Effect of Different Wood Pretreatments on the Sorption−Desorption of Linuron and Metalaxyl by Woods

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The sorption−desorption of two different pesticides, linuron and metalaxyl, by woods was studied. Sorbent/solution ratio and sorption kinetics were also determined. Untreated wood and water, NaOH, HCl, and octadecyltrimethylammonium bromide (ODTMA) treated pine (softwood) and oak (hardwood) were used as sorbents. Linuron and metalaxyl were sorbed by untreated woods up to 80 and 40%, respectively, in a short time when the sorbent/solution ratio of 1:10 was used. Sorption of pesticides was significantly higher by pine, having higher lignin content, than by oak. Freundlich sorption constants (K_f) were 96.2 and 74.4 (linuron) and 8.28 and 4.95 (metalaxyl) for untreated pine and oak woods and increased 1.04−2.35-fold (linuron) and 1.33−2.17-fold (metalaxyl) when woods were treated. The sorption was higher by HCl- and ODTMA-treated woods. Additionally, Freundlich desorption constants also indicated greater sorption irreversibility of both pesticides for treated woods than for untreated woods. The results revealed wood residues as a promising, low-cost, and environmentally friendly material to immobilize pesticides in soils, preventing water contamination. Wood treatments aimed at removing soluble wood extracts or at modifying wood chemical structure could increase their sorption capacity.

KEYWORDS: Woods; pesticides; sorption; desorption; treated woods; water pollution

INTRODUCTION

The development of innovative and effective methods for remediation of soil and water contaminated by toxic organic compounds and/or pesticides is a research area of great interest nowadays. This development involves the investigation and selection of new sorbent materials able to retain or immobilize pollutants and, if possible, at the same time able to facilitate their later degradation to prevent the transport of such compounds in soils and hence the pollution of water (*1*).

Currently, the use of new low-cost biomaterials including biomass residues such as wheat straw, crop wastes, dead leaves, wood sawdust, tree bark, etc., is being considered. The interest is to convert them into useful products since they represent unused resources and present disposal problems (*2*). The use of these residues in remediation technologies for the immobilization of soil contaminants is attractive due to their low cost and to the possibility to effectively reuse vegetative residual biomass.

Wood residues represent one of these biomaterials. They have the advantage of being readily available in large quantities from the industrial transformation of wood or from forest wastes deriving from tree harvesting. Some studies report on the use of wood residues to remove contaminants such as dyes, oils, salts, heavy metals or persistent organic pollutants from water or to immobilize these compounds in soils (*3–9*). They might have the potential to replace more expensive traditional sorbents, activated carbon, peat, modified inorganic materials, etc. (*10, 11*).

Wood is mainly composed of cellulose, lignin, and hemicellulose. Cellulose is a linear crystalline macromolecule of hydrophilic nature and lignin is an amorphous polymeric compound of hydrophobic nature (*12*). The presence of high proportions of lignin in wood could make this latter material useful for sorbing hydrophobic organic compounds, as is the case of many pesticide used in agriculture. Some studies reported the sorption capacity of lignin for hydrocarbons and lipids (*13*), and also for pesticides in studies to determine the influence of this material, as a precursor of the soil organic matter (OM), in the behavior of these compounds in soils (*14*).

However, wood residues also contain minor organic components which are soluble in water and organic solvents. They are called extractives and comprise a large number of individual low-molecular-weigh compounds such as flavonides, tannins,

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Table 1. Characteristics of Untreated and Treated Woods

		treated woods			
wood/parameter	untreated wood	water	ODTMA	HCl	NaOH
pine (*Pinus sylvestris*)					
pH	4.5 ± 0.1	4.5 ± 0.0	4.4 ± 0.1	4.0 ± 0.2	6.0 ± 0.2
total C (%)	48.4 ± 0.57	48.4 ± 0.28	50.5 ± 2.61	50.2 ± 0.28	45.5 ± 0.69
soluble C[a] (%)	1.16 ± 0.04	0.46 ± 0.01	0.14 ± 0.00	0.26 ± 0.01	0.07 ± 0.01
H (%)	6.20 ± 0.07	6.10 ± 0.12	6.19 ± 0.18	6.19 ± 0.23	5.86 ± 0.13
N (%)	0.06 ± 0.00	0.19 ± 0.01	0.25 ± 0.01	0.08 ± 0.00	0.27 ± 0.01
O (%)	45.3 ± 0.46	45.3 ± 0.26	43.1 ± 0.35	43.5 ± 0.33	48.4 ± 0.42
oak (*Quercus rubra*)					
pH	4.0 ± 0.1	4.0 ± 0.0	3.9 ± 0.1	4.0 ± 0.1	5.9 ± 0.3
total C (%)	46.5 ± 0.98	46.5 ± 1.15	48.1 ± 0.42	47.1 ± 0.16	42.1 ± 0.16
soluble C[a] (%)	2.56 ± 0.01	0.45 ± 0.01	0.08 ± 0.00	0.41 ± 0.01	0.11 ± 0.00
H (%)	5.79 ± 0.11	6.04 ± 0.20	5.94 ± 0.15	5.95 ± 0.09	5.97 ± 0.14
N (%)	0.11 ± 0.00	0.08 ± 0.00	0.19 ± 0.01	0.11 ± 0.00	0.10 ± 0.00
O (%)	47.6 ± 0.37	47.4 ± 0.52	45.8 ± 0.13	46.8 ± 0.10	51.8 ± 0.26

