**INFLUENCE OF PYROLYSIS TEMPERATURE AND HARDWOOD SPECIES ON RESULTING
BIOCHAR PROPERTIES AND THEIR EFFECT ON AZIMSULFURON SORPTION AS
COMPARED TO OTHER SORBENTS**

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ABSTRACT

Azimsulfuron is an acidic herbicide with a high water solubility which makes risk of groundwater contamination a concern. Various wood based biochars produced at different pyrolysis temperatures were characterized along with their sorption capacity for the herbicide azimsulfuron. In addition, we compared sorption on biochars with sorption on mineral sorbents such as clay minerals and iron oxides. In biochar formed at high temperatures (500°C and 700°C), FT-IR studies confirmed the increase in aromaticity. Scanning electron microscope (SEM) images of the biochars showed differences in the macroporous structure and lower size pores at higher temperatures. SSA (Specific Surface Area) of the biochars increased with pyrolysis temperature and, for all different biochars, this resulted in higher sorption of azimsulfuron. In the case of mineral sorbents, sorption is not related to SSA. Higher sorption is observed in a montmorillonite, of lower SSA, than in mixture of clay minerals with 30 % smectite (w/w). On the contrary as with the clays, sorption on the two iron oxyhydroxides increased with SSA. Desorption studies showed hysteresis. Leaching studies showed no effect on azimsulfuron retention on soil column amended with apple wood biochar, while a reduction of azimsulfuron in leachates in soil columns amended with the modified montmorillonite and alder wood biochar (500°C). Total retention was shown for alder wood biochar.

KEYWORDS: Azimsulfuron, biochar, montmorillonite, iron oxide, sorption-desorption, leaching.

43 1. Introduction

44 Biochar has been heralded as an amendment to revitalize degraded soils,
45 improve soil carbon sequestration, increase agronomic productivity, and enter into
46 future carbon trading markets (Spokas et al., 2012). The physical and chemical
47 properties of biochars are influenced by the properties of the feedstock and by
48 pyrolysis conditions such as highest treatment temperature (HTT) and furnace
49 residence time (Downie et al., 2009). Temperature is a key factor on biochar
50 properties, such as specific surface area (SSA), microporosity, and stability. With
51 increasing pyrolysis temperature, increase in aromaticity and SSA has been observed
52 (Kloss et al., 2012; García-Jaramillo et al., 2015). Characteristics of the raw feedstock
53 biomass impart specific properties to the resulting biochar, such as ash content and its
54 elemental constituents, density, and hardness. Particularly, biochar from grass, corn
55 stover, and manure feedstocks contain higher ash contents than biochar from other
56 sources (Brewer et al., 2009). Kloss et al. (2012) observed a higher ash content and
57 trace elements for straw-derived biochar than for wood-derived biochars, but lower
58 specific surface area (SSA) and microbial stability. All these biochar characteristics will
59 affect pesticide sorption on soils, which in turn determines mobility and its ability to
60 mitigate contamination of surface and groundwater. This comparison would allow the
61 determination of the optimum pyrolysis conditions to yield biochar with the most
62 appropriate properties to reduce the environmental contamination risk associated
63 with the use of agrochemicals (Cabrera et al., 2011). Brewer et al. (2009) reported
64 better sorbent properties of biochar produced at higher temperatures, as

consequence of the higher surface area and microporosity. Yang et al. (2010) considered that temperature is more important than feedstock material on the biochar effectiveness in treatment of contaminated soils. Wang et al. (2010) observed a higher sorption of the herbicide terbuthylazine in a soil amended with biochar produced at 700 °C than 350 °C, although the feedstock was the same. García-Jaramillo et al. (2015) found that biochar from alperujo compost at different pyrolysis temperatures (400, 550 and 700°C) presented a high affinity for the fungicide tricyclazole as compared with rice hull biochar (400°C pyrolysis temperature) and hardwood sawdust biochar (550°C pyrolysis temperature). This affinity was positively correlated with pyrolysis temperature, pH, SSA, and the enhanced aromaticity of the biochars. On the contrary, a negatively correlation between sorption and biochar dissolved organic carbon (DOC) was observed (García-Jaramillo et al., 2015).

