



In situ modification of activated carbons developed from a native invasive wood on removal of trace toxic metals from wastewater

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ABSTRACT

Activated carbons were developed by phosphoric acid activation of sawdust from *Prosopis rusCIFolia* wood, an indigenous invasive species of degraded lands, at moderate conditions (acid/precursor ratio = 2, 450 °C, 0.5 h). For *in situ* modification of their characteristics, either a self-generated atmosphere or flowing air was used. The activated carbons developed in the self-generated atmosphere showed higher BET surface area (2281 m²/g) and total pore volume (1.7 cm³/g) than those obtained under flowing air (1638 m²/g and 1.3 cm³/g). Conversely, the latter possessed a higher total amount of surface acidic/polar oxygen groups (2.2 meq/g) than the former (1.5 meq/g). To evaluate their metal sorption capability, adsorption isotherms of Cu(II) ion from model solutions were determined and properly described by the Langmuir model. Maximum sorption capacity (X_m) for the air-derived carbons ($X_m = 0.44$ mmol/g) almost duplicated the value for those obtained in the self-generated atmosphere ($X_m = 0.24$ mmol/g), pointing to a predominant effect of the surface functionalities on metal sequestering behaviour. The air-derived carbons also demonstrated a superior effectiveness in removing Cd(II) ions as determined from additional assays in equilibrium conditions. Accordingly, effective phosphoric acid-activated carbons from *Prosopis* wood for toxic metals removal from wastewater may be developed by *in situ* modification of their characteristics operating under flowing air.

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1. Introduction

In recent years, increasing concern over pollution of water courses arising from different anthropogenic activities has resulted in growing demand of activated carbons (ACs). They have proved to be effective for the removal of a wide variety of pollutants from aquatic ecosystems, and adsorption on ACs has been recommended to attain stringent, permissible limits for toxic metals and organic pollutants [1,2]. However, due to the expense and vast quantities of ACs required for full-scale tertiary wastewater treatment, improved, tailor-made ACs from several easily available precursors

of renewable character by different activation processes continue being investigated intensively for the sustainable production of low-cost highly effective ACs [3–17].

Prosopis rusCIFolia is a tree species indigenous to south of South America. It grows very rapidly in Chaco region, the vast plain in Argentina, Paraguay, and Bolivia. Until a few years ago, it was considered as a plague due to its ability to fast invade degraded lands turning them unproductive. A recent programme has been launched in order to control the spread of this species, and *Prosopis* wood has been introduced in the market for furniture manufacture and the timber industry [18]. In this scenario, conversion of sawdust from this wood species to ACs specifically targeted for wastewater treatment may constitute an attractive option.

Several studies in the literature have been concerned with phosphoric acid activation of lignocellulosic precursors to ACs [6,8,9,15,16,19–26]. The process has demonstrated to be particularly effective for conversion of this kind of precursors to ACs with well-developed pore structures in higher yield and at relatively lower temperatures than physical activation [27]. Most of the

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Nomenclature

C_0	metal initial concentration (mmol/L)
C_e	metal equilibrium concentration (mmol/L)
D	sample's dose (g/L)
K_L	parameter in the Langmuir model (Eq. (2)) (L/mmol)
N	number of points of experimental curves
O.F.	objective function (Eq. (4))
P	number of parameters of the isotherm model
q_e	amount of metal ion sorbed at equilibrium per unit mass of sample (mmol/g)
s	standard deviation (Eq. (5)) (%)
X_m	maximum adsorption capacity in the Langmuir model (Eq. (2)) (mmol/g)

Subscripts

calc	calculated value
exp	experimental value

studies, however, have involved thermal treatment of the impregnated precursor in inert conditions or in a restricted oxygen atmosphere.

ACs for specific use in metal removal are known to perform better when high amounts of acidic/polar oxygen groups are present on their surface. To achieve this goal, different oxidizing post-treatments of the ACs have been proposed. Yin et al. [28] have recently reviewed several techniques used to modify inherent surface functional groups for enhancing the capability and selectivity of ACs in contaminant uptakes from aqueous solutions. All of them, however, involve post-treatments of the ACs by gas- or liquid-phase oxidation using different chemical reagents. *In situ* modification of the surface characteristics of ACs during the activation process may also constitute a cost-effective alternative for the same purpose. However, it still has been scarcely examined [6,19–21,24,25].

