

PREPARATION OF SUGARCANE BAGASSE MODIFIED WITH THE THIOPHOSPHORYL FUNCTION AND ITS CAPACITY FOR CADMIUM ADSORPTION

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Sugarcane bagasse (SCB) is an important by-product from the sucro-alcohol industry in Brazil, and it is a convenient raw material for new applications. In this study, SCB was modified with thiophosphoryl chloride in order to attach the P=S chelating moiety to the fibers, aiming at the production of a new material (SCB-F) with increased cadmium adsorption capacity. The SCB-F was characterized by elemental analysis, infrared spectrometry, thermogravimetry coupled to mass spectrometry, and acid-base titration. Adsorption isotherms for Cd(II) revealed a maximum adsorption capacity (q_{max}) of 74 mg/g, over 60 times higher than that of unmodified SCB. SCB-F thus represents a potentially interesting product for the decontamination of water bodies or effluents polluted with heavy metals.

Keywords: Sugarcane; Cadmium; Thiophosphoryl chloride; Lignocellulosic residue

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INTRODUCTION

Lignocellulosic residues are cheap and abundant raw materials for the development of several chemicals. In environmental applications they have been successfully applied for the removal of heavy metal ions from both wastewater and contaminated water bodies, taking advantage of their favorable adsorptive properties (Nghah and Hanafiah 2008).

Brazil is the leading sugarcane producer (570 million tonnes annually; 33% of the world total), with 45% of it destined to produce sugar and the remainder directed to ethanol production (60% of world consumption), mostly as a fuel for the nation's car fleet. The processing of sugarcane at Brazilian sugar mills results in 92 million tonnes of sugarcane bagasse (SCB) being produced per year (Fairbairn et al. 2010; Sales and Lima 2010), which may be recycled as a fuel in the distillation process or contribute to an important agro-industrial residue that may provide a source for several chemicals such as single-cell proteins, adhesives, dyes, furfural, urea, and solvents (Reddy and Yang 2005). Also, the removal of heavy metals from waste streams or water bodies using (granular) activated carbon prepared from SCB has been proposed for the adsorption of Au, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn ions (Johns et al. 1998; Syna and Valix 2003; Ikhuoria and Onojie 2007; Soltan et al. 2007; Giraldo-Gutierrez and Moreno-Pirajan 2008), in isolation or in mixtures, as well as organic pollutants (Marshall et al. 2000).

The adsorptive properties of SCB and other agro-industrial residues have been recently reviewed (Nghah and Hanafiah 2008). In a broad sense, metal adsorption by

unmodified SCB is more favorable than that by residues such as grass stems, wood, rice husk, corncob, and plant twigs; however, other materials such as algae derivatives, Brazil nuts, chitosan and pure lignin exhibit better adsorption properties (Basso et al. 2002; Cukierman 2007; Martin-Lara et al. 2010). Moreover, the sheer amount of SCB produced as a by-product of the sugar/ethanol industry warrants its study as a potentially important material for the remediation of metal-contaminated water bodies.

Several examples of both raw and chemically-modified forms of SCB designed to enhance their natural metal-adsorption properties have been described in the literature. The strategies applied are to bind a metal-chelator moiety to the natural fiber, and/or increase the natural chelating ability of the material. The description and thermodynamic properties of some of these materials are listed in Table 1. SCB has also been used as a solid phase extractor for Cd determination in atomic spectroscopy (Borges et al. 2006) and as an extractor of Cu and Zn in livestock wastewater (De Matos et al. 2003) or of Cr(VI) in solution (Sen and Dastidar 2010). Improvements in the performance of SCB have been achieved through acidification (Sousa et al. 2009), oxidation, carboxymethylation, succinylation (Nada and Hassan 2006; Garg et al. 2009), and amidoximation (Hassan and El-Wakil 2003).