The contribution of the mineral soil constituents (i.e., clay minerals, metal oxides, humic substances) to sorption may be significant for ionic or highly polar pesticides or when the organic C content of the soil is low relative to the clay mineral content. The use of unaltered and modified clay minerals as adsorbents to prevent and remediate environmental contamination by pesticides has been a subject of great interest in environmental and agricultural chemistry (Trigo et al., 2009; Celis et al., 2012; Gámiz et al., 2015). Different studies have shown that the nature of the interlayer inorganic cation can strongly influence the adsorptive properties of clay minerals. Celis et al. (2000) showed that the herbicide hexazinone displayed very high adsorption on Fe-saturated compared to Mg-, Na-, and K-saturated Wyoming montmorillonite (SWy-2). The positive charges of ferrihydrite and goethite create a

great attraction by negative charged pesticides. Celis et al. (1999) determined that the lower pH of a poorly crystallized ferrihydrite would contribute to greater sorption on this Fe oxide since at lower pH values the oxide surface becomes more positively charged, thus increasing the attraction for 2,4-D anionic species.

Rice production under conventional flooded conditions has been associated with both environmental and health risks, such as pesticide contamination of soil and water. Azimsulfuron (**Figure 1**) is a sulfonylurea herbicide used in post-emergence control of *Echinochloa spp.*, broadleaf and sedge weeds in rice production. Azimsulfuron controls key weeds at a rate of 6-25 g active ingredient per hectarea. Because of its high water solubility and persistence its potential impact on surface water and groundwater contamination is of great concern (Brusa et al., 2001; Kim et al., 2003). The aim of this study is to characterize different wood biochars produced at different pyrolysis temperature and to determine the effects of their properties on sorption-desorption behavior of azimsulfuron compared to mineral sorbents due to the contribution of smectite clay minerals and iron oxides to the sorption of sulfonylureas (Pussino et al., 2000; Pussino et al., 2004). Chemical hydrolysis and biological degradation are the primary degradation processes of herbicides in soil (Brusa et al., 2001) so microbial degradation of sulfonylureas has been studied (Lin et al., 2010). Garcia-Jaramillo et al. (2016) used a byproduct of the olive oil industry as amendment under anoxic-flooded and oxic-unflooded condition and monitored the dissipation of azimsulfuron. The results shown that the applications of this organic amendment are an efficient strategy to reduce the negative effects derived from the application of azimsulfuron under flooded conditions. The information reported in this

paper should be useful for the implementation of the assaied materials in specific applications, such as the removal of pesticides from contaminated soil, their immobilization in soil, or the preparation of slow release formulations.

2. Materials and Methods
2.1. Chemical. Azimsulfuron (99.8 % purity) was supplied by Sigma-Aldrich, the chemical structure is shown in **Figure 1**. Azimsulfuron is a weak acid with a pKa (25 °C) of 3.6 and water solubility at 20 °C of 1050 mg L⁻¹. Its octanol/water partition coefficient (pH 7, 20°C) is 0.040 (Pesticide Properties DataBase, 2015).

2.2. Adsorbents. Biochars prepared from different hardwood trees (alder, apple, cherry, hickory, mesquite and pecan) with a thermal decomposition process at different temperatures under oxygen-limited conditions were characterized (**Table 1**). The SSA of the biochar was measured by nitrogen surface sorption, using the Brunauer, Emmett, and Telle (BET) method on a previously degassed 0.2 g sample at 80 °C for 72 h (Micromeritics ASAP 2420). Dissolved organic carbon (DOC) from the biochars was extracted by shaking 0.5 g of the sorbent with 10 mL of 0.01 M CaCl₂ for 15 minutes. The suspensions were centrifuged at 10000 rpm for 20 minutes, filtered through a 0.45 µm pore nylon filter and the solution was analyzed using a total organic carbon analyzer (TOC-VCPH. Shimadzu, Kyoto, Japan). Total C, N and H of the biochars were determined in an elemental analyzer (Truspec micro, LECO). Oxygen percentage was estimated assuming that sulfure percentage was less than 1%. The surface morphology of the sorbents was studied using a JEOL 6500 scanning electron microscope. Biochar samples were