Within this context, the present work examines the viability of employing an unexplored precursor, sawdust from a native wood species (*P. ruscifolia*), for development of ACs by phosphoric acid activation, intended for specific use in removal of trace toxic metals from wastewater. The effect of varying *in situ* the activation atmosphere involved in the thermal treatment stage of the activation process on physico-chemical characteristics and metal adsorptive behaviour of the resulting ACs was especially examined. For this purpose, ACs development was comparatively performed under mild and strong oxidation conditions. The former was attained by the atmosphere self-generated during the thermal treatment stage of the impregnated precursor, whereas the latter involved operating under a flow of air. Metal adsorption capability of the ACs developed under both atmospheres was assessed from batch assays employing dilute solutions of Cu(II) ion as a representative metal species. To further explore the metal adsorption capability of the developed ACs, additional assays were carried out using a Cd(II) ion solution at pre-established equilibrium conditions. The effectiveness of the ACs was interpreted in terms of their main physico-chemical characteristics, and compared with that determined for a commercial activated carbon.

2. Materials and methods

2.1. Preparation of the activated carbons

A piece of *P. ruscifolia* wood without bark kindly provided by GESER (Facultad de Ciencias Exactas y Naturales, Universidad

de Buenos Aires) was used for ACs preparation. It was crushed, milled, and screen-sieved. Fractions of average particle diameter of 0.75 mm were employed to obtain the ACs.

Briefly, the sawdust was impregnated with a H_3PO_4 acid aqueous solution (50 wt.%), using an acid/precursor weight ratio of 2. The impregnated samples were thermally treated at 450 °C for 0.5 h in a horizontal, fixed-bed reactor externally heated by an electric furnace. Further details of the equipment and procedure used have been reported earlier for other precursors [6,20–23]. Thermal treatment of the impregnated sawdust was carried out under either a self-generated atmosphere or a flow of air (0.1 m³/h). Air flowed through the reactor throughout the thermal treatment stage and further cooling of the samples. In order to remove the acid, the so-obtained ACs were subsequently rinsed with distilled hot water until neutral pH in the wash water was attained. Afterwards, they were dried in an oven to constant weight. Yields were evaluated from weight differences.

The ACs developed under the self-generated atmosphere and flowing air are denoted as ACS and ACF, respectively. Similar yields (40%) were attained for both atmospheres, in agreement with results reported for other precursors [6,20,23].

For the sake of comparison, a commercial activated carbon (CAC) was also used and characterized by the same methods applied to the ACs developed from *Prosopis* wood.

2.2. Characterization of the ACs

Chemical characteristics of the precursor, the ACs developed in the two activation atmospheres, and the CAC were determined by standard methods. Proximate analyses of the samples were performed according to American Society of Testing and Materials (ASTM) standards. An elemental analyzer (Carlo Erba model EA 1108) was used to assess elemental compositions of the samples.

The total and individual amounts of acidic/polar oxygen functional groups (OFGs) on the surface of the derived ACs and the commercial sample were determined following a modified procedure based on Boehm's method [20]. It enables to quantify carbonyls, phenols, lactones, and carboxyl groups by titration with a series of bases of different strength. Sodium ethoxide was used to determine the total amount of oxygen groups. Phenols, lactones, and carboxyls were quantitatively ascertained by titration with sodium hydroxide, whereas sodium bicarbonate allowed quantification of only carboxyl groups. Carbonyls were estimated by subtraction of NaOH-titrable groups from the total amount of OFGs, as determined by titration with sodium ethoxide. In turn, the quantity of phenols and lactones was evaluated by subtracting carboxyl groups from NaOH-titrable groups.

A total of 0.5 g of each sample was suspended in 50 mL of a 0.05N solution of sodium ethoxide, sodium hydroxide, or sodium bicarbonate. The slurries were stirred for 24 h and afterward filtered. A 10 mL aliquot of the resulting solutions was added to 15 mL of a 0.05N HCl acid solution. The solutions were subsequently back-titrated with 0.05N NaOH. Values are expressed as milliequivalents per gram of sample.