[a] Determined in wood extracts (1:100 ratio) after 24 h of agitation at 20 °C and expressed as percentage of total C.

terpenes, etc, which can be regarded as nonstructural wood constituents (*12*). The presence of these compounds in solution (dissolved organic carbon, DOC) could decrease the sorption capacity of organic contaminants or pesticides by woods. In this sense, the literature contains references (*15, 16*) indicating the effect of the DOC on the sorption of hydrophobic organic compounds and/or pesticides by soils treated with organic materials.

Different treatment processes of woods with acids, bases or quaternary ammonium salts have been developed to decrease the content of organic substances in solution (*6, 17, 18*). These treatments can produce structural modification of the wood residue (*19–21*) and affect the reactivity, efficiency and sorption capacity. Wood treatment processes have been tested to evaluate the sorption of heavy metals, dyes, or aromatic hydrocarbons (*17–21*). No studies report on the effect of wood treatments on the sorption of pesticides. Pesticides have a structure with different polar groups that differentiate them from the organic compounds studied; therefore, the previous work carried out with these compounds may not be directly applicable.

The aim of this work was to study the sorption–desorption of linuron (hydrophobic) and metalaxyl (sparingly hydrophobic) by pine (softwood) and oak (hardwood) untreated and treated residues. The effect of the wood/solution ratio and the sorption kinetics of pesticides by untreated woods were determined. Treatments included washing the residues with water, NaOH, HCl or octadecyltrimethylammonium (ODTMA) solutions. Results from this investigation will contribute to improve the knowledge of the sorption capacity of pesticides by woods to advance in the use of this material in the development of new technologies at preventing the pollution of soil and water.

MATERIALS AND METHODS

Pesticides. Unlabeled and ^{14}C-labeled pesticides were used in the study. ^{14}C-Linuron (specific activity 4.13 MBq mg^{-1} and 98% purity) was supplied by International Isotopes (Munich, Germany). Unlabeled linuron was supplied by Riëdel de Haën (Hannover, Germany) (>97.5% purity). ^{14}C-Metalaxyl (specific activity = 1.37 MBq mg^{-1} and 97.2% purity) and the same pesticide unlabeled (>98% purity) were kindly supplied by Novartis Crop Protection AG (Basel, Switzerland). These compounds are solids with water solubility and log K_{ow} values of 81 μg mL^{-1} and 3.00 for linuron and 8400 μg mL^{-1} and 1.75 for metalaxyl, respectively (*22*).

Wood Samples and Pretreatment Processes. Two samples representative of the different types of woods were used in this study. Pine and oak woods were obtained from a local industry in Salamanca (Spain). The woods were used in the form of sawdust. They were

grounded in a ball mill and the fraction <1 mm was selected by sieving for the study. The experiments were carried out with natural samples (untreated woods) and with the same woods chemically treated. Four different wood treatments were performed consisting in wood washed with (1) deionized water (several times), (2) 0.5 M NaOH solution, (3) 1 N HCl solution, or (4) octadecyltrimethylammonium bromide (ODTMABr) solution of concentration 2 times the cation exchange capacity of woods. In treatments 2 and 3 woods were in contact with the solutions for 8 h at 60 °C to remove nonstructural wood constituents composed of low molecular weight compounds such as tannins, terpenes, or phenolic compounds (*12*), and in treatment 4 woods were treated to prevent the elution of phenolic compounds (*13*). After treatment 2, 3, or 4 woods were washed with deionized water several times and subsequently air-dried and kept in a controlled humidity atmosphere for later use.

Characterization of Sorbents. Characteristics of untreated pine and oak woods were presented in our previous work (*23*). Elemental composition (C, N, and H) and soluble organic carbon (DOC) content (**Table 1**) were determined using an automatic analyzer Leco CHNS-932 (Leco, St. Joseph, MI) and a Shimadzu 5050 (Shimadzu, Columbia, MD) organic carbon analyzer. The FTIR spectra of untreated and treated woods were obtained using the KBr disk technique and were recorded on a Midac M Series FTIR spectrometer (Midac Corp.). All the FTIR spectra were measured in the 4000–600 cm^{-1} range by the coaddition of 64 scans with a resolution of 4 cm^{-1}. Spectral manipulation was performed using the GRAMS/32-AI software package (Thermo-Galactic).

Sorption–Desorption Experiments. Preliminary batch sorption experiments were conducted in duplicate with untreated woods to study the effect of the sorbent/solution ratio and of sorption equilibrium time. Wood samples of 25, 50, 100, 250, 500, and 1000 mg were treated with 10 mL of an aqueous solution of each pesticide at a concentration of 25 mg L^{-1} and at an activity of 200 kBq L^{-1}. The suspensions were shaken intermittently at 2–3 h intervals for 24 h in a thermostated chamber at 20 ± 2 °C. Subsequently, the suspensions were centrifuged at 5045g for 15 min, and the pesticide concentrations were determined. The sorption kinetics of pesticides by pine and oak were determined by equilibrating wood samples of 100 mg with 10 mL of a aqueous solution of each pesticide at 25 mg L^{-1} (200 kBq L^{-1}) for time periods of 0.5, 1, 1.5, 2, 3, 8, 14, 24, 38, 43, and 72 h.

