxic metal sequestering medium for environmental applications (Hasany and Ahmad, 2006; Sousa et al., 2007).

Coconut fibers have metal adsorption capacity as a result of both ion exchange and chemical coordination processes at appropriate sites, however, with low selectivity (Latif and Jaafar, 1989; Espinola et al., 1998, 1999; Omgbu et al., 1998; Hasany and Ahmad, 2004, 2006). In order to improve their adsorption capacity by means of adding new coordination sites for the metal, a number of functionalization strategies have been devised (Table 1). Low and colleagues (1997) produced functionalized coconut fibers with aminopolycarboxylates (nitrilotriacetate and EDTA), formaldehyde and phosphoryl chloride ($POCl_3$). Sreedhar and Anirudhan (2000) prepared an acrylamide copolymer with coconut fiber to produce a sorption system for Hg^{2+}. In spite of interesting results, the reaction requires the acrylamide monomer, which is highly toxic. Baes and colleagues (1996) activated coconut fibers with sulfuric acid and formaldehyde as a cross-linking agent. The final product showed high affinity for Cu^{2+} and Pb^{2+}.

Ligands that display the thiophosphoryl function, $P{=}S$, such as Cyanex302® (Chart 1) are marketed as chelators for the heterogeneous extraction of metals from acid liquors in hydrometallurgical processes (Swain et al., 2007). The thiophosphoryl function and its analogues have previously been incorporated into carbohydrates (Kaushik et al., 1989; Yalpani, 1992), but in Yalpani's study the thiophosphorylating agent (TA) employed was the highly toxic and inflammable P_4S_{10}. Thiophosphoryl chloride, $Cl_3P{=}S$, is comparatively less reactive (Corbridge, 1990).

Thiophosphorylation of the whole fiber (without chemical separation of cellulose, hemicellulose and lignin) has not been attempted with *C. nucifera* fibers. The interest in this source of biopolymers arises from the increasing importance that this product has been receiving in the Brazilian market, with 57 thousand hectares planted in 2001. In addition, the increased consumption

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Table 1

Modifications to coconut fibers and their adsorption capacity for metal ions.

Modification	Cation	Metal solution[a]	Adsorption capacity (mmol g^{-1})[b]	Ref.
Natural coconut	Cd2+	dw; pH 7	2.55	Pino et al. (2006)
	Ag^+	Acetic acid/acetate 0.10 M; pH 6	0.57	Hasany and Ahmad (2004)
Acrylamide copolymer	Hg^{2+}	dw; pH 6; 60 °C	0.70	Sreedhar and Anirudhan (2000)
NTA	Cr^{3+}	dw; pH 4.5	0.50	Low et al. (1997)
EDTA	Cr^{3+}	dw; pH 4.5	N.D.	Low et al. (1997)
NaOH	Cr^{3+}	dw; pH 4.5	N.D.	Low et al. (1997)
H_2SO_4	Cr^{3+}	dw; pH 4.5	0.28	Low et al. (1997)
	Pb^{2+}	dw; pH 6	4.62	Baes et al. (1996)
	Cu^{2+}	dw; pH 6	3.58	Baes et al. (1996)
	Ni^{2+}	dw; pH 6	1.86	Baes et al. (1996)
Formaldehyde	Cr^{3+}	dw; pH 4.5	N.D.	Baes et al. (1996)
$Cl_3P{=}O$	Cr^{3+}	dw; pH 4.5	N.D.	Low et al. (1997)

[a] dw = deionized water.
[b] N.D. = not determined.

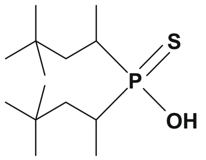

Chart 1.

of coconut water brings with it the important environmental issue of the residue destination, since 80–85% of the coconut mass is discarded (Rosa et al., 2001).

