Characterization of Corn (*Zea mays*) Leaf Powder and Its Adsorption Properties Regarding Cu(II) and Cd(II) from Aqueous Samples

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In this study, a green adsorbent made of corn leaf powder was applied in the removal of Cu(II) and Cd(II) from water samples. The material was characterized by Fourier transform infrared (FTIR) spectroscopy, which indicated the existence of amine (1375 and 1249 cm^{-1}) and carboxylic groups (1730 cm^{-1}). Elemental analysis corroborated the results of FTIR, indicating that the substance consisted of 0.63% sulfur and 0.46% nitrogen. The NMR results indicated that thiamine and methionine may be present in the corn leaf substances, which can act in coordination with metal species. Scanning electron microscopy (SEM) indicated the existence of pores of approximately 15 μm in diameter and a homogeneous particle size. Equilibrium adsorption was attained in 5 min, and the obtained data were applied to a pseudo-second-order kinetic model (r^2 = 0.999 for Cu(II) and Cd(II)). Selective adsorption of Cu(II) was attained at pH 3.0, and the maximum adsorption capacities were attained at pH 6.0. Adsorption isotherms were adjusted to a modified Langmuir equation and the maximum number of moles adsorbed of Cu(II) and Cd(II) were 0.089 and 0.071 mmol g^{-1}, respectively. The results are superior to many materials currently employed in metal removal from aqueous samples.

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INTRODUCTION

Environmental contamination with toxic substances such as pesticides, dyes, pharmaceuticals, and potentially toxic metal species is increasing each year. This behavior can be attributed to the increasing demand for industrialized and non-industrialized products by a population that is continually increasing. High population size and the non-sustainability of production methods are primarily responsible for this environmental contamination.

Among several types of contaminants, potentially toxic and toxic metal species are responsible for numerous deleterious health effects on living organisms (Manahan 2000; Ke and Wang 2001). In addition to their effects on health, scientific interest concerning these substances has focused on the non-degradability and the possibility to overcome bioaccumulation and biomagnification processes in the environment (Manahan 2000; Caihuan and Wang 2001).

In the last two decades, several methods, such as co-precipitation reactions (Soylak *et al.* 2007; Bulut *et al.* 2008), liquid-liquid extraction (Visser *et al.* 2001; Morizono *et al.* 2011), resin adsorption (Tanco *et al.* 2002), and solid-phase extraction (Alcantara *et al.* 2004; Madrakian *et al.* 2008; Ferreira *et al.* 2011; Filho *et al.* 2013), have been successfully applied in the removal of metal species from aqueous samples. Among these methods, solid-phase extraction is still widely applied, possibly because of the development of new adsorbent materials and the possibility of anchoring different molecular ligands onto material surfaces (Alcantara *et al.* 2004; Madrakian *et al.* 2008; Mahmoud *et al.* 2010; Ferreira *et al.* 2011; Prado *et al.* 2011; Filho *et al.* 2013; Hajiaghababaei *et al.* 2013; Jorgeto *et al.* 2013).

In general, the synthesis of new materials is the attempt to attach to a solid phase surface molecules containing Lewis base atoms, such as nitrogen, sulfur, oxygen (nonbonding electron carriers), and organic groups such as carboxylic groups, which may be involved in the coordination and ion exchange process, respectively (Alcantara *et al.* 2004; Madrakian *et al.* 2008; Filho *et al.* 2013; Jorgeto *et al.* 2013). Although it is possible to create a material with the desired characteristics, the steps involved in material surface modification may generate toxic residues due to the solvents used and may also have high costs (Ferreira *et al.* 2011; Souza *et al.* 2011; Filho *et al.* 2013; Jorgetto *et al.* 2013), making large-scale production for environmental purposes impossible.

As an alternative to synthetic materials, several adsorbents that have been produced through simple treatment of organic, naturally available, materials may be applied as adsorbents in solid phase extraction procedures. Materials such as banana peels (Castro 2011), coconut shells (Souza *et al.* 2010), peanut husks and peanut hull ash (Ricordel *et al.* 2001; Liao *et al.* 2011), *Pinus* bark (Gundogdu *et al.* 2009), grasses (Hossain *et al.* 2012), sugarcane bagasse (Soliman *et al.* 2011), agricultural waste and clarified sludge (Singha and Das 2013; Naiya *et al.* 2008), and rice husk ash (Naiya *et al.* 2009a) have been applied after simple treatment in the solid-phase extraction and pre-concentration of metal species.

The extraction capacity of these natural materials is related to the existence of Lewis base atoms in their structures, which may form covalent bonds (with electron pair sharing) with metal species in solution and in the presence of carboxylic groups (Castro *et al.* 2011; Martins *et al.* 2013). In addition to their low cost and easy preparation, some of these materials can be reused for several adsorption/desorption cycles (Castro *et al.* 2011; Martins *et al.* 2013).