Sorption–desorption experiments were carried out with untreated and treated residues using the batch equilibrium technique. Sorption isotherms were obtained equilibrating duplicate 100 mg wood samples with 10 mL of an aqueous solution of each pesticide at concentrations of 1, 5, 10, 15, 20, and 25 mg L^{-1}. Wood-free controls were also treated in the same way as the samples to quantify the loss of compounds through mechanisms other than sorption to wood. The suspensions were shaken and centrifuged as indicated above.

Desorption isotherms of the pesticides were studied in wood samples initially treated with 25 mg L^{-1} solution of each pesticide during the

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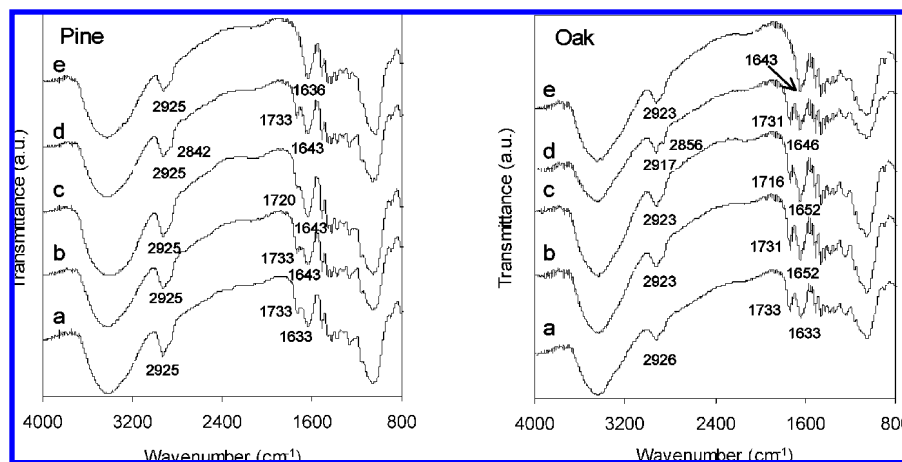
Figure 1. FTIR spectra of pine and oak woods: untreated wood (a), and woods treated with water (b), HCl (c), ODTMA (d), and NaOH (e).

sorption study by four sequential decant-refill steps. After sorption equilibrium had been reached, 5 mL was removed from the solution and immediately replaced by 5 mL of deionized water. The resuspended samples were shaken as indicated above, after which the suspensions were centrifuged and the desorbed pesticide was measured.

Pesticide Analysis. Pesticide equilibrium concentration was determined mixing 1.0 mL of supernatant solution with 4.0 mL of scintillation liquid and its activity was measured in disintegrations per minute (dpm) on a Beckman LS6500 liquid scintillation counter (Beckman Instruments Inc., Fullerton, CA). The dpm value recorded was related to the dpm obtained for the aliquots of the respective standards of the pesticide solutions. In all solutions, determinations were carried out in duplicate, and the coefficient of variation was always <2%. The amount of pesticide sorbed was considered to be the difference between that initially present in solution and that remaining after equilibration with the soil. The amount of compound sorbed by the wood at each desorption step was calculated as the difference between the initially sorbed and the initially desorbed amount. Desorption percentage was calculated as the final sorbed concentration divided by the sorbed concentration before the desorption steps. Calculations were based on the assumption that no degradation of linuron and metalaxyl occurred during sorption studies. To check this, preliminary studies using unlabeled pesticides were carried out. Determinations were performed using HPLC with a Waters chromatograph (Waters Associates, Milford, MA) following the method of Rodriguez-Cruz et al. (*10*).

RESULTS AND DISCUSSION

Characterization of Sorbents. Results from **Table 1** indicated a decrease in the amount of DOC in woods after pretreatments. This decrease varied between 60 and 94% for pine washed with water and NaOH solution, and between 82 and 97% for oak washed with water and ODTMABr solution. Total organic carbon (TOC) content was similar in water washed woods, but increased after HCl and ODTMABr treatments (4−5%) and decreased after NaOH treatment (6−9%) (**Table 1**). These variations in the contents of DOC and TOC revealed that treatments altered the wood chemical structure (*17, 20*). This was estimated by FTIR spectra analysis of the treated and untreated woods.