In this study, we report the reaction of the TAs $Cl_3P{=}S$, $(CH_3O)_2ClP{=}S$ or $(CH_3CH_2O)_2ClP{=}S$ with whole fibers of green coconut (*C. nucifera*) and the production of three functionalized fibers (FFs): F1 (treated with $Cl_3P{=}S$); F2 (treated with $(CH_3O)_2ClP{=}S$) and F3 (treated with $(CH_3CH_2O)_2ClP{=}S$) in order to obtain a sorption system for Cd^{2+} ions. Functionalization of whole fibers is proposed as a means to simplify the procedure. The functionalized fibers, as well as the natural precursor (FN) were characterized by means of elemental and thermal analysis, and infrared spectroscopy. In all studies, Cd^{2+} added in buffered solutions (citrate and HEPES) which may mimic the presence of environmental ligands, therefore representing better the ability of the materials to adsorb toxic metals in a real situation.

2. Methods

2.1. Materials

Coconut fibers were prepared (Rosa et al., 2001) and provided by EMBRAPA Tropical Agroindustry (Fortaleza, Brazil), dried at 80 °C for 4 h and kept in a desiccator. HEPES (sodium 4-(2-hydroxyethyl)piperazine-1-ethanesulfonate), sodium citrate tribasic, EDTA, pyridine, $CuSO_4{\cdot}5H_2O$, CaH_2, Cd^{2+} atomic absorption standard, $Cl_3P{=}S$, $(CH_3O)_2ClP{=}S$ and $(CH_3CH_2O)_2ClP{=}S$ were acquired from Sigma–Aldrich and used as received.

2.2. Instrumentation

Infrared spectra in KBr pellets were registered in a Bomem MB-100 FTIR instrument. Elemental analysis (C, H, N, S) was performed in a Perkin Elmer Series II CHNS/O 2400 analyzer. Contents of P and Cd were determined in a Spectroflame ICP-OES instrument. Thermal decomposition profiles were recorded in a Shimadzu TG 50 instrument (50 mL min^{-1} air flow, 10 °C min^{-1} heating rate). An Orion 420A+ pH meter (Thermo Electron) was used in the titration procedures. Shaking was conducted in a New Brunswick controlled environment incubator (New Brunswick Scientific).

2.3. Coupling reaction

The method was an adaptation of a literature protocol for the thiophosphorylation of cotton fiber (Kaushik et al., 1989). Two grams of coconut fiber were treated with 200 mL pyridine (previously dried over CaH_2 and freshly distilled) for 1 h at 90 °C in a two-neck flask with a mechanical stirrer and a rubber septum. Two milliliters of $PSCl_3$, $(CH_3O)_2ClP{=}S$ or $(CH_3CH_2O)_2ClP{=}S$ in glass syringes with stainless steel needles were slowly added over the suspension, and the reaction system was kept under further reflux and stirring for 2.5 h. The solid was washed with 10×100 mL distilled water and 5×100 mL ethanol, and dried under vacuum in a desiccator. For comparative purposes, the natural fiber FN was submitted to the same procedure except for the addition of the TA.

2.4. Coconut fiber acid–base titration

Samples of 1.0 g of the fibers were suspended in 50.0 mL of distilled water and titrated with 0.5 mL aliquots of NaOH 0.010 M (FN) or 0.10 M (F1, F2 and F3) under stirring at 25 °C. The titration curves were adjusted by the CurTiPot program version 3.2.3 (Gutz, 2007) (smooth = 50%; 1000 points interpolated).

2.5. Adsorption kinetics

Fiber samples (*ca.* 60 mg) were transferred to 15-mL plastic vials and treated with 5.0 mL of a buffered solution (citrate 0.05 M, Na_2HPO_4 0.10 M, pH 5; HEPES 0.02 M, pH 7) of 890 μM Cd^{2+} (prepared by the dilution of Cd^{2+} standard in buffer, filtration and pH and concentration verification prior to the measurements) and shaken (150 rpm) at 25 °C for 24 h. The supernatants were collected at regular intervals and analyzed by ICP-OES.