Because of these advantages and its high availability, in the present work a powder obtained from corn (*Zea mays*) leaf was investigated for its capacity to remove Cu(II) and Cd(II) ions from aqueous samples. Several parameters, such as pH, that influence the adsorption process, the kinetic model involved, the maximum adsorption capacity, and the point of zero charge (pHpzc) were investigated. The material surface was characterized through Fourier transform infrared (FTIR) spectroscopy, elemental analysis, and ^{13}C nuclear magnetic resonance spectroscopy (NMR) to identify groups involved in metal ion coordination and by scanning electron microscopy (SEM) to verify the particle size homogeneity.

EXPERIMENTAL

Materials

All reagents were of analytical grade. Metal ion (Cu(II) and Cd(II)) solutions were prepared daily after dissolving their respective nitrate salts (Sigma-Aldrich; Steinheim, Germany) in ultrapure water (Direct-Q system, Millipore, France). Nitric acid solution (Vetec, Brazil) was previously distilled in a quartz sub-boiling system (Marconi, Brazil). Metal standard solutions used in the spectrometer calibration were prepared after stepwise dilution from a 1000 mg L^{-1} stock solution (SpecSol, Brazil).

Methods

Adsorbent preparation

Corn leaves were collected from a local market (Botucatu City, São Paulo, Brazil) and washed carefully with ultrapure water to remove dust particles. Leaves were cut into small pieces, placed in paper bags, and left in an air circulation drying oven for 48 h at 80 °C. Dried corn leaves were minced in a ball mill using a FRITSCH Pulverisette 6 (Brazil) for 50 min at 500 rpm. After pulverization, the corn leaf powder was sieved and the fraction between 45 and 63 μm was selected to perform the experiments.

Surface characterization

Diffuse reflectance infrared Fourier transform (DRIFT) spectra of the corn leaf powder were recorded on a spectrometer (Nicolet Nexus 670, USA) equipped with a Smart Collector, using 200 scans and a resolution of 4 cm^{-1}. The FTIR spectra were obtained through the tablet method, where 1 mg of sample was mixed with 500 mg of KBr. Elemental analysis was performed using an elemental analyzer (Thermo Finnigan Flash 1112 Series EA CHNS, Italy) with 2.00 mg of corn leaf powder.

High-resolution ^{13}C-NMR spectra of the powder were obtained with a Varian INOVA spectrometer under a magnetic field of 9.4 T. Samples were spun up to 7 kHz in 7-mm silicon nitride rotors in the magic angle condition. The ^{13}C spectra were obtained from single pulse direct experiments and also from {^{1}H}-^{13}C cross polarization experiments (CP-MAS). In the direct experiments, a single π/2-pulse of 3.0 μs was used on ^{13}C, with a recycle delay of 80 s, and 1024 signals were collected. In the {^{1}H}-^{13}C cross-polarization experiments, a single π/2-pulse of 3.5 μs was used on ^{1}H with a contact time of 1 ms, a recycle delay of 2 s, and 24,000 signals were collected. High-power proton decoupling was applied during the acquisition period in direct and CP experiments. A solid adamantane sample was used as a secondary standard for the ^{13}C isotropic chemical shift and also for calibration of the {^{1}H}-^{13}C CP-MAS conditions.

Scanning electron micrographs of corn leaf particles were obtained using a FEI (Quanta 200, USA) microscope equipped with an Everhart-Thornley secondary electron detector and operating at an accelerating voltage of 10 and 12.5 kV. Sample particles were dispersed in isopropanol, and the suspension was dropped into a glass laminula that was pasted onto an aluminum surface stub. After drying, the sample was coated with gold to a thickness of ~30 nm.

Surface area investigation and pore size distribution were determined using a Micromeritics ASAP 2010 apparatus (Micromeritics Instrument Corporation) with 2.0 g of corn leaf powder.

Batch extraction procedure

The primary objective of this step was to investigate parameters related to metal/surface interactions. Aliquots containing 1.8 mL of metal solution were transferred to a 5-mL plastic tube with 0.01 g of adsorbent powder. The conditions were adjusted according to the experiment. Kinetics investigations were performed in intervals of 1 to 240 min of stirring time with metal solutions of 75 mg L^{-1}. The influence of pH on the adsorption process was investigated over a range of 1 to 6 with a stirring time set at 30 min and solution concentration kept constant at 75 mg L^{-1}. The maximum adsorption capacity was determined using 0.01 g of adsorbent with a dynamic contact time of 30 min and metal solution concentration ranging from 1 to 300 mg L^{-1}.