previously sputtered with gold in order to improve their conductivity for improved image quality. The surface functional groups of the biochar were determined using a Nicolet Series II Magna-IR System 750 FTIR spectrometer, recording the spectrum region from 4000 to 400 cm^{-1} with a resolution of 2 cm^{-1} (University of Minnesota CharFac facility). For selected biochars, the pore size distribution (40- 0.004 μm) was determined by mercury intrusion porosimetry technique using an Autopore 5500. For each sample, 1 g of biochar was heated at 90 $^{\circ}\text{C}$ for 24 h before analysis.

Mineral sorbents were also used in this study. SWy-2 Na-rich Wyoming montmorillonite and a white clay (68 % of smectite) were modified with Fe through ion exchange reactions using successive treatments with a FeCl_3 1M solution at a rate 1:10 (g:mL), washed with distilled water till chloride free and then freeze-dried. Two iron oxyhydroxide minerals [Ferrihydrite ($\text{Fe}^{3+}\text{O}_3 \cdot 0.5 \text{H}_2\text{O}$) and Goethite ($\alpha\text{-FeO(OH)}$)] were also used as sorbents. Goethite was purchased from SIGMA Aldrich and ferrihydrite was synthesized according to Celis et al. (1999).

2.3. Adsorption-Desorption Experiments.

The adsorption of azimsulfuron to the different sorbents was measured at a single initial herbicide concentration ($C_i = 1 \text{ mg L}^{-1}$) using the batch equilibration procedure. Duplicate 20 mg of adsorbent were equilibrated with 8 mL of 1 mg L^{-1} azimsulfuron solution by shaking at $20 \pm 2^{\circ}\text{C}$ for 24 h. Sorption kinetics were performed (data not shown) and indicate that equilibrium is reached within 24 h. After equilibration, the suspensions were centrifuged and 4 mL of the supernatant solution was removed for analysis. The concentration of herbicide in the supernatant solutions

(C_e) was determined by HPLC as described below. Differences between the initial (C_i) and equilibrium (C_e) solution concentration were assumed to be sorbed (C_s). The sorption coefficient (K_d) was calculated as C_s/C_e .

Adsorption-desorption isotherms of azimsulfuron on selected samples were also obtained. Duplicated 20 mg adsorbent samples were equilibrated with 8 mL of herbicide initial solutions ($C_i = 1, 1.5, 2, \text{ and } 5 \text{ mg L}^{-1}$) by shaking mechanically at $20 \pm 2^\circ\text{C}$ for 24 h. After equilibration, the suspensions were centrifuged and 4 mL of the supernatant solutions was removed for analysis. The herbicide concentration in the supernatant solutions was determined by HPLC. The amount of herbicide adsorbed was calculated by difference between the initial and the equilibrium solution concentration. Desorption was measured immediately after adsorption from the highest equilibrium concentration of the adsorption isotherm, that is, that corresponding to $C_i = 5 \text{ mg L}^{-1}$. The 4 mL of supernatant removed for the adsorption analysis was replaced with 4 mL of distilled water. After shaking at $20 \pm 2^\circ\text{C}$ for 24 h, the suspensions were centrifuged, and the herbicide concentration was determined in the supernatant. This desorption procedure was repeated three times. A desorption hysteresis coefficient was also calculated, $H = (1/n_{f\text{-des}}) / (1/n_f) \times 100$.