Table 1. Chemical Derivatives of SCB that act as Metal Adsorbents and their Langmuir Adsorption Parameters (q_{\max} , maximum adsorbate amount; b , binding constant)

Modification/ Treatment	Metal	q_{\max} (mg/g)	b (L/mg)	Condition	Reference	
None	Cd	10.7	0.25	Ground, sieved 150 μm	Basso et al. 2002	
		10.1	0.25		Cukierman 2007	
		2.58	0.0178		Joseph et al. 2009	
	Pb	69.06	0.1127		Garg U et al. 2008	
		6.37	nr		Martin-Lara et al. 2010	
		11.63	0.087		Dos Santos et al. 2010	
		6.87	0.0120		Dos Santos et al. 2010	
NaOH	Cu	1.77	0.0123	Joseph et al. 2009		
		30.68	0.101	Dos Santos et al. 2010		
H ₂ SO ₄	Pb	11.87	0.0111	Dos Santos et al. 2010		
		7.30	nr	Martin-Lara et al. 2010		
Citric acid	Cu	31.53	0.00212	Dos Santos et al. 2010		
		24.89	5.44 \times 10 ⁻⁴	Fiber was neutralized with NaOH	Dos Santos et al. 2010	
		52.63	0.011	Dos Santos et al. 2010		
Anaerobically digested	Cd	35.09	0.007	Fiber was neutralized with NaOH	Dos Santos et al. 2010	
		6.0	0.280	Joseph et al. 2009		
Acrylamide copol + diethylenetria- mine	Zn	3.3	0.339	Joseph et al. 2009		
		Hg	769.2	nr	26.2% graft	Ma et al. 2010
			833.3	nr	35.0% graft	Ma et al. 2010
917.4	nr		58.3% graft	Ma et al. 2010		

Table 1. (Continued)

Modification/ Treatment	Metal	q_{\max} (mg/g)	b (L/mg)	Condition	Reference
Succinic acid	Cu	114	0.431		Karnitz et al. 2007
		185.2	0.540	Fiber was neutralized	Gurgel et al. 2008
		185.2	0.307	2×mercerized, neutralized	Gurgel et al. 2008
	Cd	196	0.103		Karnitz et al. 2007
		212.8	0.940	Fiber was neutralized	Gurgel et al. 2008
		256.4	1.700	2×mercerized, neutralized	Gurgel et al. 2008
	Pb	189	0.110		Karnitz et al. 2007
		416.7	1.000	Fiber was neutralized	Gurgel et al. 2008
		500.0	0.952	2×mercerized, neutralized	Gurgel et al. 2008
	Zn	125	0.115		Pereira et al. 2009
Succinyl- ethylenediamine	Cu	139	0.173		Karnitz et al. 2007
	Cd	164	0.068		Karnitz et al. 2007
	Pb	189	0.125		Karnitz et al. 2007
Succinyl- triethylenetetra- mine	Cu	133	0.014		Karnitz et al. 2007
		69.4	1.092	2×mercerized	Gurgel and Gil 2009
	Cd	313	0.004		Karnitz et al. 2007
		106.4	0.947	2×mercerized	Gurgel and Gil 2009
	Pb	313	0.121		Karnitz et al. 2007
		222.2	1.072	2×mercerized	Gurgel and Gil 2009
Xanthated	Cd	219	nr	Charred fiber	Homagai et al. 2010
	Pb	327	nr	Charred fiber	Homagai et al. 2010
	Ni	148	nr	Charred fiber	Homagai et al. 2010
	Zn	157	nr	Charred fiber	Homagai et al. 2010
	Cu	185	nr	Charred fiber	Homagai et al. 2010
EDTA	Zn	105.26	0.043		Pereira et al. 2010
		45.45	0.550	Zn from electroplating wastewater	Pereira et al. 2010
	Cu	56.2	0.141	pH 3	Karnitz et al. 2009
		59.2	0.367	mercerized, pH 3	Karnitz et al. 2009
		70.9	2.140	2×mercerized, pH 3	Karnitz et al. 2009
		66.7	1.950	pH 5.3	Karnitz et al. 2009
		76.9	0.807	mercerized, pH 5.3	Karnitz et al. 2009
		92.6	1.370	2×mercerized, pH 5.3	Karnitz et al. 2009
	Cd	104.0	0.525	2×mercerized, pH 3	Karnitz et al. 2009
		149.0	1.340	2×mercerized, pH 5.3	Karnitz et al. 2009
	Pb	238.0	0.600	2×mercerized, pH 3	Karnitz et al. 2009
		333.0	0.205	2×mercerized, pH 5.3	Karnitz et al. 2009
	Ca	46.1	0.965	2×mercerized, pH 5.5	Karnitz et al. 2010
54.1		5.140	2×mercerized, pH 10	Karnitz et al. 2010	
Mg	23.5	4.390	2×mercerized, pH 5.5	Karnitz et al. 2010	
	42.6	1.360	2×mercerized, pH 9	Karnitz et al. 2010	