Spectra (**Figure 1**) indicated for all samples a broad and strong band around 3400 cm^{-1} corresponding to OH stretching vibration (not free), a strong band in the region of 2950−2800 cm^{-1} corresponding to CH stretching vibration in methyl/methylene groups, an absorption band around 1733 cm^{-1} mainly due to C=O stretching in acetyl ester groups (hemicelullose) or in unconjugated ketone and conjugated carboxylic groups (lignin), and absorption bands in the regions 1600−1500 and 1460−650 cm^{-1} attributed to

aromatic ring carbon stretching (1589, 1507 cm^{-1}), CH deformation in methyl/methylene groups (1462, 1424 cm^{-1}), and C−O deformation (1269−1238 cm^{-1}), respectively (*20, 24*). The comparison of the different spectra indicated the total removal or displacement to lower wavenumbers of C=O band at 1733 cm^{-1} in both NaOH-treated woods and the partial removal of this band in the HCl-treated woods. Furthermore, small differences in intensity of bands at 2844 and 2856 cm^{-1} in ODTMA treated woods and around 1450 cm^{-1} in all treated samples show that some changes in the chemical structure of the woods have occurred by the treatments (*20, 25*). These changes could be explained by the hydrolysis of a portion of cellulose or hemicellulose from woods cleaving glycosidic linkages (decrease of C=O band intensity after HCl treatment) (*12, 20, 24*), by the degradation of polysaccharides to aliphatic carboxylic acids (decrease of C=O band wavenumber converted to carboxylate by NaOH treatment) or by the adsorption of ODTMA organic cation with a 18C aliphatic chain by woods (increase of CH band intensity) (*12, 21, 26*).

Effect of Sorbent/Solution Ratio on Sorption. An initial sorption study was carried by untreated pine and oak woods using different sorbent/solution ratios to optimize the experimental conditions of pesticide sorption. **Figure 2** shows the variation in the amount of pesticide sorbed (Cs), expressed in mg kg^{-1} of sorbent and in percent as a function of the amount of the sorbent in suspension. An increase in the sorption of linuron by pine (from 17.1 to 86.5%) and oak (from 13.5 to 83.1%) and in the sorption of metalaxyl by the same woods [from 4.61 to 41.1% (pine) and from 2.63 to 31.8% (oak)] was observed when the wood/solution ratio was increased from 1:400 to 1:10 (weight-based). Sorption of linuron at the different sorbent/solution ratios was higher than that of metalaxyl due to the higher hydrophobic character of linuron. The increase in sorption efficiency (% sorbed pesticide) on increasing the concentration of the sorbent was initially rapid, due to greater number of available sorption sites, after which sorption became stable. However, the intensity of sorption [sorbed pesticide (mg)/amount of sorbent (kg)] decreased when the concentration of sorbent increased. Numerous investigators have also observed this fact when studying sorption of pesticides and organic compounds by soils and sediments (*27*). Four main causes have been indicated to explain this: The incomplete phase separation of colloidal-sized material, nonattainment of sorption equilibrium, the particle-induced desorption of the reversibly sorbed fraction of organic compound, and aggregation of
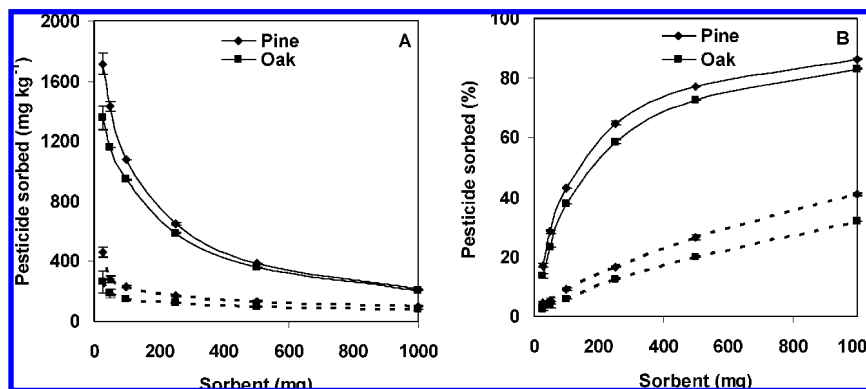
Figure 2. Influence of the sorbent amount in suspension on the sorption of linuron (solid line) and metalaxyl (dashed line) by woods. Pesticide sorbed is expressed in mg kg^{-1} of sorbent (**A**) and in percentage (**B**). Bars represent ± standard deviation of the mean. (Solution volume = 10 mL, initial concentration of pesticides = 25 mg L^{-1}.)
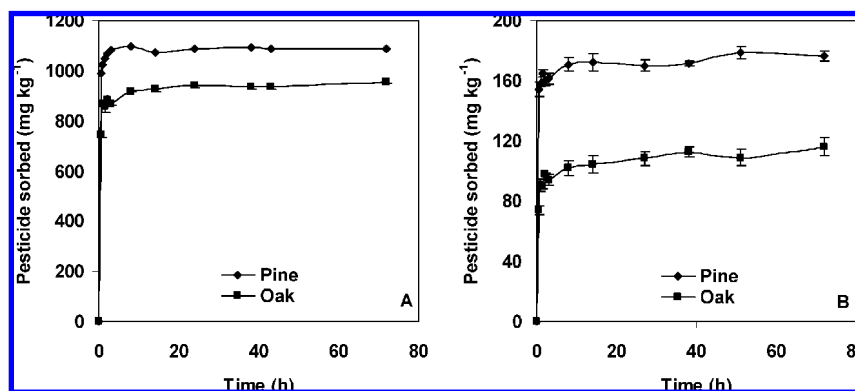
Figure 3. Sorption kinetics of linuron (**A**) and metalaxyl (**B**) by woods. Bars represent ± standard deviation of the mean.