2.4. Leaching experiments

Leaching was studied in 30 cm length × 3.1 cm internal diameter glass columns. The top 5 cm were filled with sea sand and the bottom 5 cm with sea sand plus glass wool, to prevent losses of soil during the experiment. The other 20 cm were hand packed with air-dried sandy soil (95.7 % Sand; 1.2 % Lime and 3 % Clay; pH = 8.48; Total Organic Carbon = 0.5%), then saturated with deionized water and allowed to drain for 24 h. The calculated pore volume of the columns after saturation was 55.1 ± 1.5 mL (0.92 volumetric ratio). The top of the columns was amended with apple wood biochar pyrolysed at 500°C, alder wood biochar pyrolysed at 500° and 700°Cor SW-Fe at a rate of 10 % mixing 9 g of soil and 1 g of sorbent. The amount of azimsulfuron corresponding to an application rate of 1 kg ha^{-1} was applied to the top of duplicate soil columns. Duplicate unamended soil columns were also prepared. Apple wood biochar was selected due the importance of this crop in Spain and for its moderate K_d value (**Table 1**) which convert it in a possible strategy to reduce extensive transport losses associate with the application of azimsulfuron. On the contrary, alder wood biochar was selected for its high sorption capacity and its possible use to remove pesticides from contaminated soil and their immobilization. To compare mineral sorbents with biochars, SW-Fe was selected due to its high sorption capacity compared to the others inorganic sorbents.

2.5. Herbicide Analysis. Azimsulfuron was analyzed by HPLC using a Waters 600E chromatograph coupled to a Waters 996 diode-array detector. The analytical conditions were Novapack C18 column (150 mm length x 3.9 mm i.d.); eluent mixture, 65:35 diluted Acetic Acid (0.06 %)/acetonitrile at a flow rate of 1 mL min^{-1} ; 100 μL injection volume; and UV detection at 240 nm (28). The limit of

detection (LOD) and limit of quantification (LOQ) were determined using signal to noise ratios of 3 to 10 respectively.

3. RESULTS AND DISCUSSION

3.1. Characterization of sorbents

3.1.1. FT-IR studies of biochar

The ATR-FTIR spectra of feedstocks and biochars obtained at 350, 500 and 700°C are displayed in **Figure 2**. FTIR spectroscopy showed characteristic absorption bands of cellulose and hemicelluloses corresponding to polysaccharides ($1000 - 1200\text{ cm}^{-1}$) in the raw materials that lose their intensity with increasing temperatures (Haberhauer and Gerzabek, 1999; Schwanninger et al., 2004). The increase in pyrolysis temperature also decreased the intensity of the O-H stretching of the hydroxyl groups at $3200 - 3400\text{ cm}^{-1}$, due to the loss of hydration, and the C-H stretching of the aliphatic vibration groups ($2980 - 2820\text{ cm}^{-1}$). The absorption intensities at $1610 - 1740\text{ cm}^{-1}$, corresponding to C=O stretching of ketones and other carbonyl structures of the feedstocks (Mimmo et al., 2014) are no longer detected in the biochar with pyrolysis temperature $> 350^\circ\text{C}$. The band at 1030 cm^{-1} , corresponding to C-O and C-O-C stretching, characteristic of the anomeric region of cellulose-like structure (Haberhauer and Gerzabek, 1999; Schwanninger et al., 2004) also is not apparent in the biochars. Intensity of the peaks corresponding to aromatic C=O and C=C stretching at 1590 cm^{-1} increased with pyrolysis temperature as well as that corresponding of aryl C-H and/or

aryl C-O groups ($700 - 850 \text{ cm}^{-1}$) (Tatzber et al., 2007, 2009). Pyrolysis also resulted in the formation of carboxylic and carbonylic groups (1700 cm^{-1}), that Sharma et al. (2004) attributed to carbohydrate decomposition. The 350°C pyrolysis temperature pecan and apple wood biochars, maintain a certain hydration and a carbohydrate-like structure showing characteristic peaks between 1200 and 1000 cm^{-1} due to C-O-C and C-O stretching and the characteristic hydroxyl group at $3200 - 3400 \text{ cm}^{-1}$ (**Figure 2**). In biochar formed at 500°C and 700°C pyrolysis temperature, the O-H stretching bands are virtually absent, while the bands associated with vibrations of aromatic structures, such as 3070 to 3000 cm^{-1} corresponding to the C - H aromatic stretching vibration increased. At 350°C pyrolysis temperature, in alder, cherry, hickory and mesquite wood biochar, the absorption bands of cellulose and hemicelluloses ($1000 - 1200 \text{ cm}^{-1}$) practically disappeared. Oak biochar spectra at the three different pyrolysis temperatures are very similar, showing a higher surface chemistry stability as compared with other wood feedstocks. Mimmo et al. (2014) found that at low pyrolysis temperatures ($< 360^{\circ}\text{C}$) biochars behave like the feedstock and maintain a certain hydration and a carbohydrate structure, due to the partial chemical conversions occurring at these conditions.