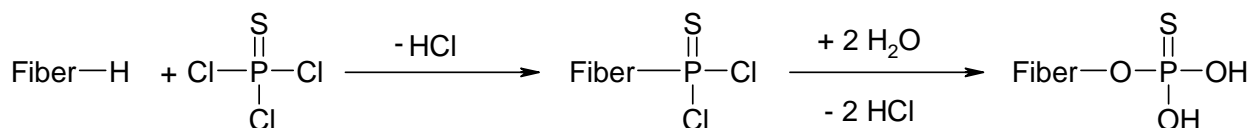
We have previously demonstrated that the introduction of a thiophosphoryl (P=S) moiety into coconut fibers increases the maximum amount of Cd binding by a factor of 30 (De Sousa et al. 2010). The thiophosphoryl chelator Cyanex302® is extensively used

in hydrometallurgical applications. Also, being a sulfur-containing chelator moiety, thiophosphoryls are of particular interesting for the removal of heavy metals from water bodies. Thus, herein we report the insertion of a P=S function into native SCB and the results of a subsequent study on the physicochemical and Cd adsorption characteristics of the modified product. We successfully obtained a modified SCB with a 64-fold increase in Cd binding capacity, thereby adding value to and providing an alternative use for this agro-industrial residue.

EXPERIMENTAL

Preparation of the Functionalized SCB (SCB-F)

SCB was procured from local producers of sugarcane syrup and was ground in a domestic blender. Fibers were dried in an oven at 100°C for 2 h, resulting in the loss of *ca.* 7% moisture. Ground fibers so treated were kept in a desiccator until use. PSCl₃ and CaH₂ were purchased from Sigma-Aldrich, and pyridine was obtained from Vetec (Brazil). The coupling reaction (Scheme 1) of the fibers with PSCl₃ is described elsewhere (De Sousa et al. 2010), starting from *ca* 1 g of SCB in 100 mL of dry pyridine and 1 mL of PSCl₃ under reflux. The product was washed with chloroform (3×10 mL), acetone (1×20 mL) and distilled water (10×10 mL), generating SCB-F. The functionalized fiber was dried in an oven at 100°C for 1 h.



Scheme 1.

Physico-chemical Characterization

Elemental analysis was performed on a Perkin-Elmer CHN 2400 (C, H, N, S) analyzer or a Spectro Ciros CCD ICP-OES (P) spectrometer. FTIR spectra were obtained on a Bomem MB100 instrument with KBr pellets. The determinations using thermogravimetry coupled to mass spectrometry (MS) were carried on an STA 409 PC Luxx – QMS 403C Aëolos system in alumina crucibles under synthetic air at a heating rate of 10°C.min⁻¹. Acid-base titrations (25°C) were performed with 1.000 g of SCB or 0.441 g of SCB dispersed in distilled water and titrated with 0.01 M NaOH (SCB) or 0.1 M NaOH (SCB-F). The pH was determined using a Gehaka PG1800 pH meter.

Cd(II) Adsorption Measurements

Cd(II) stock solutions were prepared from anhydrous CdCl₂ (Sigma) in 1% pure HNO₃ (Vetec) prepared with double-distilled water. Fiber samples (*ca* 50 mg) were transferred to Falcon tubes, treated with Cd solutions (0 to 2000 ppm final concentration) and shaken at 25°C, 150 rpm for 18 h. The tubes were centrifuged (10 min at 7000×g), and the supernatants were collected and filtered through pipette tips with cotton filling to remove debris. The Cd concentrations were determined by ICP-OES in a Spectro Ciros CCD system.