Table 2. Sorption Rate Constants for First- (K_1) and Second-Order (K_2) Kinetics, Sorbed Maximum Amounts (Cs), and Correlation Coefficients (r^2) of These Kinetic Models

pesticide	wood	Cs^a (mg kg^{-1})	first-order kinetic model			second-order kinetic model		
			Cs^b (mg kg^{-1})	K_1 (h^{-1})	r^2	Cs^b (mg kg^{-1})	K_2 (kg mg^{-1} h^{-1})	r^2
linuron	pine	1084	392	1.864	0.93	1111	0.023	0.99
	oak	934	122	0.252	0.80	909	0.004	0.99
metalaxyl	pine	171	17.7	0.375	0.76	177	0.019	0.99
	oak	110	28.5	0.172	0.87	105	0.011	0.99

^{a} Amount sorbed determined experimentally. ^{b} Amount sorbed calculated from kinetic models.

particles. This last factor has been usually pointed out in studies using woods as sorbents (*6*). Aggregation of particles would cause a decrease in surface area for sorption and an increase in the diffusional path length. The increase in the diffusional path length (factor influencing the sorbent tortuosity or diffusional resistance of organic compound) (*28*) could result in nonattainment of sorption equilibrium during short-term sorption experiments. With the aim to minimize these effects a ratio of 1:100 was chosen to carry out sorption studies. The results obtained initially pointed to the good sorption capacities of the pesticides by the woods and the influence in this process of the type of wood and the nature of the pesticide used.

Sorption Kinetic Study. Sorption kinetics of pesticides by untreated woods were determined to establish the sorbent/sorbate equilibrium time before studying the sorption isotherms. A rapid initial sorption for both pesticides was followed by a much slower sorption rate to finally reach equilibrium. For linuron equilibrium was reached at about 3 or 8 h of contact between the pine or oak and the pesticide solution. In the case of metalaxyl equilibrium in presence of pine or oak was reached

after 8 h of contact between the solution and the sorbent (**Figure 3**). Mackay and Gschwend (*5*) reported also fast kinetics of sorption of toluene by pine and fir woods even when woods of different sizes were used.

First-order [log (Cs − C) = log Cs − $K_{1-sorp}t$/2.3] and pseudo-second-order [t/C = (1/$K_{2-sorp}C_s^2$) + (t/C_s)] kinetic models (*29*) were checked to calculate the kinetic parameters of sorption. Cs and *C* are the amounts of pesticide sorbed (mg kg^{-1}) by the wood samples at equilibrium and at time *t*. K_{1-sorp} and K_{2-sorp} are the first-order (h^{-1}) and second-order (kg mg^{-1} h^{-1}) rate constants. The maximum amounts sorbed (Cs) and the rate constants for the two models were determined from linear plots of the previous equations. **Table 2** shows the values of these parameters, together with the correlation coefficients obtained for all the systems. The results obtained indicated that the sorption kinetics was better described by the pseudo-second-order process.

Sorption rate constants for both pesticides were higher by pine than by oak wood. In our previous work (*23*) we indicated that lignin is the component responsible for the sorption of these pesticides by woods and pine wood has higher lignin content

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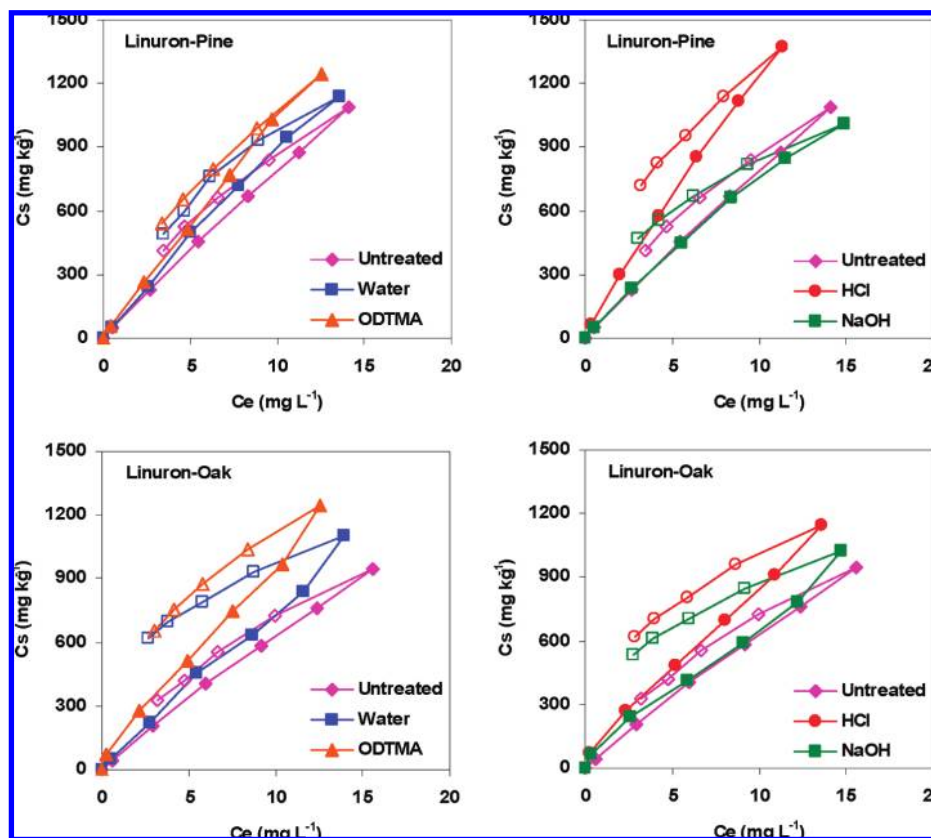
Figure 4. Sorption−desorption isotherms of linuron by untreated and treated pine and oak woods (solid symbols correspond to sorption and open symbols to desorption).