2.6. Competition studies with EDTA

Fiber samples (*ca.* 60 mg) were pre-treated with 5.0 mL of Cd^{2+} solution (890 μM; pH 7) for 30 min. The samples were then filtered, washed 5 times with distilled water and treated with 5.0 mL of 100 mM EDTA in 15-mL plastic vials. The vials were shaken at 150 rpm at 25 °C for 24 h, and aliquots of the supernatant were collected at intervals and analyzed for metal contents by ICP-OES.

2.7. Cd^{2+} adsorption isotherms

Fiber samples (*ca.* 100 mg) were transferred to 15-mL plastic vials and treated with 20.0 mL of Cd^{2+} solutions in citrate buffer (pH = 5), with metal concentrations ranging from 0 to 100 ppm.

The tubes were shaken at 150 rpm for 24 h at 25 °C and subsequently centrifuged at 13,000g for 5 min. Supernatants were collected and their metal contents were determined by ICP-OES. Adsorption isotherms were built according to the linearized Langmuir model described in Eq. (1) (Langmuir, 1918; Sreedhar and Anirudhan, 2000):

$$\frac{1}{q_e} = \frac{1}{c_e b q_{\max}} + \frac{1}{q_{\max}} \tag{1}$$

where q_e is the equilibrium amount adsorbed (mmol g^{-1}); c_e is the equilibrium concentration of the adsorbate (mmol L^{-1}); and $q_{\max}$ and b (L mmol^{-1}), Langmuir constants related to the maximum adsorption capacity and binding energy, respectively. These parameters are derived from the intercept ($q_{\max}$) and slope (b) of plots of $1/c_e$ versus $1/q_e$.

3. Results and discussion

The elemental composition of the fibers is shown in Table 2. It can be observed that the treatment of coconut fibers with the TAs resulted in a 7- to 10-fold increase in S content and 24- to 30-fold increase in P content, compared to FN. There was no apparent correlation between the substituent in the TA starting material (Cl, CH_3O or CH_2CH_3O) and the amount of P or S incorporated into the fiber, except for a consistent decrease in %S for F2 (similar results were found after at least two coupling attempts). P:S ratios in all three cases were roughly equal to unity, which would imply that the P═S bond remains intact after the coupling step (F1 and F3) or that at least part of the P atoms are involved in a P═S bond (F2). These results are in marked contrast with previously reported data on the coupling of cellulose from cotton fibers and $Cl_3P{=}S$, where the final P:S ratio was *ca.* 4.5 (Kaushik et al., 1989). The authors suggested that the harsh washing conditions employed in their study (boiling detergent + HCO_3^- for 3 h) might have led to the partial replacement of S by O in the phosphate ester group. Our results indicate that under gentler washing conditions, the TAs introduce the desired S atom to build the coordination site for heavy metals in coconut fibers, with negligible loss due to side reactions.

Chloride derivatives of the TAs were chosen due to the possibility of their undergoing dehydration reactions with OH groups potentially present in the components of the fiber, with the subsequent release of the strong, volatile HCl (Chart 2).

Therefore, the P═S group should have remained intact after the reaction (for $Cl_3P{=}S$, the washing step might induce further hydrolysis at the P atom). Confirming this hypothesis, in all the FFs, the IR spectra had peaks at *ca.* 680–770 cm^{-1} which can be attributed to the P═S stretching (Fig. 1) (Marsault-Herail and Tartar, 1968; Olie and Stufkens, 1976), further indicating the effective coupling of the desired function to the material. This stretching is absent in the natural, unmodified fiber FN.