Besides, identification of surface functionalities of the ACs was complementary conducted by Fourier Transform Infrared (FT-IR) spectroscopy. The spectra were recorded using a Nicolet Magna IR 550 spectrometer within the wavenumber range of 400–4000 cm⁻¹. Each sample was mixed with KBr and then ground in an agate mortar at an approximate ratio of 1:100 for preparation of the pellets. The resulting mixture was finally pressed. The background obtained from a scan of pure KBr was automatically subtracted from the sample spectra.

N₂ adsorption/desorption isotherms at (–196 °C) for the derived ACs were determined with a Micromeritics surface analyzer. Tex-

tural properties were assessed from the isotherms, according to conventional procedures depicted in detail in own previous studies [20–22].

2.3. Metal adsorption experiments

The capability of the prepared ACs to remove Cu(II) ions was investigated using model dilute solutions. A stock solution (1000 mg/L) was first prepared by dissolving the necessary amount of analytical grade $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in distilled water. Afterwards, it was diluted to obtain standard solutions of concentrations ranging between 5 and 400 mg/L.

Batch adsorption experiments using particles of 325 μm -average size were carried out at a constant temperature of 28 °C and pH 6. The latter was selected on the basis of previous studies dealing with copper uptake by other developed ACs and/or commercial samples [29–31]. Concentrations of Cu(II) ion in solution were determined by UV–vis absorption spectrophotometry, according to a standard technique based on the formation of a brown compound of dithiocarbamate of Cu, followed by subsequent extraction of this compound with an organic solvent, and further analysis of the organic phase by spectrophotometry [32].

The effect of the sample's dose on adsorption of Cu(II) ions was examined by contacting different weighed amounts of each sample (0.05–1 g), including the CAC used for comparison, with 100 mL of 50 mg/L metal solutions under pre-established equilibrium conditions. Equilibrium was thoroughly verified for all the investigated systems from preliminary experiments performed for different prolonged contact times. Capped glass flasks containing the slurries were kept in a shaker at 500 rpm and controlled temperature (28 °C) for a period of 24 h. To check for any significant pH drift during the tests, the pH was recorded at the start and at the end of each experiment. No variations were determined with pH values maintained within 0.3 units. Once equilibrium was attained, the slurries were filtered through 0.45 μm membranes and metal concentrations in solution were determined as described above. The amount of Cu(II) ions sorbed at equilibrium per carbon mass unit (q_e) was calculated according to the following expression:

$$q_e = \frac{C_0 - C_e}{D} \quad (1)$$

where C_0 , C_e denote the initial and equilibrium metal concentrations, respectively, and D , the dose of sample used.

Adsorption isotherms were determined by contacting 0.4 g of each sample with 100 mL of solution of initial metal concentration in the range 5–400 mg/mL. The general procedures depicted above were followed, keeping the same experimental conditions.

Besides, to further explore the performance of the derived ACs in removing toxic metals, some additional batch assays were conducted using a dilute cadmium solution of 20 ppm initial concentration and sample's dose of 0.2 g. The solution was prepared by dissolving the necessary amount of analytical grade $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in distilled water. Concentrations of Cd(II) ion in solution were determined using a selective ion electrode (Cole-Parmer 27502-07). The same procedure and experimental conditions as those used in Cu(II) ion adsorption assays were applied. Equilibrium attainment was also thoroughly verified for these assays.

Duplicate experiments were at least conducted for every investigated system. Differences between replicates were less than 2% in all of the cases. Average values are reported. Furthermore, solute and adsorbent free blanks were used for control in all the tests.

Table 1

Proximate and elemental analyses of the sawdust from *Prosopis ruscifolia* wood used as a precursor

Proximate analysis	wt.%, dry basis
Volatile matter	75.4
Ash	2.4
Fixed carbon ^a	22.2
Elemental analysis	wt.%, dry-ash free basis
C	47.1
H	6.2
N	0.4
O ^a	46.3

^a Estimated by difference.