(24.4%) than oak wood (18.2%). Sorption equilibrium conditions must occur by sorbate diffusion through the cellulose crystalline polymer of the wood until to get the intercellularly lignin-rich tissue between adjoining cellulose (*5*). The diffusion of sorbate into the matrix of lignin (three-dimensional network of polymer chains, with a relatively open, flexible structure perforated with voids) could be similar to the diffusion of organic solutes into the matrix of organic matter of soils indicated by Brusseau and Rao (*30*) to describe the sorption of organic solutes by natural sorbents. The sorption equilibrium might be limited in part by tortuous diffusion through the cellulose polymer (*5*), this process being possibly influenced by the hydrophobic character of the pesticide. Thus, rate constants in pine are higher for linuron (more hydrophobic, K_{ow} = 3.00) and in oak for metalaxyl (slightly hydrophobic, K_{ow} = 1.75). An enhanced diffusion of metalaxyl in cellulose might occur in oak with greater content in this hydrophilic polymer. The higher affinity of metalaxyl than of linuron by cellulose relative to lignin has been indicated by Rodriguez-Cruz et al. (*31*) in a study of the sorption of pesticides by woods components.

Influence of the Wood Pretreatment on the Pesticide Sorption. Figures 4 and **5** show the sorption−desorption isotherms corresponding to linuron and metalaxyl by untreated and treated woods. The sorption isotherms were in general of L-type of the Giles classification (*32*). Experimental data were well fitted to the linearized Freundlich equations for sorption (log Cs = log K_f + n_f log Ce) and desorption (log Cs = log K_{fd} + n_{fd} log Ce) with *r* values ≥0.99 and ≥0.93, respectively. K_f (mg$^{1-n_f}$ L^{n_f} kg^{-1}) and n_f and K_{fd} (mg$^{1-n_{fd}}$ L$^{n_{fd}}$ kg^{-1}) and n_{fd} are two characteristic constants of pesticide sorption and desorption, respectively. Cs (mg kg^{-1}) is the amount of pesticide sorbed, and Ce (mg L^{-1}) is the equilibrium concentration of pesticide in solution.

The n_f values obtained in the sorption of the pesticides by the untreated and treated woods varied between 0.69 and 1.00 for linuron and between 0.74 and 1.02 for metalaxyl. In general, they can be considered outside the 0.95 < n_f < 1.05 range suggested by Pignatello et al. (*33*) as suitable for an isotherm to be considered linear. The isotherms obtained can be considered nonlinear and a dual-reactive domain model of sorption of pesticides by woods (*33*) or a partitioning mechanism and additional specific interactions of pesticides with the active groups of wood components (*34*) could be used to interpret this nonlinearity.

Sorption constants of both pesticides by the untreated woods are included in **Table 3**. They are higher for pine wood with greater lignin content than for oak wood and they are also higher for the more hydrophobic pesticide linuron than for metalaxyl (*23*). After wood treatments, sorption constants increased for both pesticides. K_f values increased 1.04−1.61 times (pine) and 1.15−2.35 (oak) for linuron and 1.44−2.17 times (pine) and 1.33−1.90 (oak) for metalaxyl. For linuron the increase of sorption constants was greater for treated oak wood than for treated pine wood. Oak wood contains higher soluble C fraction than pine wood (**Table 1**), and linuron could be sorbed by this soluble C pool in untreated wood decreasing sorption. Sorption of linuron by DOC from soils amended with liquid amendments has been indicated in previous works (*35, 36*). Differences in the sorption of metalaxyl by treated pine and oak when compared with untreated woods were lesser than for linuron, being the influence of DOM in the sorption of metalaxyl lesser (*15*).