Thermal decomposition events are summarized in Table 3. All the fibers underwent a slight weight loss at $t < 100$ °C (t_1), in agreement with water and/or pyridine (BP = 65 °C) elimination. In addition, the FFs had lower thermodecomposition temperatures (t_2) than FN, which is in agreement with similar experiments conducted with thiophosphorylated cotton fibers (Kaushik et al., 1989). During the functionalization process, 6-chlorodeoxycellulose may form, and this intermediate has a distinctive thermodecomposition profile (dehalogenation starts at *ca.* 200 °C). The HCl liberated during the 6-chlorodeoxycellulose decomposition is the cause of the different thermal decomposition profiles observed for FFs (not shown). This observation indicates that thermal analysis is a useful tool to characterize the proposed functionalizations. In contrast to FN, all the FFs showed 3–5% mass residue at 900 °C, suggesting the formation of stable phosphates, oxides or sulfates at this temperature.

According to the kinetic profiles (Fig. 2), after 10 min most of the Cd^{2+} present in solution was adsorbed by the fibers at both pH 5 and 7. The difference in the amounts of adsorbed metal at different pH values may be due to the deprotonation of coordinating groups of the fibers (see below), which renders it an overall negative charge.

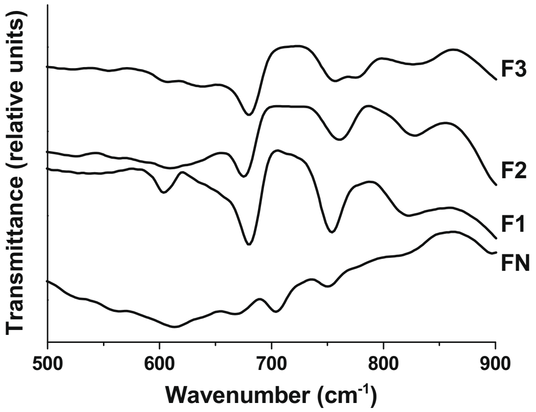

Fig. 1. Infrared spectra of the fibers in KBr pellets.

Table 2
Elemental composition of the studied fibers.

	%C	%H	%N	%S	%P	P:S
FN	46.01	5.42	1.98	0.54	0.19	0.35
F1	39.74	3.81	2.99	5.33	4.58	0.86
F2	40.27	4.50	2.31	3.55	4.98	1.40
F3	41.27	4.65	2.37	5.36	5.72	1.07

Table 3
Thermal decomposition events.

	t_1 (°C)	t_2 (°C)	Residue at 900 °C (weight%)
FN	55.01	316.40	0.03
F1	51.23	246.60	4.62
F2	49.49	271.30	4.60
F3	50.36	260.40	3.49

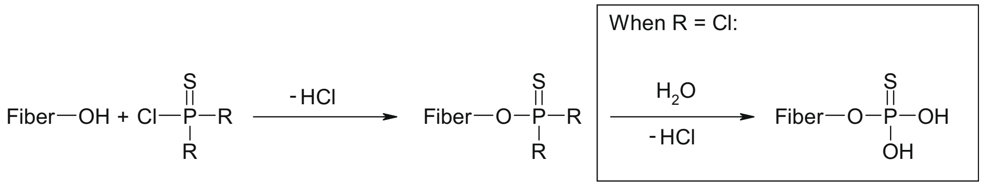

Chart 2.