3.1.2. SEM studies of biochars and iron oxides

Together with heating rate, feedstock characteristics determine the physical properties of biochar, which will affect their different sorption behavior. **Figure 3** shows the SEM images of selected biochars. Biochar images at $3000\times$ magnification show the pores shapes and sizes, which could be related with the sorbent sorption capacity. As it can be seen in the figures, the structure of biochar retains major characteristics of the

physical structure of the original feedstock. The SEM images of the biochars showed differences in the macroporous (approximately 1 μm diameter) structure and higher abundance of lower size pores at higher temperatures.

Figure 3 also shows the SEM images of the two selected iron oxyhydroxides, goethite and ferrihydrite. As it can be seen, goethite has a crystalline structure whereas ferrihydrite possesses an amorphous structure.

3.1.3. SSA Measurements and Pore size distribution

Table 1 shows specific surface area (SSA) measurements of the biochars, clays and iron oxyhydroxides. Biochars produced at 350°C do not exceed 2.6 $\text{m}^2 \text{g}^{-1}$ and, in general, increase in the pyrolysis temperature to 500 °C did not cause a great increase in SSA (Kloss S., 2012). Only for cherry wood biochar, a considerable enlargement was observed when the pyrolysis temperature increase from 350 °C and 500°C (From 0.72 to 118.88 $\text{m}^2 \text{g}^{-1}$). An increase to 700°C resulted in an increase in SSA for all biochars which can be related with changes in the physical structure at high temperatures. This has also been observed by Keiluweit et al. (2010), who found an increase in SSA with pyrolysis temperature for wood based chars, with an average value of 350 $\text{m}^2 \text{g}^{-1}$ for the biochars created at pyrolysis temperature of 700°C. The clay CTI-Fe has a higher SSA than the pure montmorillonite SWy-Fe, and the amorphous ferrihydrite a much higher SSA than goethite. These results are in agreement with SEM micrographs (**Figure 3**).

In addition to structural differences, there are also chemical changes. Our FTIR characterization indicated that the absorption bands of cellulose and hemicelluloses

almost disappeared and the bands associated with vibrations of aromatic vibration increased.

Variations of organic carbon (OC) were observed between biochars due to differences in the feedstock and pyrolysis conditions (**Table 1**). Alder, cherry, mesquite and oak wood biochars show an increase in OC (%) with pyrolysis temperature increase from 350 °C to 700 °C. The higher temperature of biochar production results in a higher recalcitrant OC structure to microbial mineralization and hydrophobic character of the biochar. On the contrary, the OC (%) of apple and pecan wood biochar decreased from 350°C to 700 °C temperature. Increasing pyrolysis temperature tended to increase the C contents and decrease H contents in the biochar (**Table 1**). Atomic ratios (H/C and O/C) decreased with pyrolysis temperature for all biochars. Lower H/C ratios demonstrate an increased aromaticity by pyrolysis and therefore indicate higher stability of the material (Keiluweit et al., 2010 and Uchimiya et al., 2010). O/C ratio decrease with pyrolysis temperature would be attribute to removal of polar surface functional groups (**Table 1**). (

The pore size distributions for alder and apple wood chips biochars obtained at 500°C and 700°C are shown in **Figure 4**. The increase in cumulative volume with temperature, from 2500 to 3500 mm³/g (alder wood) and 1200-1700 mm³/g (apple wood), correlates to the SSA measurements. For alder wood chips, the maximum relative volume (mm³/g) (**Figure 4**) distribution is located in the macropores range (10 - 100 µm) with lower pore volume in the small (0.01 - 0.25 µm) and medium (0.25 - 4.5 µm) range and a small development of micropores is observed with increasing carbonization temperature. On the other hand, the volume of mesopores significantly

increases with temperature. Apple wood biochar, as alder wood biochar, have a maximum located in the macropores region (10 - 100 μm), but the distribution is more homogeneous and the absolute pore volumes (mm^3/g) are smaller. On the contrary, with increasing pyrolysis temperature in apple wood biochar there was no increase in micropores, but a development of macroporosity. This agrees with Bagreev et al. (2001) who observed an increase predominantly in the mesoporous region with minor micro-pore contribution for biochars from municipal sewage sludge pyrolyzed at temperatures between 400 and 950 $^{\circ}\text{C}$.