In general, K_f slightly increased in water- and NaOH-treated woods for both pesticides. This could be due to the low decrease of DOC for water treated woods and the greater decrease of TOC for alkali-treated woods (**Table 1**). Alkali-treated woods
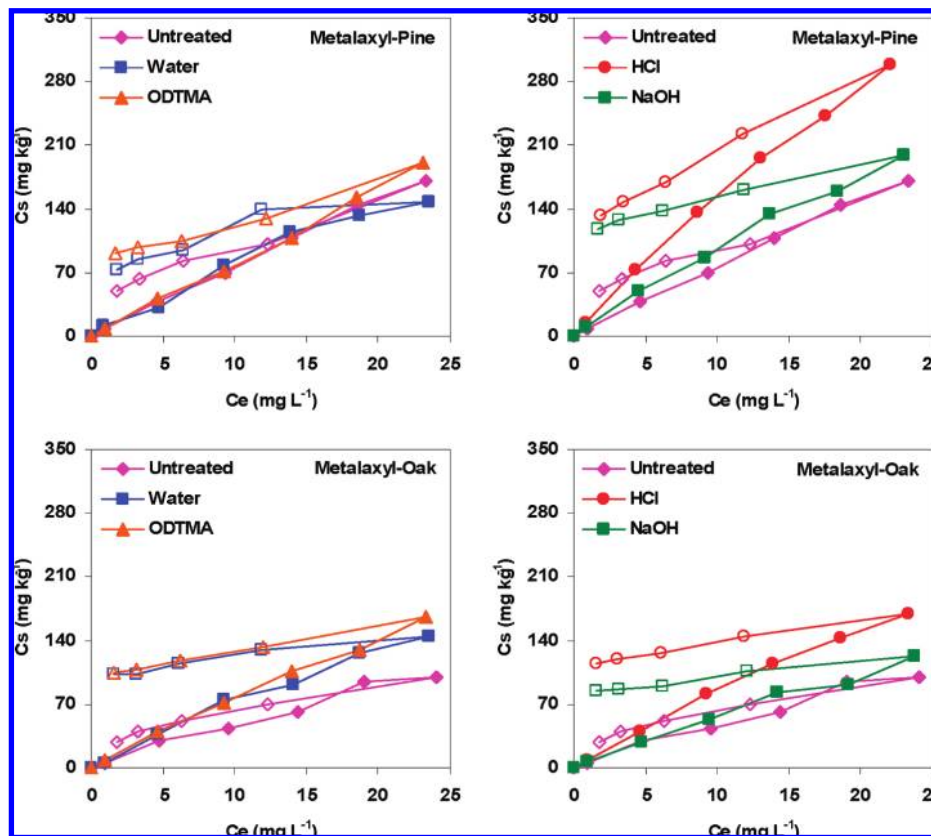
Figure 5. Sorption−desorption isotherms of metalaxyl by untreated and treated pine and oak woods (solid symbols correspond to sorption and open symbols to desorption).

Table 3. Freundlich Sorption (K_f and n_f) and Desorption (K_{fd} and n_{fd}) Coefficients of Linuron and Metalaxyl by Untreated and Treated Pine and Oak Woods, Hysteresis Coefficients (H), and Sorbed (A) and Desorbed (D) Amounts

pesticide/wood treatment	$K_f \pm SD^a$ (mg$^{1-n_f}$ L^{n_f} kg^{-1})	$n_f \pm SD$	A^b (%)	$K_{fd} \pm SD$ (mg$^{1-n_{fd}}$ L$^{n_{fd}}$ kg^{-1})	$n_{fd} \pm SD$	$H \pm SD$	D^c (%)
linuron/pine							
untreated	96.2 ± 0.07	1.00 ± 0.00	43.4	179 ± 18.3	0.68 ± 0.04	1.34 ± 0.08	62.2
water	99.7 ± 3.04	0.95 ± 0.02	45.6	236 ± 43.3	0.62 ± 0.08	1.55 ± 0.18	56.8
ODTMA	116 ± 1.02	0.95 ± 0.01	49.6	247 ± 0.13	0.64 ± 0.00	1.49 ± 0.01	56.5
HCl	155 ± 0.50	0.91 ± 0.01	54.8	400 ± 47.7	0.50 ± 0.04	1.80 ± 0.14	47.5
NaOH	97.0 ± 0.17	0.88 ± 0.00	40.4	275 ± 13.3	0.48 ± 0.02	1.82 ± 0.07	53.9
linuron/oak							
untreated	74.4 ± 0.63	0.93 ± 0.01	37.7	148 ± 9.77	0.68 ± 0.03	1.36 ± 0.05	65.1
water	85.6 ± 6.12	0.95 ± 0.04	44.1	433 ± 17.2	0.35 ± 0.02	2.71 ± 0.13	44.0
ODTMA	175 ± 0.91	0.73 ± 0.00	49.9	392 ± 0.50	0.46 ± 0.01	1.59 ± 0.02	47.6
HCl	165 ± 1.34	0.70 ± 0.00	45.8	408 ± 24.8	0.39 ± 0.02	1.78 ± 0.07	46.1
NaOH	137 ± 1.67	0.69 ± 0.00	41.0	360 ± 19.8	0.39 ± 0.02	1.79 ± 0.07	47.8
metalaxyl/pine							
untreated	8.28 ± 0.38	0.97 ± 0.01	6.81	36.4 ± 3.85	0.46 ± 0.05	2.13 ± 0.23	70.6
water	11.9 ± 0.70	0.81 ± 0.02	5.92	59.4 ± 46.2	0.30 ± 0.02	2.71 ± 0.15	51.2
ODTMA	16.1 ± 0.57	0.74 ± 0.02	7.62	72.0 ± 28.8	0.27 ± 0.01	2.74 ± 0.13	52.3
HCl	18.0 ± 0.19	0.92 ± 0.01	12.0	100 ± 12.9	0.33 ± 0.04	2.78 ± 0.37	55.8
NaOH	12.2 ± 0.11	0.90 ± 0.01	7.99	103 ± 28.5	0.19 ± 0.01	4.61 ± 0.26	40.7
metalaxyl/oak							
untreated	4.95 ± 0.71	0.98 ± 0.05	3.95	22.1 ± 0.91	0.47 ± 0.02	2.09 ± 0.10	70.9
water	6.49 ± 0.89	1.02 ± 0.07	5.75	92.9 ± 6.35	0.13 ± 0.02	7.76 ± 1.59	28.3
ODTMA	8.55 ± 1.73	0.95 ± 0.14	6.63	90.6 ± 9.39	0.17 ± 0.01	5.55 ± 0.55	37.2
HCl	9.39 ± 0.51	0.94 ± 0.03	6.76	103 ± 30.4	0.14 ± 0.01	6.54 ± 0.61	32.2
NaOH	6.56 ± 0.36	0.93 ± 0.01	4.92	75.3 ± 1.05	0.14 ± 0.05	6.68 ± 0.29	31.2