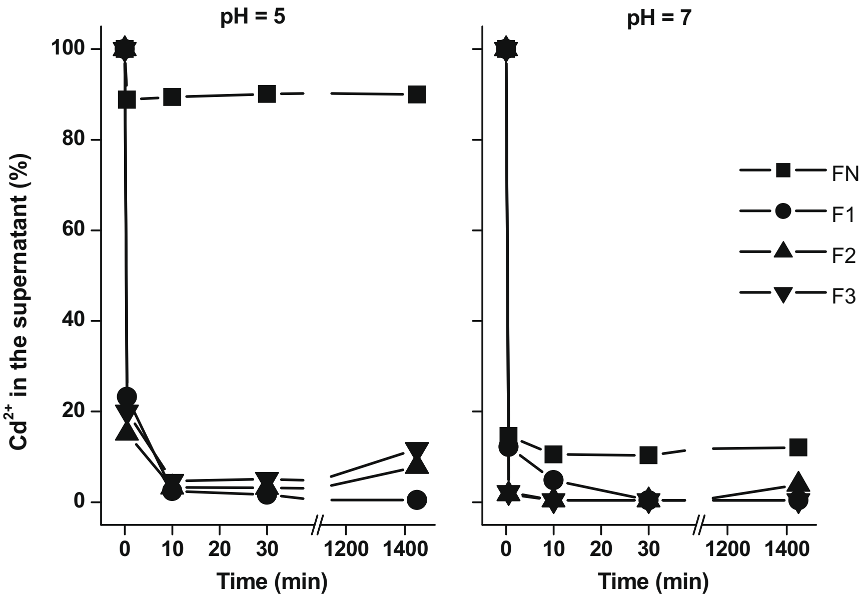

Fig. 2. Kinetic profile of Cd^{2+} adsorption by the fibers at different pH values (t = 25 °C).

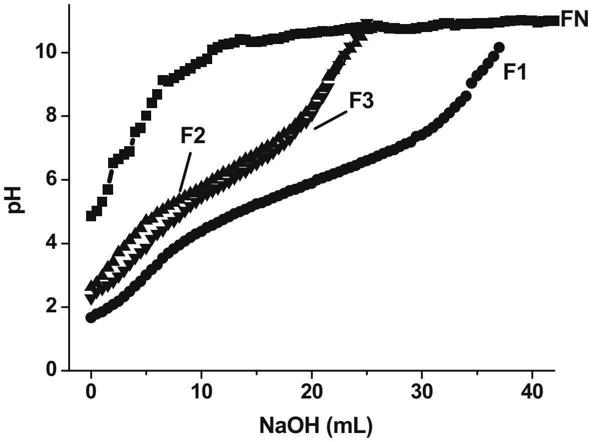

Fig. 3. Volumetric titration curves with NaOH 0.010 M (FN) or 0.10 M (F1, F2 and F3).

Fig. 3 shows the titration curve of the fibers. For FN, it is possible to derive three p*K*a values at *ca.* 5.5, 7.5 and 9.4, corresponding fairly well to reported values for carboxylic acids, phenones and phenols, respectively, present in other lignocellulosic materials (Sjöström, 1993). At pH 5, only part of the carboxylic acids will be available for metal coordination, while at pH 7 more functional groups might participate in metal sequestration. Since the proposition is a system to adsorb toxic trace metals from natural waters, which may be slightly acidic due to the decomposition of organic matter, further adsorption studies were conducted at pH 5 only.

A marked difference is observed between FN and the FFs in the titration profiles (Fig. 3). Tiophosporylation renders the coconut fibers much more acid than the natural material, which can be observed both by the pH of their aqueous suspensions (~2 for FF's against 5 for FN) and by the fact that, in order to consume equivalent volumes of the titrant, NaOH concentration was 10 times more concentrated for FF's than for FN. Therefore, at any environmentally relevant pH value, the overall charge of FF's will be more negative than that of FN, making the electrostatic component of adsorption a more important effect for them than in the case of the natural fiber.

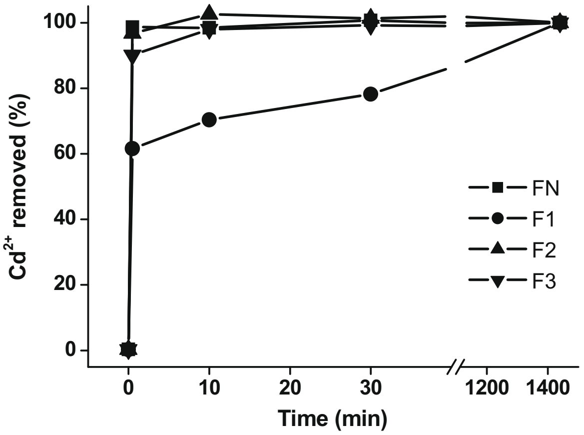

Fig. 4. Metal desorption from the fibers mediated by EDTA as a function of time (pH = 5; t = 25 °C).