3.2. Sorption studies

Azimsulfuron distribution coefficients (K_d values) were calculated at a single initial concentration of 1 mg L^{-1} (**Table 1**). Except for pecan and cherry, that have K_d values at 350 $^{\circ}\text{C}$ higher than at 500 $^{\circ}\text{C}$, increase in pyrolysis temperature increased K_d . In general, higher K_d values correspond with SSA, which also increases with pyrolysis temperature (García-Jaramillo et al., 2015, Wang et al., 2010 and Yu et al., 2010). At the pH of the biochar solutions, azimsulfuron molecules are mostly in the anionic form. Thereby, repulsion between azimsulfuron and negative groups on the biochar surface is expected. However, the highest K_d values corresponded to the biochars of higher pH: Alder (700 $^{\circ}\text{C}$) (8.89), apple (700 $^{\circ}\text{C}$) (8.59) and hickory (700 $^{\circ}\text{C}$) (9.86). Although, azimsulfuron sorption on alder wood (700 $^{\circ}\text{C}$) is ten times higher than with hickory wood (700 $^{\circ}\text{C}$), despite the slight pH difference. These biochars also have very high SSA. Discarding hydrolytical degradation of the herbicide at high pH, which according to Boschín et al. (2007) is faster at acidic than at neutral or weakly basic conditions ($t_{1/2}$ 161 d at pH 8.7), these results suggest other interactions such as hydrophobic or

specific interactions rather than anion binding take place on biochars, and that these interactions would be favored by increased SSA. The presence of hydrophobic forces are in agreement with the increase in H/C ratios (**Table 1**) and aromatic vibration bands with temperature showed in FTIR characterization (**Figure 2**). Moreover, the presence of aromatic C=O stretching, that increase with pyrolysis temperature, could mask the impact of pH on the sorption of herbicides (Tessmer et al., 1997). The lower K_d values correspond to biochars with higher DOC content. The SSA could be reduce by the DOC, which decreases with increasing pyrolysis temperature for all biochars. DOC molecules can block biochar external surfaces competing with pesticide molecules for sorption sites (Pignatello et al., 2006; García-Jaramillo et al., 2015; Cabrera et al., 2014). Therefore, according to K_d values at 1 mg L⁻¹ initial concentration, adsorption of azimsulfuron can be related to pyrolysis temperature, SSA and DOC. The higher sorption of azimsulfuron on alder wood 700°C compared to other biochars of similar physicochemical properties also indicates the importance of feedstock characteristics (Mimmo et al., 2014). Porosity studies also showed differences in total pore volumes (higher in alder wood biochar than in apple wood biochar) and less microporosity in alder wood biochar than in apple wood biochar. This is also observed for cherry and pecan biochars, with an increase of SSA not correlating with significant K_d increases.

In the case of mineral sorbents, a different behavior is observed. K_d values for the two clays (SW-Fe and CTI-Fe) are not related to SSA. Higher sorption is observed in SWy-Fe montmorillonite, of lower SSA, than in CTI-Fe, of higher SSA (**Table 1**). CTI-Fe is a mixture of different clay minerals with only 30 % of smectite, whereas SWy-Fe is pure montmorillonite. Montmorillonite minerals have internal surfaces, not measurable by

N₂, available to water molecules and some pesticides (Laird et al., 1992, Hermosín et al., 1993, Celis et al 1997). Also, the acidic water surrounding Fe³⁺ saturating ions in SWy-Fe montmorillonite, which have been shown to be 4 pH units lower than the pH of the bulk solution (Bailey et al., 1968), could contribute to this higher sorption. This has been observed for other polar pesticides (Celis et al., 1997; Cox et al., 1998, 2000). According to Pinna et al. (2004), azimsulfuron sorption on iron-clays involves protonation of one of the two basic nitrogen atoms of the pyrimidine ring by this acidic water.