^{a} Standard deviation of duplicates. ^{b} Pesticide sorption (expressed as percentage) from an initial concentration of 25 mg L^{-1}. ^{c} Pesticide desorption (expressed as percentage) after sorption from an initial concentration of 25 mg L^{-1}.

must increase its polar character and therefore its polarity index [(O + N)/C] as observed by Huang et al. (*20*). Some studies (*37, 38*) indicated that sorption of organic compounds decreased when polarity index of sorbents increased.

The highest increase of K_f was seen for HCl and ODTMABr treatments. HCl could hydrolyze the soluble extracts fraction of hemicellulose, increasing the relative percentage of lignin (aromatic carbon) (*17*), which is the main wood component

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responsible for the sorption of non ionic pesticides (*5, 23, 39*). Huang et al. (*20*) also found that increased sorption of PAH by acid hydrolyzed wood was due to a facilitated access of PAH molecules to the hydrolyzed wood aromatic cores.

Treatment with ODTMABr might increase the hydrophobic surface of wood by cation exchange of the organic cation ODTMA, and enhance the sorption of pesticides as indicated for other inorganic materials modified with this organic cation (*11*). The same increase of hydrophobicity was shown to occur with woods modified with fatty acids and vegetable oils (*18*) for the treatment of oil spills and with quaternized wood for removal of dyes (*40*).

Desorption isotherms of pesticides from woods (**Figures 4** and **5**) showed hysteresis. Hysteresis coefficients, *H*, determined as the n_f/n_{fd} ratio are reported in **Table 3**. These *H* values increased for the pesticide desorption from the treated woods indicating an increase in the sorption irreversibility after treatments. Therefore, the K_{fd} values, i.e., sorbed amounts of pesticides after desorption, were greater for treated wood samples than those from untreated wood samples (1.3−3-fold for linuron and 1.6−5-fold for metalaxyl). A greater irreversibility of PAH sorption from hydrolyzed woods has been also found by Huang et al. (*20*) and attributed by these authors as due to a much more condensed matrix of the treated woods.

The amount of pesticide sorbed by the different woods at an initial concentration of 25 mg L^{-1}, corresponding to the maximum concentration of pesticide used in the isotherms, varied between 37.7 and 54.8% (linuron) and between 3.95 and 12.0% (metalaxyl) (**Table 3**). These sorbed amounts are higher than those obtained in the sorption of the same pesticides by natural inorganic materials like low-cost natural clay minerals, and in the range obtained using ODTMA modified clay minerals proposed as sorbents of the pesticides studied in our previous papers (*10, 11*). The amount of pesticide desorbed after four desorption cycles from the treated wood was lower than that from the untreated wood and varied between 44.0 and 65.1% (linuron) and between 28.3 and 70.9% (metalaxyl) (**Table 3**). Desorbed amounts from treated woods were in general lesser than those from low cost clay minerals modified with ODTMA (*11*).

In summary, pine and oak woods could be used as natural sorbents in the immobilization of pesticides from different scenarios of pollution and to reduce pesticide flows into surface and groundwater. Results indicated the influence of type of wood (greater sorption by pine wood with higher lignin content) and the nature of pesticide (greater sorption for the more hydrophobic pesticide linuron). The sorption−desorption isotherms indicated that treatment of wood increased pesticide sorption and decreased sorption irreversibility. Treatments with HCl and ODTMA produced the highest sorption capacity of wood due to the induced structural changes in the original materials. Results obtained allow us to judge the potential use of woody materials as one of the sorbents that can be used to develop remediation technologies of soil and water contaminated by pesticides. These materials could be considered a low-cost alternative to more expensive materials, such as activated carbon, peat, zeolites, synthetic resins, or modified inorganic materials. However, any site application of the wood technology requires a detailed cost effectiveness analysis and the evaluation of the risks arising from wastewater production by wood treatment processes. The application of wood pretreatments must be always justified by an increase of sorption capacities of modified sorbents.

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