RESULTS AND DISCUSSION

Sugarcane bagasse is composed of cellulose (32 to 48%), hemicellulose (19 to 24%), and lignin (23 to 32%) (Reddy and Yang 2005). Lignin is the major metal-adsorption species in lignocellulosic materials, presenting several acidic functions such as phenols and carboxylic acids (Basso et al. 2002) that are prone to derivatization. The presence of reactive acid groups in this fiber, similar to those of coconut fibers, provided the basis for its coupling with PSCl_3 after elimination of HCl , as described by De Sousa et al. (2010) and references therein. Table 2 shows the results of the elemental analysis of the fibers before and after the functionalization.

Table 2. Elemental Analysis (%) of the Fibers

	C	H	N	P	S
SCB	44.80	6.40	0.41	0.01	<0.05
SCB-F	39.69	5.16	1.47	4.08	2.99

The composition of SCB was well within previously reported values (C: 42.4 to 46.9%; H: 5.6 to 6.2%; N: 0.1 to 1.2% (Basso et al. 2002; Cukierman 2007; Garg et al. 2008; Garg et al. 2009; Joseph et al. 2009; Karnitz et al. 2009). The hydrogen content in SCB and nitrogen content in SCB-F were slightly increased by the persistence of solvents (water or pyridine, respectively) in the final products, which was confirmed by MS determinations (see below). The P:S ratio in SCB-F was around unity, indicating that the P=S function was successfully inserted. Caution should be taken in the final wash of SCB-F, since harsh conditions may promote further hydrolysis of P=S to P=O and deplete the fiber of the crucial sulfur atom required to enhance the coordination to heavy metal ions (De Sousa et al. 2010). Indeed, in our study, we observed a slight decrease in the S content in relation to P.

The IR spectra of both fibers (Fig. 1) further illustrate the effect of thiophosphorylation on SCB. Our results are in agreement with previous attributions of the main vibrational features of SCB (Garg et al. 2008) (Table 3).

Table 3. FTIR Absorption Frequencies (cm^{-1}) for the Fibers

Adsorbent	O-H	C-H	C=O	-CH ₃	P=S
SCB	3444	2899	1738	1040	absent
SCB-F	3450	2921	absent	1039	680, 756

The complex nature of the materials under study complicates straightforward FTIR attributions. Nevertheless it was noted that the carboxylic C=O stretching at 1738 cm^{-1} disappeared upon SCB functionalization, indicating that this is a site for P=S coupling to the fiber. In addition, SCB-F exhibits two distinct peaks at 680 and 756 cm^{-1} which are indicative of P=S stretching (Marsault-Herail and Tartar 1968; Olie and Stufkens 1976).

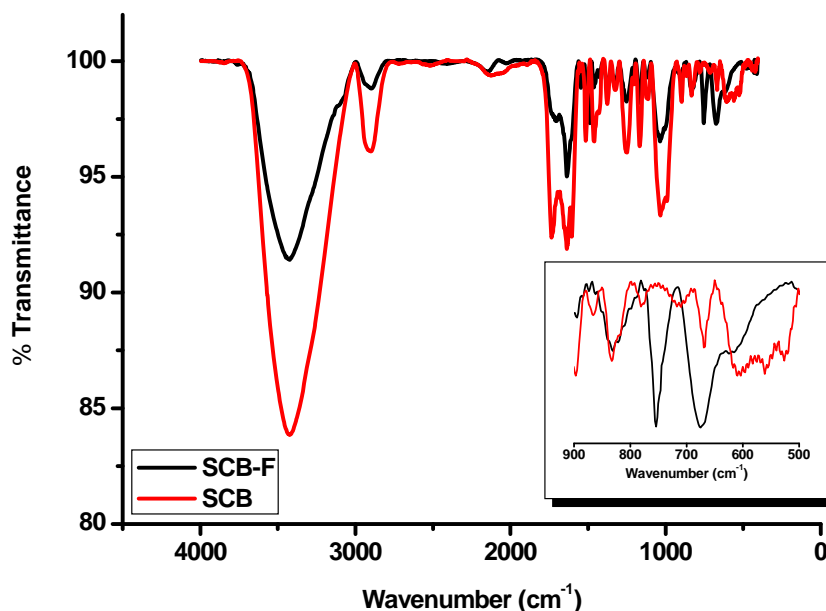


Fig. 1. FTIR spectra of SCB and SCB-F in KBr pellets. Inset: the P=S stretching frequency region