3. Results and discussion

Table 1 lists chemical characteristics of the precursor, whereas those of the activated carbons derived under both atmospheres and the commercial sample are summarized in Table 2. As inferred from comparison of the results in Tables 1 and 2, noticeable changes in the precursor occurred due to the activation process, in turn depending on the activation atmosphere. In particular, contents of ash and elemental oxygen of the ACF were markedly higher than those of the ACS, in agreement with the stronger oxidation conditions involved in the thermal treatment stage used in the preparation of the former.

The total and individual contents of surface acidic/polar oxygen functional groups of the derived ACs and the CAC are illustrated in Fig. 1. As observed in this figure, *in situ* modification of the activation atmosphere pronouncedly affected the development of oxygen functionalities on the carbons' surface, in agreement with

Table 2

Chemical characteristics of the activated carbons developed under the self-generated atmosphere (ACS) and flowing air (ACF), and the commercial sample (CAC)

Sample	ACS	ACF	CAC
Ash (%)	3	8	6
%C	88.0	81.1	89.4
%H	2.4	2.1	0.6
%N	0.2	0.3	0.6
%O ^a	9.4	16.5	8.9
%S	0.0	0.0	0.5

^a Estimated by difference.

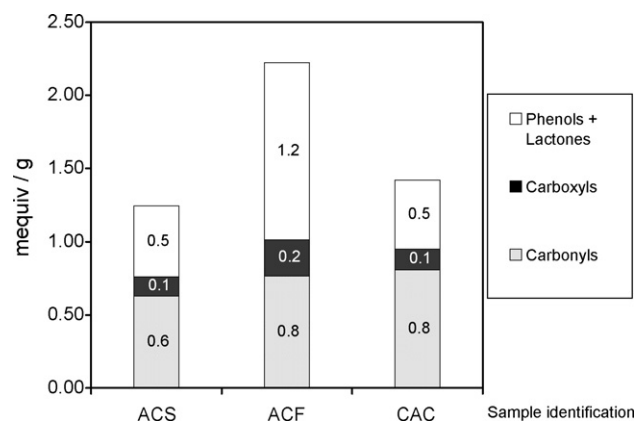


Fig. 1. Total and individual quantities of surface acidic/polar oxygen functional groups determined for the activated carbons developed from the native wood sawdust under the self-generated atmosphere (ACS) and flowing air (ACF), and the commercial activated carbon (CAC).

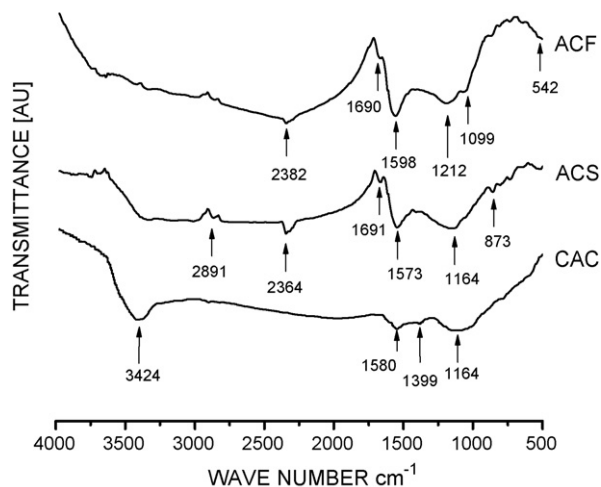


Fig. 2. FT-IR spectra for the activated carbons developed from the native wood sawdust under the self-generated atmosphere (ACS) and flowing air (ACF), and the commercial activated carbon (CAC).

results reported for ACs derived from other precursors through different activation strategies [19–21,25]. The ACF obtained under severe oxidation conditions exhibited a larger total content of oxygen functional groups than the ACS developed with a limited supply of oxygen. The trend agrees with the elemental oxygen content of these samples, as assessed by elemental analysis (Table 2). Likewise, the total content of the CAC was slightly larger than the one for the ACS.