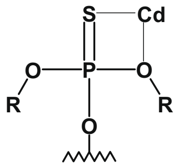

Chart 3.

Competition studies between EDTA and the fibers by Cd^{2+} ions (Fig. 4) showed that, in the first few minutes of metal extraction, only 60% of the metal bound to F1 is mobilized by the chelator, as opposed to the near completion of this process for the other fibers. This indicates that EDTA takes more time to stablish equilibrium conditions with F1-bound Cd^{2+}. If the coordination mode is identical for the three FFs, this indicates that Cd^{2+} is more strongly bound to F1 than to the other fibers.

According to the scheme shown in Chart 2, F1 is unique among the FFs since no alkyl functions are bound to the oxygen atom. In Chart 3, the structure of the resulting Cd^{2+} complex formed with

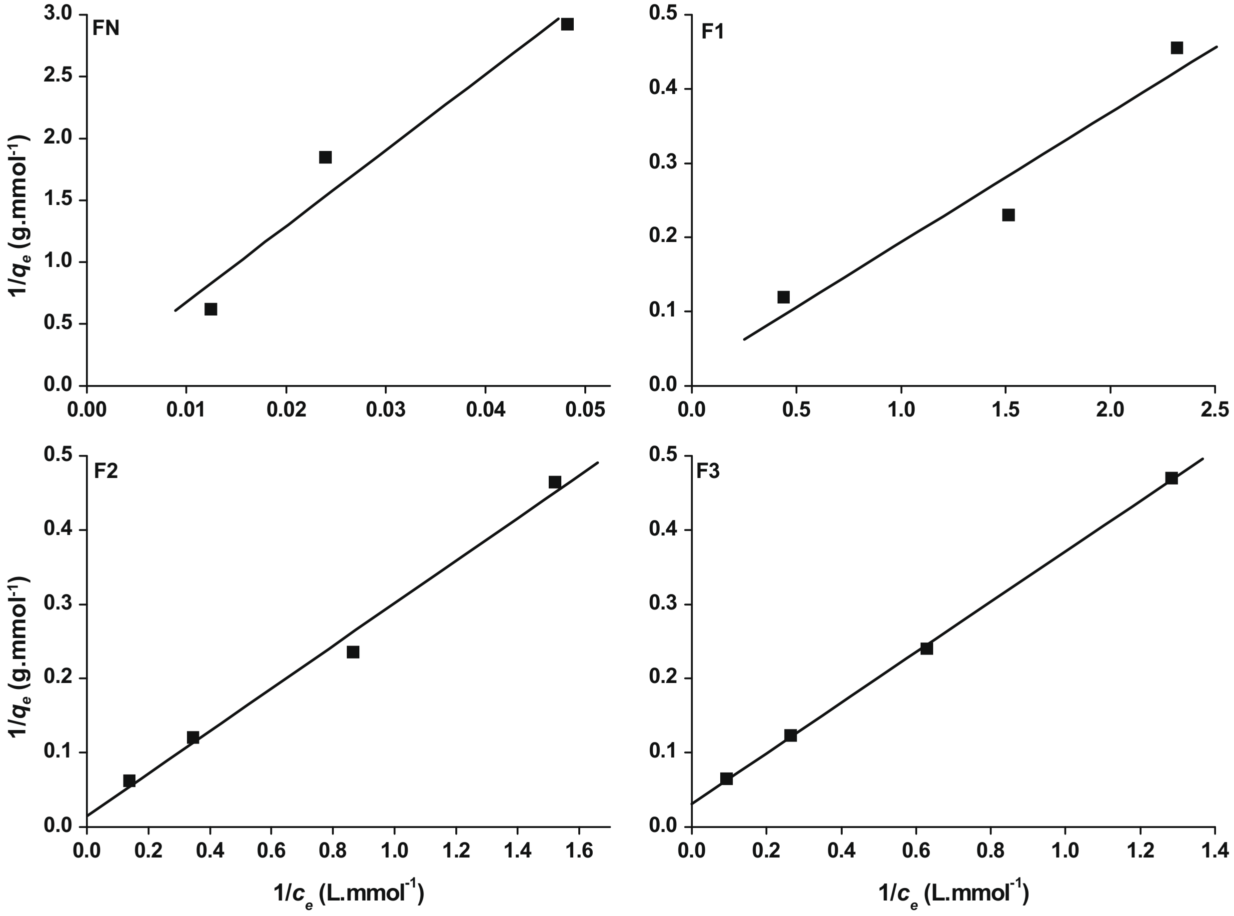

Fig. 5. Adsorption isotherms for the fibers at pH 5 and 25 °C. c_e = equilibrium concentration; q_e = amount of metal adsorbed.

the FFs is proposed. In this case, electrodonating groups such as CH_3 or CH_2CH_3 would increase the electronic density over the O atom, thus 'hardening' the base and rendering its cadmium complex less stable. Given the 'soft' character of Cd^{2+} (Pearson, 1963), it is therefore expected that the less electrodonating group (H) bound to the oxygen would provide a stronger binding site for the metal and thus explain the difference in the profiles presented in Fig. 4.

Other important contribution to explain the highest adsorption capacity of F1 is the fact that, at any environmentally relevant pH value, this fiber will have the most negative overall charge in comparison with the other fibers, as showed in the titration experiments (Fig. 3). Therefore, the unique ability of F1 to adsorb Cd^{2+} ions could be explained by a successful combination of coordination and electrostatic effects.

The Langmuir adsorption model is widely used to describe adsorbate–adsorbent equilibria and adsorption capacity for a monolayer coverage of the adsorbent at a constant temperature (Langmuir, 1918). Fig. 5 shows the adsorption isotherms for Cd^{2+} at 25 °C and pH 5. It can be observed that all the FFs adjusted well to this model, adsorbing higher amounts of Cd^{2+} than the natural fiber, with maximum binding