In all batch experiments, the supernatant was separated from the solid phase through vacuum filtration in order to minimize the contact between metal species and filter paper. Metal species (Cu(II) and Cd(II)) were determined by an atomic absorption spectrometer (Shimadzu AA6800) equipped with a flame (FAAS) and graphite-furnace (GFAAS) module after appropriate dilution. The monochromator of the equipment was adjusted to 324.7 and 228.8 nm, which are the most sensitive spectral lines for copper and cadmium, respectively. The number of divalent metal moles separated by a unit mass of adsorbent, N_f (mmol g^{-1}), was calculated based on the following equation:

$$N_f = \frac{n_i - n_s}{m} \tag{1}$$

where n_i is the initial number of moles of the metal ion in the solution phase, n_s is the number of moles of metal ion in the supernatant, after the extraction, and m is the mass of adsorbent used. The residual metal concentration in the supernatant was determined by FAAS.

To improve the characterization of the adsorbent surface, the point of zero charge (pHpzc) was determined using 20 mg of adsorbent. First, 50-mL samples of a 0.01 M NaCl solution were transferred into various Erlenmeyer flasks. Their pH was adjusted to various values between 1 to 12 by the addition of diluted HCl and NaOH solutions (Tan *et al.* 2008). The mixtures were stirred for 24 h, and the final pH of the solutions was recorded using a calibrated pH meter (Metrohm Model 827, Switzerland).

Statistical analysis

All modeling, graphics and data analysis presented in this work were built using ORIGIN PRO 8.5 software (OriginLab, USA). Variance analysis utilized the Tukey test ($P < 0.05$) using SAS Version 9 (SAS Institute, Cary, NC). The analysis of each repetition was accomplished in triplicate.

RESULTS AND DISCUSSION

Surface Characterization

To identify organic groups that may have been involved in metal coordination and/or extraction from aqueous solution, the organic corn leaf powder was subjected to FTIR analysis. The infrared spectrum of the solid sample, shown in Fig. 1, led to the identification of several important bands related to the material composition. The bands

observed in the region of 3390 and 2916 cm^{-1} were assigned to OH and CH stretch vibrations, which were expected because cellulose is the primary constituent of leaves. The presence of carboxylic groups was demonstrated by the existence of an absorption band in the region of 1730 cm^{-1}. The strong band at 1640 cm^{-1} may be assigned to OH vibration from glycoside units. Those bands that appeared at 1375 and 1249 cm^{-1} may be assigned to N-H vibration from aromatic amines. The absorption bands located from 1000 to 1200 cm^{-1} may be assigned to C-O stretching vibrations from alcoholic groups.
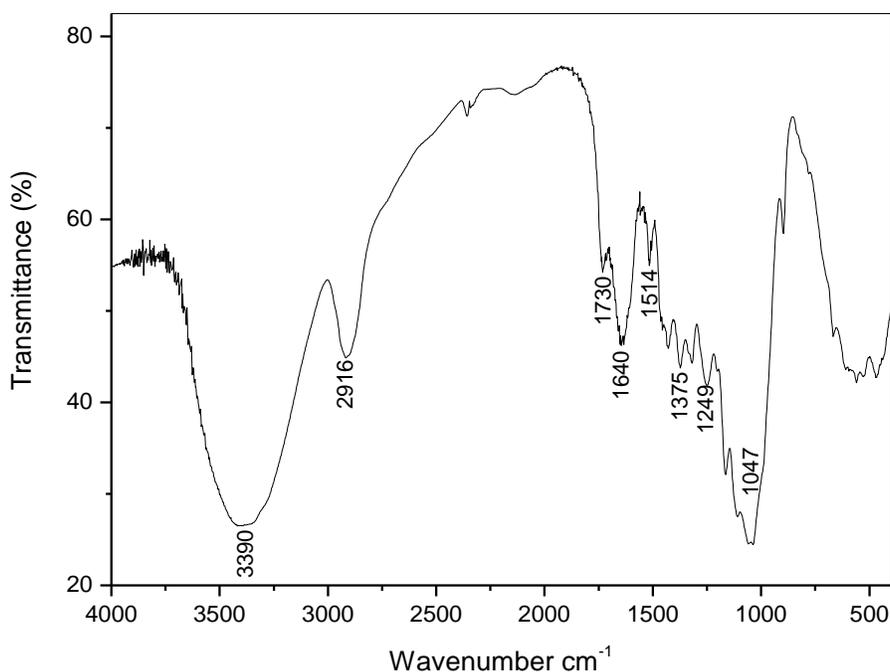

Fig. 1. Infrared spectrum of corn leaf powder with some organic group absorption bands; measuring conditions: 200 scans; resolution 4 cm^{-1}; room temperature (28 °C)