On the contrary as with the clays, sorption on the two iron oxyhydroxide minerals increase with SSA. For ferrihydrite and goethite, the positive charged surfaces create an attraction by the negative charge of anionic pesticides (Iglesias et al., 2010). Sorption on iron oxides was directly related to SSA and inversely related to pH. The lower sorption of azimsulfuron on goethite as compared to ferrihydrite would be related to its crystalline structure, resulting in a lower total SSA, which is confirmed in the SEM images (**Figure 3**).

Adsorption-desorption isotherms of azimsulfuron on selected sorbents are shown in **Figure 5**. Alder wood and apple wood biochars at 500°C and 700°C were selected because of their high sorption (**Table 1**), with higher values for alder wood biochar (5672 and 156 L kg⁻¹ at 700°C and 500°C respectively) than for apple wood biochar (546 and 71 L kg⁻¹ at 700°C and 500°C respectively), despite the higher SSA of the apple biochar (**Table 1**). Adsorption-desorption studies were also performed with the four mineral sorbents, SWy-Fe, CTI-Fe, ferrihydrite and goethite. Sorption data was described by the Freundlich equation and sorption coefficients are given in **Table 2**.

Slopes of sorption isotherms were > 1 , typical of S-type curves and indicate that sorption is facilitated by high solute concentrations. This behavior is observed when: 1.-sorbent-solute specific interactions take place, 2.- moderate attraction between sorbed herbicide molecules and/or 3.-solute molecules and solvent molecules compete for sorption sites (Giles et al., 1960). Pusino et al. (2004) and Pinna et al. (2004) found an S-type sorption for azimsulfuron on a clay loam soil and on an iron-rich clay sorbent. Because the significant differences between $1/n_f$ values for all sorbents, K_f values can't be compared directly. Differences on sorption values between alder wood and apple wood biochar would be related with their differences pore size distribution (**Figure 4**). Desorption isotherms graphs shown in **Figure 5** together with sorption isotherms, show irreversible sorption behavior.

3.3. Leaching experiments

The effect of amendment addition on the cumulative breakthrough curves (BTC's) of azimsulfuron in soil columns are shown in **Figure 6**. At the pH of the soil solution (8.48), 100 % of azimsulfuron molecules are anionic and a high solubility was expected ($\text{pH } 7 = 1050 \text{ mg L}^{-1}$ and $\text{pH } 9 = 6540 \text{ mg L}^{-1}$) which implies a low retention of azimsulfuron. In addition to this, due to the soil characteristic (95.7 % sand and 0.5 % OC) low soil sorption is expected. Leaching of the herbicide in soil column amended with SW-Fe result in lower azimsulfuron concentration in leachates, which is illustrated by the flattening of the breakthrough curves (BTC) when compared to unamended soil. This also translated into lower total leached amounts during the first 100 mL (65 % for unamended soil and 47% for SW-Fe). In addition, the application of SW-Fe also resulted in the retardation of the maximum concentration peak of the BTC. The

flattening of the BTCs of alder wood biochar (500°C) shows a maximum concentration peak to large volumes of water added as compared with the unamended soil and the total amount of azimsulfuron leached were reduced by the application of the biochar (80%). On the contrary, the leaching of azimsulfuron on the column amended with apple wood biochar shows higher concentrations in leachates during the first 80 mL leached than in the soil unamended followed by lower concentrations. As was expected, due to its high K_d value (5272.7 L Kg⁻¹), the concentration of azimsulfuron in the leachates of the soil amended with alder wood biochar was null.