All the ACs showed minor proportions of carboxylic groups, likely because they become unstable at the temperature used in the thermal treatment stage. Temperature-sensitive surface functionalities, such as carboxylic groups, on ACs obtained by phosphoric acid activation reportedly arise from acidic hydrolysis of the raw material used as a precursor, and begin to decompose at relatively low temperatures ($>250^{\circ}\text{C}$) [16]. Nevertheless, the content of carboxylic groups for the ACF duplicated the one for the ACS and CAC.

The ACF also exhibited a major contribution of phenols and lactones, almost twice the contents of the ACS and CAC, suggesting that the strong oxidation atmosphere imposed by the flow of air favoured a preferential development of these functionalities upon activation, whereas the content of carbonyls was intermediate. Seemingly, these groups are formed through the reaction between the precursor and air present during activation. In contrast, the ACS and CAC exhibited larger proportions of carbonyls than of phenols and lactones. Accordingly, the results indicate that *in situ* modification of the activation atmosphere not only influenced the total amount of acidic/polar surface oxygen groups, but also the relative proportions of the individual functionalities present on the surface of the resulting ACs.

To gain insight into the effect of modifying the activation atmosphere on the developed surface functionalities, FT-IR spectra for the ACs derived from the native wood sawdust in both atmospheres are illustrated in Fig. 2. The spectrum for the CAC is also included in the same figure.

The spectra for the ACs developed under both atmospheres show absorption bands between 500 and 850 cm^{-1} , that may be assigned to aromatics substituted by aliphatic groups. For the CAC, no absorption is observed in this region or it might be masked. These results suggest a lower content of substituting aliphatic groups in the aromatic rings for the latter and might be related to the lower content of elemental hydrogen determined for the commercial sample compared to that for the native wood-derived ACs (Table 2).

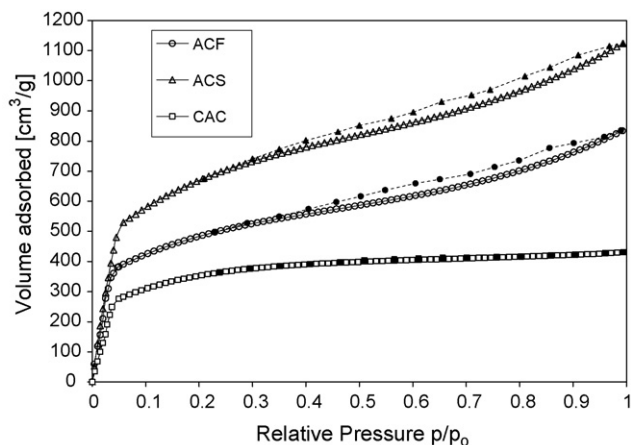


Fig. 3. N_2 adsorption (empty symbols) and desorption (solid symbols) isotherms for the activated carbons developed from the native wood sawdust under the self-generated atmosphere (ACS) and flowing air (ACF), and the commercial activated carbon (CAC).

The spectra for the developed ACs also display a broad band between 950 and 1300 cm^{-1} , frequently found in ACs obtained by phosphoric acid activation [16,33,35,37]. Presumably, absorption in this region arises from superposition of signals corresponding to oxygen functional groups, like ethers, phenols and lactones, and to phosphorous-containing groups to compounds containing P(V) in their structure [35]. Formation of the latter, which are thermally stable even at high activation temperatures, has been attributed to the reaction between the precursor or its acidic hydrolysis products and H_3PO_4 acid or other forms of phosphorous-containing acids, arising from pyro- or polyphosphoric acids formed at the activation temperature [16]. The broad bands at 1000 – 1300 cm^{-1} have been assigned to C–O single bonds such as those in ethers, phenols, acids and esters [34,35].

In addition, the band between 1400 and 1750 cm^{-1} is preferentially assigned to carboxyl groups, quinones, ketones, lactones, diketone and keto-ester, and keto-enol [34,36]. The latter band is more pronounced for ACF, whereas the relation of intensities is slightly opposite for the ACS. For the CAC sample, an important absorption band appears at 900 and 1300 cm^{-1} resulting from phenol or ether-like structures.