An aliquot of 2.0 mg of corn leaf powder was characterized through elemental analysis to determine the percent of total nitrogen and sulfur. Knowledge of these species is important because they can act as metal adsorptive sites. These species, among others such as oxygen, have free electron pairs (Lewis base) that can be shared with metals, resulting in coordination through covalent bonds. The results obtained through FTIR analysis were confirmed by the elemental analysis, which demonstrated the presence of nitrogen (0.46%), sulfur (0.63%), carbon (40.12%), and hydrogen (6.05%). Although there are sulfur atoms in this sample, their identification was not possible using FTIR analysis due to the low intensity of the corresponding absorption bands. Based on these results and taking into account the fact that corn leaf is a natural and organic material, it is important to keep in mind that only a fraction of total nitrogen and sulfur will be available at the particle surface to participate in the extraction reaction. Thus, elemental analysis and FTIR characterization techniques were applied to determine the potential of the material to be used in solid phase extraction procedures.

Figure 2 shows the ^{13}C-NMR spectrum of corn leaf powder. Although the spectrum obtained in the corn sample is too broad to discuss detailed resonance assignments, it is still possible to observe a good correlation between the partially resolved peaks and those

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reported in the literature for cassava husk powder (Jorgetto *et al.* 2014). The main resonance at 74.3 ppm corresponds to COH in glucoside (G) and thiamine (T). The shoulder at 62 ppm and the resolved resonance at 104.5 ppm can both be correlated with COH carbons from G. The two resonances at 174 ppm and 181 ppm corresponds respectively to COOH in methionine (M) and N=CN in T. The resonances between 146 ppm and 153 ppm can be attributed to C=C and N=C-S in T, respectively. The shoulder at 55.5 ppm corresponds to CN carbons in T and M. Shoulders at 112 ppm and 82 ppm are consistent with apiosyl (A) CO carbons observed in cassava husks. Therefore, the results indicate that thiamine and methionine may be present in the corn leaves, corroborating the results obtained by elemental analysis.
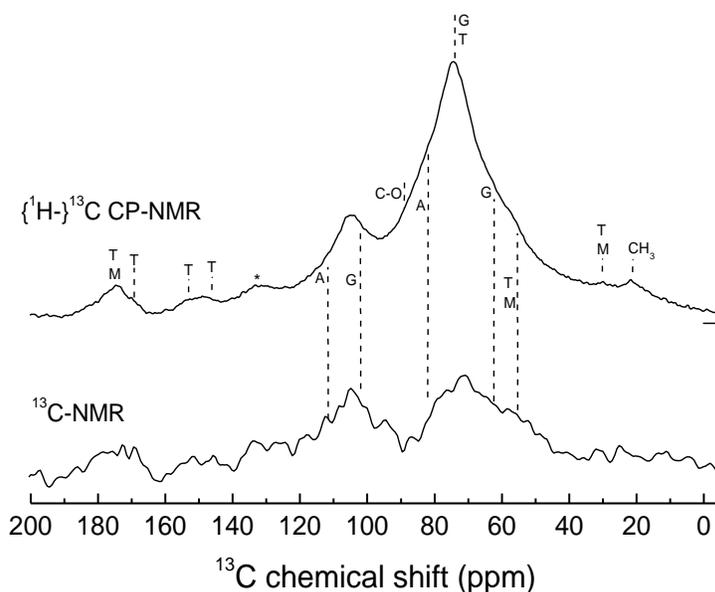

Fig. 2. ^{13}C NMR spectra obtained through {^{1}H}-^{13}C cross-polarization technique (upper trace) and with direct polarization of ^{13}C (lower trace). Code for resonance identification: T= thiamine, M= methionine, G= glucoside, A= apiosyl.

Based on the characterization performed, an illustration related to metal/surface interaction was developed and is represented in Fig. 3. Adsorption may occur at different adsorption sites, through covalent bonds with electron pair sharing with Lewis base groups or *via* ion exchange processes at carboxylic groups. As the present material is natural, the grinding process is important because it makes available some groups existing in the inner portion of the leaf and results in new pores being available, creating many small channels in the leaf structure.
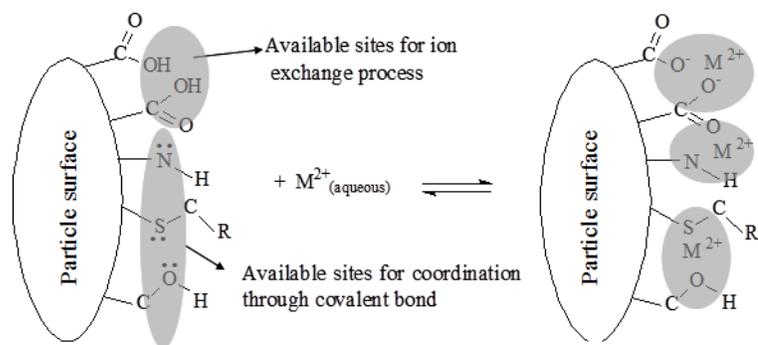
Fig. 3. Scheme of metal interaction with organic groups existing on the material surface during the adsorption process