capacities (q_{max}) of around 0.2–5.0 mmol metal/g fiber (Table 4). The F1 fiber gives a higher q_{max} for this metal than the untreated fiber at neutral pH in deionized water (Table 1; Pino et al., 2006). A comparison of F1 with other modified fibers is difficult since the studies deal with different metals (Table 1). The relatively low q_{max} values obtained in this experiment for FN, F2 and F3 may be due to the high concentration of chelating buffering agents chosen to perform our studies, which compete with the fiber binding sites for metal adsorption. The effect of a number of interfering anions (including chelators) on the percentage of Cd^{2+} sorption to unmodified coconut fiber has been previously studied (Hasany and Ahmad, 2006). Citrate alone would decrease this figure to *ca.* 7%; phosphate ions were not evaluated. If all these competing ligands are not removed from the medium, a lower adsorption capacity for all the coconut fibers would be expected. Since removing these ligands may be technically difficult and costly in a real setup (considering that their concentrations are typically more than a 100 times higher than that of the trace metals), it is proposed here that the performance of heavy metal adsorbents should be studied in a model that accommodates this effect, such as the buffered solutions employed in this study.

Table 4
Langmuir parameters for Cd^{2+} adsorption in the different fibers (pH 5, 25 °C, citrate–hydrogenphosphate buffer).

Fiber	q_{max} (mmol g^{-1})	b (L mmol^{-1})	R^2
FN	0.14	0.001	0.943
F1	4.71	0.108	0.926
F2	0.62	0.050	0.989
F3	0.28	0.092	0.999

4. Conclusions

In this study, coconut fibers were successfully functionalized in order to provide adsorbents for Cd^{2+} that offer a better performance than the unmodified fiber. In particular, fiber modification with $Cl_3P{=}S$ resulted in a material which forms stable complexes with Cd^{2+}, showing high binding capacity for this metal. The underlying objective of providing new uses for an otherwise discarded residue was therefore achieved, and this strategy may contribute to preventing the build up of solid wastes in areas close to major urban settlements.

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