The ACS and ACF also present an intense band at 1550 and 1650 cm^{-1} resulting from C=C stretching vibrations in aromatic rings enhanced by polar functional groups [34,35]. This band has a lower intensity for the CAC spectrum.

The presence of a band at around 1690 cm^{-1} is also observed for the *Prosopis* wood-based ACs (ACS and ACF). It may be due to the stretching vibrations of C=O moieties in carboxylic acid groups, esters, lactones and quinones [34,36,37]. ACS and ACF also show absorption bands at 2300 and 2900 cm^{-1} . The peaks at 2380 cm^{-1} for the ACF and at 2364 cm^{-1} for the ACS, may be assigned to carbon-oxygen bonds in ketene groups [34]. The peak at 2890 cm^{-1} could be originated from C–H stretching in $-\text{CH}_2-$ and CH_3 groups [34–37]. These bands are absent in the FT-IR spectrum of the CAC.

In addition, the OH bond corresponding to alcohols, phenols and water chemisorbed is in the range between 3600 and 3200 cm^{-1} [34,35,37]. This band is more intense for the CAC than for the ACS and ACF. In summary, main differences in the spectra of the wood-based ACs are found in the region comprised between 500 and 1700 cm^{-1} , that might affect their adsorptive behaviour.

Fig. 3 shows N_2 adsorption/desorption isotherms for the derived ACs and the commercial samples. Textural characteristics evaluated from the isotherms are listed in Table 3. The shape of the adsorption

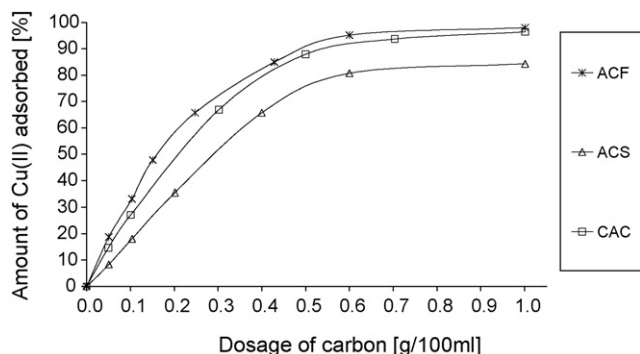


Fig. 4. Effect of the sample's dose on Cu(II) ion adsorption at equilibrium conditions for the activated carbons developed from the native wood sawdust under the self-generated atmosphere (ACS) and flowing air (ACF), and the commercial activated carbon (CAC). Experimental conditions: $C_0 = 50$ mg/L; pH 6; $t = 24$ h; $T = 28^\circ\text{C}$.

isotherms for both ACs developed from *Prosopis* wood was similar and showed characteristics between those of Type I and II, according to IUPAC classification. They point to the presence of micro- and mesopores. The shape of these isotherms, however, differed substantially from that for the CAC. The latter was characteristic of Type I isotherms, indicating microporous structures.

The results in Table 3 indicate that BET surface area (S_{BET}) and total pore volume (V_T) of the developed ACs were substantially higher than those for the CAC. They also evidence that the stronger oxidation conditions generated by the air flow induced a reduction in the development of porous structures and of mesopores, in comparison with the results obtained for the ACS. This might be due to an enhanced development of porosity at the outer surface of the precursor's particle and/or to pore blockage occasioned by the larger formation of ash (Table 2), in turn resulting from carbon oxidation because of the greater presence of oxygen in the thermal treatment stage.

The effect of the sample's dose on removal of Cu(II) ions from solutions of 20 ppm is illustrated in Fig. 4. As expected, increasing the dosage led to enhancements in Cu(II) ion adsorption for the three ACs. Noticeable differences between ACS and ACF samples may be seen for fixed doses. The ACF developed under stronger oxidation conditions than the ACS showed a better performance, slightly superior to that determined for the CAC.