Point of zero charge (pHpzc) is the point where the curve of the final pH *versus* the initial pH intersects the straight line corresponding to pH initial = pH final. At this point, the net surface charge of the adsorbent is 0. As shown in Fig. 4, pHpzc was determined to be 6.1. This indicates that the adsorbent acquires a positive charge below pH 6.1 due to the protonation of hydroxyl, carboxylic, and amine groups. Above pH 6.1, the material surface is negatively charged and adsorption may be favored. The pHpzc value found is slightly acidic, suggesting a predominance of acidic groups on the material surface (Jorgetto *et al.* 2014).
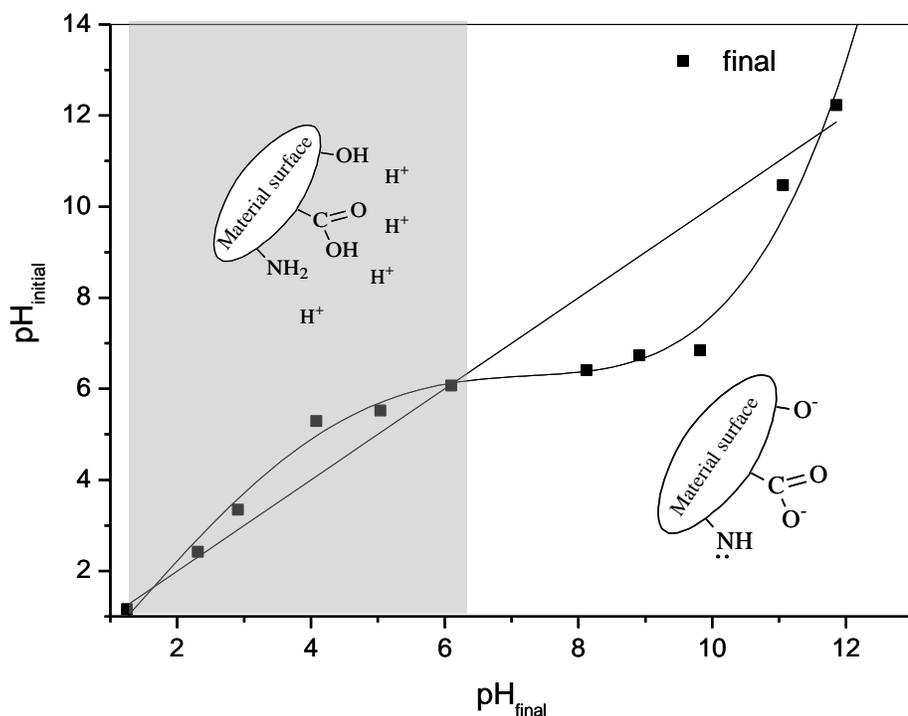

Fig. 4. Point of zero charge (pHpzc) determination for surface particles of corn leaf powder

As the obtained powder was fractionated before use, it was analyzed by SEM to determine its homogeneity. According to Fig. 5a, particle size was not homogenous and

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some particles present elongated format. Despite the low specific surface area of cellulose-based materials (Castro *et al.* 2011; Jorgetto *et al.* 2013; Martins *et al.* 2013), it is possible to observe the existence of irregular channels of approximately 10 µm in diameter (Figs. 5b, 5c, and 5d), which allowed the metal solution to contact the inner particles.
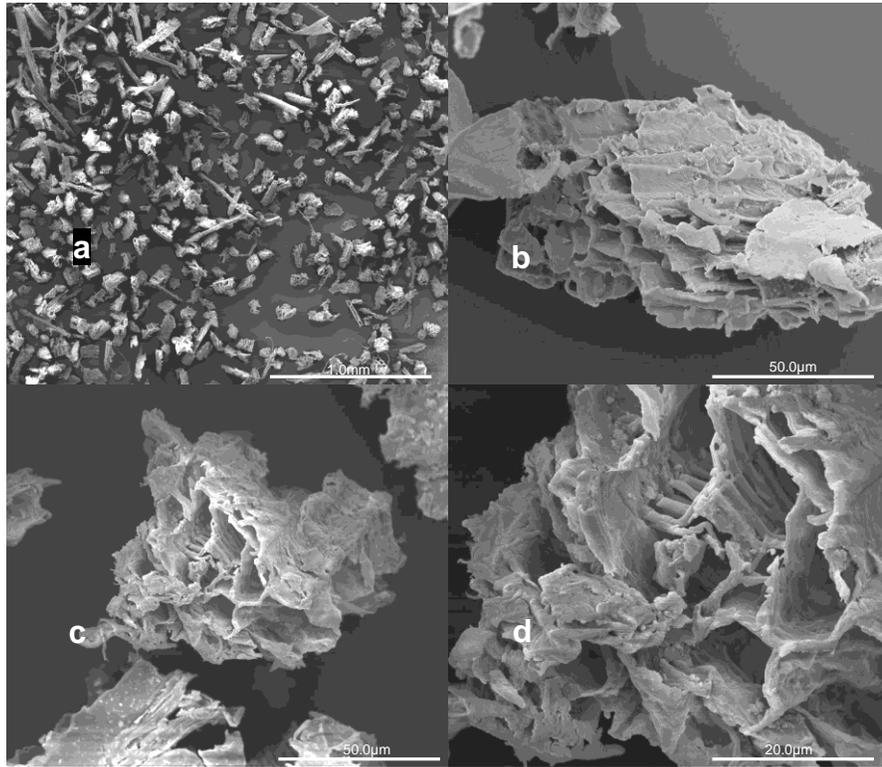