Further studies were performed on SCB and SCB-F by thermal analysis, followed by mass spectrometry characterization of the volatiles generated during decomposition (Fig. 2). At temperatures lower than 100°C, both fibers lost ca. 2.6% of adsorbed H₂O. Both types of fibers displayed two exothermic decomposition events, although at different temperatures, evidencing the different chemical natures of the materials. The first thermodecomposition event of SCB occurred at ca. 310°C, which was higher than that for SCB-F (220°C). A similar decrease in the temperature at which decomposition begins was previously observed for coconut fibers treated with PSCl₃, which may be related to the formation of chlorinated derivatives of cellulose (which have distinct decomposition profiles) during the functionalization reaction (De Sousa et al. 2010). For both fibers, this first event probably corresponds to the burning of organic material (evidenced by the generation of CO₂ and H₂O), and traces of pyridine (C₅H₅N; bp = 115°C) are released from within the SCB-F fibers.

The second thermodecomposition step occurs at higher temperatures for SCB-F (~600°C) as compared to SCB (480°C) and in the case of SCB probably corresponds to the oxidation of carbonized material, evidenced by the release of CO₂ without concomitant generation of H₂O. For SCB-F, this burning of carbon is also associated with the elimination of SO₂, which is not related to the oxidation of the thiophosphorylating agent, since PSCl₃ has a much lower boiling point (125°C). Therefore, in SCB-F the P=S group is chemically attached to the fiber and is not a simple mixture of SCB and PSCl₃.

Finally, the ash content was increased for the functionalized fiber (3.94%) as opposed to the basal 1.24% observed in SCB, which agrees with previous reports (Reddy and Yang 2005) and is consistent with the formation of solid, inorganic phosphates.