Fig. 5 shows the experimental Cu(II) ion adsorption isotherms obtained for both developed ACs and the commercial activated carbon. In order to represent the experimental data and accounting for the shape of the isotherms, the Langmuir model was applied. It is described by the following equation [38]:

$$\text{Langmuir model: } q_e = \frac{K_L X_m C_e}{1 + K_L C_e} \quad (2)$$

Model characteristic parameters were estimated by non-linear regression analysis for a 5% significance level, by minimising the following objective function:

$$\text{O.F.} = \sum (q_{ei} - q_{ei, \text{calc}})^2 \quad (4)$$

Table 3

Textural properties of the activated carbons developed in the self-generated atmosphere (ACS) and flowing air (ACF), and the commercial sample (CAC)

Parameter	ACS	ACF	CAC
S_{BET} (m^2/g)	2281	1638	1200
V_T (cm^3/g)	1.73	1.28	0.66
V_{micro} (%)	67	71	93
V_{meso} (%)	33	29	7
r (\AA)	15	16	11

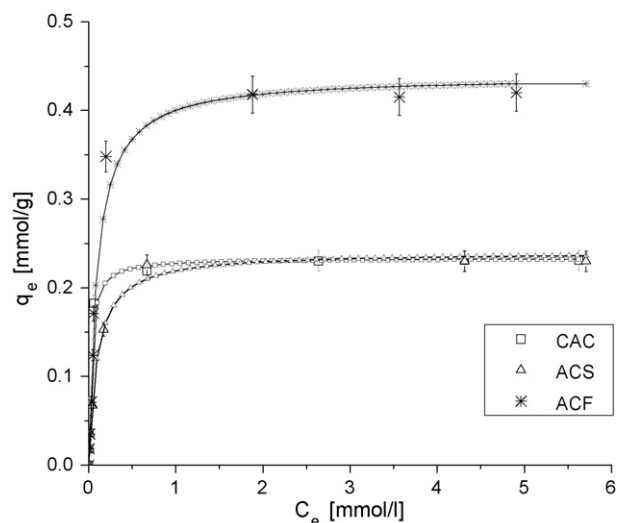


Fig. 5. Adsorption isotherms of Cu(II) ions onto the activated carbons developed from the native wood sawdust under the self-generated atmosphere (ACS) and flowing air (ACF), and the commercial activated carbon (CAC). Comparison between the experimental data (points) and predictions of the Langmuir model (solid lines). Experimental conditions: $C_0 = 5\text{--}400$ mg/L; pH 6; $T = 28^\circ\text{C}$; carbon dose = 0.4 g/100 mL.

The appropriateness of the model to represent the experimental data was examined from the standard deviation (s), which was estimated according to:

$$s = 100 \left[\frac{\sum_{i=1}^N (q_{ei, \text{exp}} - q_{ei, \text{est}})^2}{N - P} \right]^{1/2} \quad (5)$$

The estimated characteristic parameters of the Langmuir model along with the corresponding R^2 values are summarized in Table 4. Model predictions are shown in Fig. 5. As may be appreciated in the figure, the Langmuir model enables to represent properly the experimental data with high R^2 values (Table 4).

The results in Table 4 indicate a pronouncedly higher maximum adsorption capacity for the ACF than for the ACS and the commercial sample. As may be appreciated in the table, similar X_m values were obtained for the two latter. The found trend clearly points to a predominant influence of the acidic/polar oxygen functional groups present on the surface of the ACs over that exerted by the porous structures. The ACF with a relatively less developed porous matrix (Table 3) but with a higher amount of acidic/polar oxygen functionalities (Fig. 1) showed the greatest potentiality for Cu(II) ion removal, likely because dissociation or polarization of these functionalities renders to the surface of the ACs immersed in aqueous media anionic characteristics that favour their behaviour as cationic exchangers. Based on present results and on predictions of a reported surface complexation model for copper adsorption onto activated carbons [35], carboxylic groups and phenols could be the main functionalities involved in copper binding for the experi-

Table 4

Langmuir model parameters estimated for the adsorption Isotherms of Cu(II) ion onto the activated carbons developed in the self-generated atmosphere (ACS) and flowing air (ACF), and the commercial sample (CAC)

Sample	Parameter			
	X_m (mmol/g)	K_L (L/mmol)	s (%)	R^2
ACS	0.24	10.3	0.8	0.99
ACF	0.44	10.3	2.5	0.98
CAC	0.23	38.4	1.0	0.99