Fig. 5. SEM images of particles obtained through grinding and fractionation

The specific surface area analysis provided the value of 1.423 ±0.012 m^2 g^{-1}. As may be noted from Fig. 6 (inset), corn leaf powder does not have a great pore volume, as it is much smaller than 10^{-5} cm^3 g^{-1}, which may explain the low surface area detected. This implies that the material is practically non-porous, a fact corroborated by characteristics of the adsorption desorption isotherm, depicted in Fig. 6. The majority of pores had an average diameter of 1.0 nm, and there was also a small amount of pores with an average diameter in the range of 10 to 50 nm.
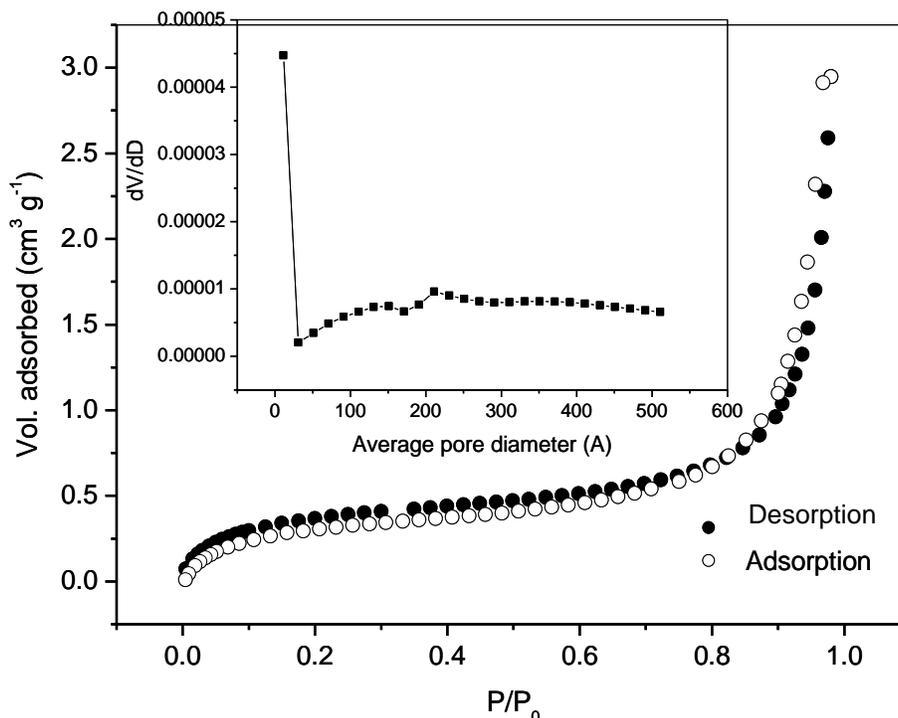
Fig. 6. Nitrogen adsorption and desorption isotherms and distribution of pore diameter (inserted figure)

Adsorption Experiments

An important characteristic of adsorbents used in solid phase extraction procedures is the time necessary to achieve sorption equilibrium. Usually, a material that presents fast kinetics may be applied to pre-concentration systems through the use of small columns filled with adsorbent; during column experiments the contact time between metal solution and solid phase is reduced. This system achieved dynamic equilibrium within 5 min. According to the literature, it is normally incorrect to use simple kinetic models like equations of first and second order to describe the adsorption by heterogeneous surface due to the fact that the transport phenomena and chemical reactions onto these surfaces be experimentally inseparable. This way the kinetic data obtained for Cu(II) and Cd(II) were applied to the pseudo-second-order (Ho and Mckay 1999) and intraparticle diffusion kinetic models (Weber and Morris 1963).