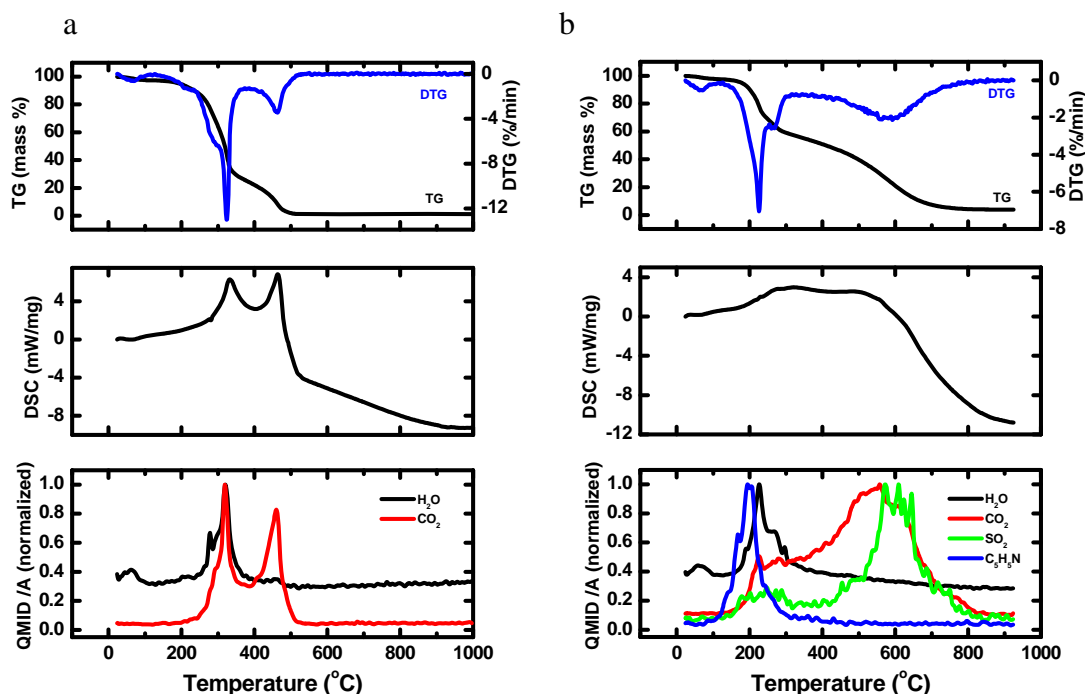


Fig. 2. Thermal analysis of (a) SCB and (b) SCB-F. Upper panels: thermogravimetric (TG) and differential thermogravimetric (DTG) curves; middle panels: differential scanning calorimetry (DSC) curve; lower panels: mass spectrometry spectra for the thermal degradation products

Acid-base titration with NaOH (Fig. 3) revealed a greatly increased buffer capacity of SCB-F as compared to SCB, considering the amount of base uptake. Specifically, two acid groups are added per P=S group (see Chart 1). SCB-F has a plateau at *ca.* pH 3 (pK_{a1}) and two stoichiometric points at pH 4.5 and 9.1, giving a pK_{a2} of 6.8, which is considerably higher than that of SCB (5.7). Both pK_a figures for SCB-F are consistent with the values for other phosphorus acids such as H_3PO_3 (2.00 and 6.59, respectively) or H_3PO_4 (2.12 and 7.21, respectively).

The increase in acid content is a function of the amount of thiophosphoryl groups coupled to the fiber on a 2:1 (H^+ :P) basis (Scheme 1). Therefore, from the amount of P in SCB-F (4.08%; 1.31 mmol P/g_{fiber}; Table 2) it is possible to determine that SCB-F should have an acid content of 2.62 mmol H^+ /g_{fiber}. The second stoichiometric point (when all acid is neutralized) for SCB-F was reached with the addition of 2.15 mmol of OH^- per gram of fiber, which agrees well with the expected value. In comparison, SCB displayed only 0.1 mmol H^+ /g_{fiber}, *ca* 20× lower than its functionalized counterpart.

The adsorption of Cd ions onto SCB-F follows the Langmuir model (Eq. 1), providing a good correlation (Figure 4 and Table 4). The linearized form of the adsorption isotherm is described by Eq. 1,

$$\frac{q_e}{c_e} = \frac{bq_{max}}{1 + c_e b} \quad (1)$$

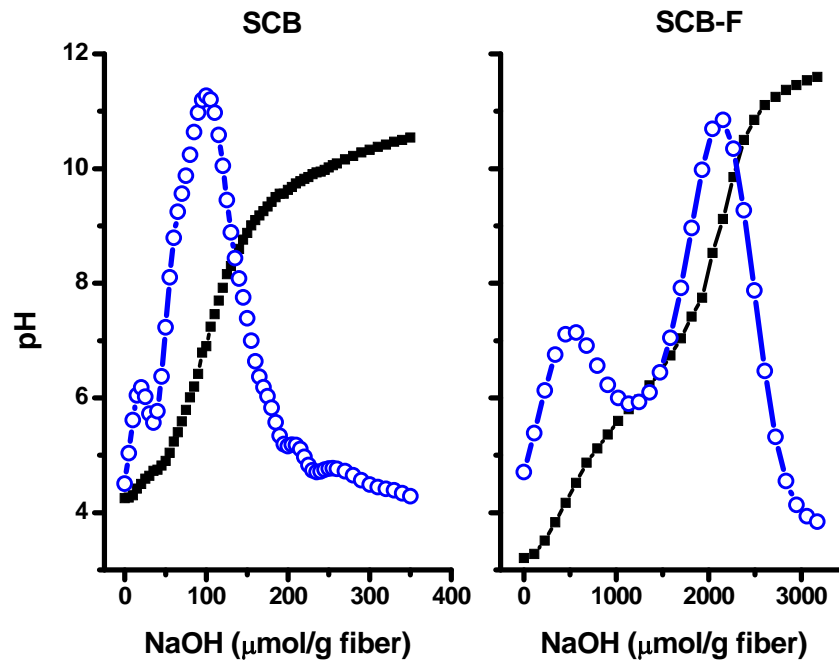


Fig. 3. Acid-base titration curves of SCB and SCB-F (filled squares) and the first derivatives (open circles)

where q_e is the amount adsorbed at equilibrium (mg/g); c_e is the equilibrium concentration of the adsorbate (mg/L); and q_{\max} and b (L/mg) are the Langmuir constants related to the maximum adsorption capacity and binding energy, respectively.