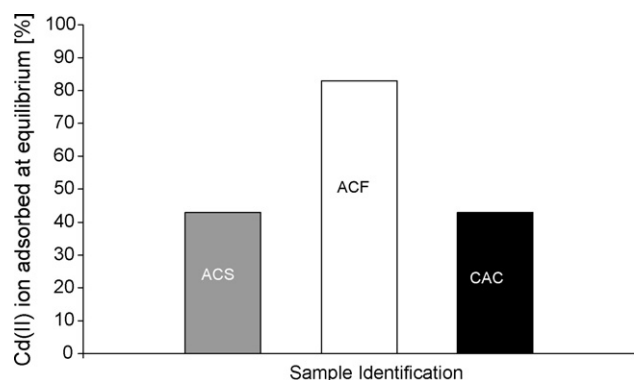


Fig. 6. Effectiveness of the activated carbons developed from the native wood sawdust under the self-generated atmosphere (ACS) and flowing air (ACF), and the commercial activated carbon (CAC) in equilibrium adsorption of Cd(II) ions.

mental conditions used in this study. Seemingly, carboxylic groups are involved in Cu(II) adsorption through the formation of a monodentate charged complex (RCOOCu^+), whereas phenolic groups appear to form a hydrated neutral complex (ROCuOH), the role of the latter having a greater influence on adsorption from more concentrated solutions [35]. Values of the K_L parameter estimated for the ACs developed from the native wood were similar, regardless of the activation atmosphere involved in the thermal treatment stage. However, they differed considerably from that estimated for the commercial sample, suggesting that the inherent nature of the precursor dominantly influences the affinity of the carbons towards Cu(II) ions in solution.

Results obtained for Cd(II) ion adsorption onto the developed ACs and the commercial carbon evidenced the same trend as that determined for Cu(II) ion adsorption. Fig. 6 shows the results obtained for the adsorption of Cd(II) ions onto each sample using solutions of 20 ppm initial concentration. As may be appreciated in the figure, the ACF exhibited the highest effectiveness in the removal of both metal species, whereas the ACS and the CAC showed a similar performance. The behaviour is also consistent with the content of surface acidic oxygen functionalities characterizing the samples (Fig. 1).

4. Conclusions

Phosphoric acid activation of wood sawdust from the native invasive species *P. ruscifolia* led to ACs with highly developed porous structures, which were markedly dependent on the activation atmosphere involved in the thermal treatment stage. The ACs obtained in the self-generated atmosphere showed higher BET surface area and total pore volume ($2281 \text{ m}^2/\text{g}$, $1.7 \text{ cm}^3/\text{g}$) than those derived under flowing air attaining values of $1638 \text{ m}^2/\text{g}$ and $1.3 \text{ cm}^3/\text{g}$, respectively. Modification of the activation atmosphere was also found to exert a strong influence on the development of acidic/polar oxygen functionalities of the ACs, affecting both the total content of these groups and relative proportions of the individual functionalities present on the surface of the resulting ACs.

The ACs obtained under flowing air showed a higher effectiveness in Cu(II) ion adsorption compared to those resulting from the self-generated atmosphere. As judged from modelling of the experimental adsorption isotherms, the maximum adsorption capacity for the former ($X_m = 0.44 \text{ mmol/g}$) almost duplicated those determined for the latter ($X_m = 0.24 \text{ mmol/g}$), and for the commercial sample used for comparison ($X_m = 0.23 \text{ mmol/g}$). The trend was further verified from additional assays using model dilute solutions of Cd(II) ion. For the two metallic species investigated, the adsorptive behaviour of the ACs was in full accordance with their total content

of surface acidic/polar oxygen groups, pointing to a predominant influence of these functionalities on metal adsorption.

Overall, present results indicate that effective ACs for specific use in metal removal from dilute aqueous media may be developed through phosphoric acid activation of *P. ruscifolia* wood, as an alternative precursor, by *in situ* modification of their surface characteristics operating under flowing air and moderate process conditions.

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