According to the literature, this model implies that metal extraction process occurs *via* coordination through free electron pair sharing from atoms of the material surface. The pseudo-second-order kinetic model in its linearized form is represented by the following equation:

$$\frac{t}{N_{ft}} = \frac{1}{K N_f{}^2} + \frac{1}{N_f} t \tag{2}$$

where N_{ft} is related to the adsorption capacity in a given time (mmol g^{-1}), K represents the adsorption rate constant, and t is the time that the mixture was stirred.

The intraparticle diffusion equation is represented by Eq. 3.

$$q_t = k_{dif}t^{1/2} + C \qquad (3)$$

where qt is the amount of adsorbed metal (mg g^{-1}), t is the stirring time (min), C is a constant related to diffusion (mg g^{-1}), and K_{dif} may be obtained by the slope of the plot (mg g^{-1} min$^{-0.5}$). In order to quantify the applicability of each model, the determination coefficient (R^2), was calculated from these plots. The obtained values are shown in Table 1.

Table 1. Obtained parameters of applied kinetic models

Metal	Pseudo-second-order			Webber and Morris		
	N_f (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	r^2	k_{dif} (mg g^{-1} min$^{-0,5}$)	C (mg g^{-1})	r^2
Cu(II)	5.213	-0.1636	0.9993	-0.0569	5.7965	0.8396
Cd(II)	7.559	0.1241	0.9998	0.0367	7.0311	0.6038

As can be seen by the determination coefficient (R^2) from Table 1, the adsorption mechanism for Cu(II) and Cd(II) followed the pseudo-second order model. Another fact attesting to good agreement with this model is the similarity of the experimental N_{ft} values, 0.085 mmol g^{-1} (5.397 mg g^{-1}) and 0.066 mmol g^{-1} (7.419 mg g^{-1}), and the calculated values, 0.082 (5.213 mg g^{-1}) and 0.067 (7.559 mg g^{-1}) mmol g^{-1}, for Cu(II) and Cd(II), respectively, indicating that chemisorption mechanism is mainly responsible for metal adsorption.

The influence of metal solution pH on the extraction process was investigated in a range of 1 to 6; experiments with pH above this value were not performed due to the risk of cation hydrolysis. Figure 6 presents a plot of the adsorption capacity as a function of pH. At lower pH values, adsorption was not favored, which may be attributed to the protonation of adsorption sites, which is more intense as pH values decrease. Similar results have also been reported in the literature for adsorbents that contain carboxylic and amine groups as adsorptive sites (Castro *et al.* 2011; Ferreira *et al.* 2011). For copper ions, at pH values from 3 to 6, the adsorption remained practically constant; for cadmium ions, adsorption occurred successfully at pH values above 5. The great difference between the behavior of these two metal species was clearly observed at pH 3.0, where Cu(II) adsorption was almost at a maximum and cadmium adsorption was almost at a minimum. This suggests that Cu(II) can easily displace hydronium ions from adsorption sites; hence, the present material may be applied in the solid extraction of Cu(II) from acidic solutions, such as industrial effluents. Another interesting application that may be exploited is the selective extraction of Cu(II) or Cd(II) by controlling the solution pH.
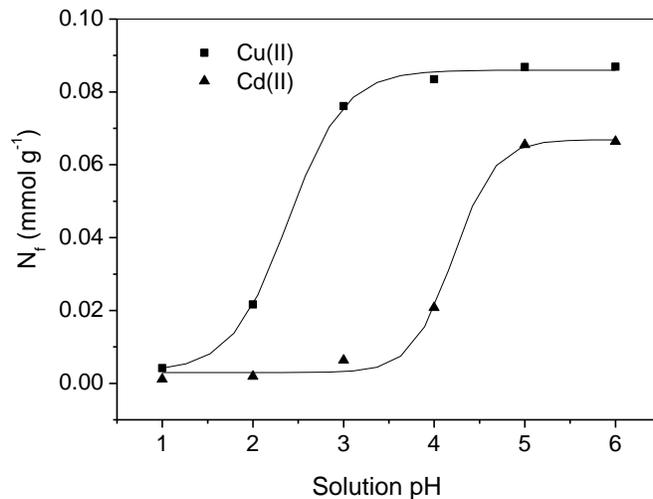
Fig. 7. Effect of solution pH on adsorption of Cu(II) and Cd(II) in aqueous medium