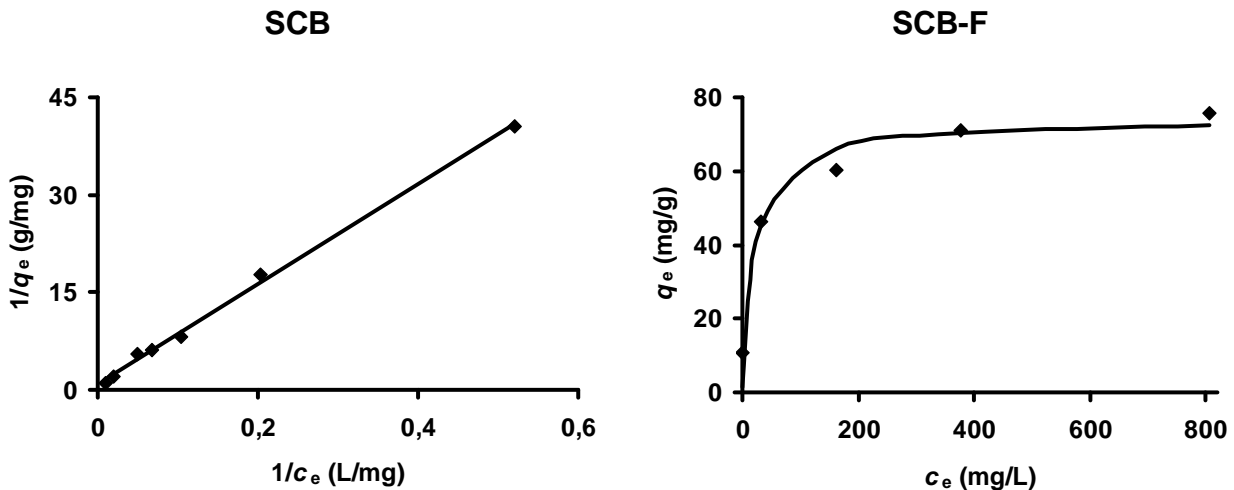


Fig. 4. Langmuir adsorption isotherms for SCB (linearized) and SCB-F (non-linearized) treated with Cd ions.

Table 4. Langmuir Parameters for the Adsorption of Cd ($t = 25^{\circ}\text{C}$)

	q_{\max} (mg/g)	b (L/mg)	r^2
SCB	1.15	0.0113	0.998
SCB-F	74.1	0.0491	0.951

A plot of $1/q_e$ against $1/c_e$ makes it possible to obtain q_{\max} (intercept) and b (slope), and this was done for the SCB starting material. Inspection of these data shows that q_{\max} of SCB-F was increased by over sixty-fold in relation to the unmodified SCB. Also, as expected, the binding constant (b) was higher for SCB-F due to the insertion of several chelator moieties.

According to the elemental analysis (Table 2), sulfur is present at a concentration of 0.93 mmol/g in SCB-F. The maximum adsorption capacity of this material for Cd indicates saturation at 0.66 mmol Cd/g, which results in a sulfur binding occupancy of 0.70. This indicates that not all available coordination sites are occupied by the metal even after prolonged (18 h) exposure, and that the most plausible metal-to-ligand ratio for the cadmium ions is 1:1, as previously proposed (De Sousa et al. 2010).

CONCLUSIONS

1. Thiophosphorylation of SCB resulted in a new material with increased adsorption properties towards cadmium in aqueous systems.
2. Functionalization of abundant lignocellulosic materials with chelator moieties tailored to heavy metals represents an interesting alternative for the use of these residues.

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