The ion exchange capacity of corn leaf powder was characterized by its capacity to adsorb Cu(II) and Cd(II) from aqueous solution, which was determined by the saturation range of the metal loading isotherms depicted in Fig. 8. The isotherm data were applied to the linearized Langmuir equation (Eq. 3) (Langmuir 1932):

$$\frac{C_s}{N_f} = \frac{C_s}{N_s} + \frac{1}{N_s b} \tag{3}$$

where C_s is the equilibrium solution concentration (mmol L^{-1}), N_f is the amount of metal ions adsorbed onto the material surface (mmol g^{-1}), N_s is the maximum adsorption capacity (mmol g^{-1}), which is related to the number of available adsorption sites, and b is a constant that is related to the affinity of metal ions with the solid matrix.
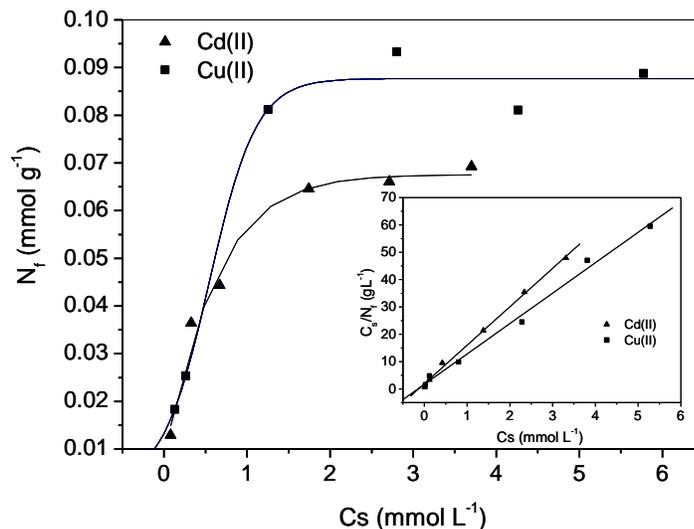

Fig. 8. Adsorption isotherms for Cu(II) and Cd(II) in aqueous solution at room temperature (28 °C) and linear shape of adsorption isotherms of Cu(II) and Cd(II) (inset)

As can be seen in the plot of C_s/N_f as a function of C_s (inset in Fig. 8), the Langmuir model presents a good agreement with the experimental data. Through this linearization, equations 4 and 5 were obtained for copper and cadmium, respectively:

$$y = 1.67 + 11.12x \tag{4}$$

$$y = 1.92 + 14.06x \tag{5}$$

Using these equations, the N_s values were obtained from the angular coefficient ($1/N_s$) as 0.089 and 0.071 mmol g^{-1} for Cu(II) and Cd(II), respectively. Because of the similarity of the N_s values with those established by the plateau attained in isotherms from Fig. 8, it is possible to infer that all or almost all existing adsorption sites at the material surface were used in the coordination of metal species.

The use of natural adsorbents has increased because their adsorption capacity has been determined to be similar to that obtained with synthetic adsorbents. Table 2 presents a comparison of the adsorption capacities of several natural and synthetic adsorbents.

Table 2. Comparison of the Cu(II) and Cd(II) Adsorption Capacity of Several Natural and Synthetic Adsorbents

Material type	Adsorption capacity (mmol g^{-1})		Ref.
	Cu(II)	Cd(II)	
Dithiooxamide-modified cellulose	0.058	0.072	(Jorgetto *et al.* 2013b)
Amidoamidoxime-modified silica	0.016	------	(Ngeontae *et al.* 2009)
Raw rice husks	------	0.076	(Kumar and Bandyopadhyay 2006)
Gaomiaozi Country bentonite	0.10	------	(Li *et al.* 2009)
Cassava husk powder	0.14	0.109	(Jorgetto *et al.* 2013a; 2014)
Coconut copra meal	------	0.044	(Ho and Ofomaja 2006)
Sawdust	0.104	------	(Li *et al.* 2006)
Clarified Sludge	------	0.32	(Naiya *et al.* 2008)
Activated alumina	------	0.31	(Naiya *et al.* 2009b)
Saw dust	------	0.23	(Naiya *et al.* 2009c)
Neem bark	------	0.227	(Naiya *et al.* 2009c)
Peanut hulls	------	0.053	(Brown *et al.* 2000)
Corn leaf powder	0.089	0.071	This study

In addition to its adsorption capacity, which is similar to that of other materials, corn leaf powder requires a very simple treatment before it can be applied in extraction. This leads to low costs and is in accordance with green chemistry principles because its production does not generate any kind of toxic residues, and it may be used for an environmental purpose.

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CONCLUSIONS

1. The characterization of corn leaf powder revealed the existence of Lewis base groups, which were demonstrated to be active in the adsorption of Cu(II) and Cd(II) ions from an aqueous medium.

2. The efficient grinding and fractionation process enabled the achievement of a homogeneous and porous material. This simple and rapid treatment makes corn leaf an attractive alternative to synthetic adsorbent materials.

3. The study of the effect of pH on the adsorption capacity demonstrated that the selective adsorption of Cu(II) may be achieved at pH 3.0, which may be useful in some industrial processes.

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