For the soil amended with apple wood biochar at 10 %, a low concentration of azimsulfuron in the leachates was expected due to the high sorption capacity obtained at 1 ppm (**Table 1**). The pH around biochar particles would initially increase the soil solution due to the Lewis basicity of the π -electrons (Contescu et al. 1998), and then decrease due to the potential formation of acidic functional groups on biochar surfaces (Cheng et al. 2006; Cheng and Lehmann 2009). This dissolution reaction would explain the high concentration in the first 80 mL leached and the subsequent decrease when compared to leaching in the unamended soil. The total amount of azimsulfuron leached from amended soil columns was lower (82% for apple wood and 89 % for SW-Fe) than that leached from unamended soil (93 %), as a result of the increase in the adsorption capacity of the soil upon amendment with the sorbents.

4. Conclusions

Our results indicate that together with heating rate, feedstock characteristics determine biochar physical properties which controlled the different sorption behavior. The most significant changes in biochar structure and properties were found for those pyrolysed at 700°C. Comparing biochar sorption values with the two modified clays and the two iron oxyhydroxides, except for oak and pecan wood biochars, K_d values of biochar pyrolysis at 700°C are higher than the K_d value for SW-Fe (149 L kg⁻¹) and Ferihydrite (155 L kg⁻¹). In all cases a higher sorption values of azimsulfuron on biochar pyrolysed at 700°C were observed as compared with CTI-Fe and goethite. Sorption-desorption results for selected samples show an irreversible sorption behavior. Leaching studies showed no effect on azimsulfuron retention on soil column amended with apple wood biochar and a reduction of azimsulfuron in leachates in soil columns amended with SW-Fe and alder wood biochar (500°C). In addition, a lower percentage of azimsulfuron leached at the end of the experiment for the soil column amended with apple wood biochar was observed as compared to the percentage of azimsulfuron leached for the soil column amended with SW-Fe and null for the soil column amended with alder wood biochar (700°C).

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FIGURE CAPTIONS

Figure 1. Chemical structure of azimsulfuron.

Figure 2. FTIR spectra of raws and biochars of Alder , Apple , Cherry , Hickory , Mesquite , Oak and Pecan woods.

Figure 3. SEM image of biochar samples at different temperatures: (a, b, c) Alder wood chips, (d and e) Apple wood chips, (f and g) Cherry wood, (h and i) Oak wood, (j and k) Pecan wood, (l) ferrihydrite and (m) goethite.

Figure 4. Pure size distribution of Alder wood (BC242 and BC228) and Apple wood biochars (BC220 and BC215).

Figure 5. Azimsulfuron adsorption-desorption Isotherms for Alder wood biochars (BC248 and BC228), Apple wood biochars (BC220 and BC215), SW-Fe, CTI-Fe, Goethite and Ferrihydrite.

Figure 6. Relative (left) and cumulative (right) breakthrough curves of azimsulfuron in soil columns amended and unamended with Sw-Fe and Apple wood biochar.

Table 1 . Physicochemical Properties of biochars and sorption values at 1 ppm.

Table 2. Freundlich sorption parameters for azimsulfuron for Alder wood biochars (BC228 and BC242), Apple wood biochars (BC215 and BC220), SW-Fe, CTI Fe, Goethite and Ferrihydrite.

Figure 1. Chemical structure of azimsulfuron.

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Figure 2. FTIR spectra of raws and biochars of alder, apple , cherry , hickory , mesquite , oak and pecan woods.

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Figure 4. Pore size distribution of alder and apple wood biochars at 500 and 700 °C. .

Figure 5. Azimsulfuron adsorption (open?) and desorption(closed symbol) isotherms for alder wood biocharsapple wood biochars, SW-Fe, CTI-Fe, goethite and ferrihydrite.

Figure 6. Relative (left) and cumulative (right) breakthrough curves of azimsulfuron in soil columns amended and unamended with SW-Fe and apple wood biochar.

Table 1 . Physicochemical Properties of biochars and sorption values at 1 ppm.

Biochar	Wood Feedstock	T (°C)	pH	SSA (m ² /g)	C (%)	H (%)	N (%)	O (%)	N/C	H/C	O/C	DOC (mg/L)	Kd (L kg ⁻¹)
BC228	Alder	700	8.89	249.64	82.99	1.33	0.31	15.18	1.01	0.19	0.24	6.5	5672.7 ± 156.1
BC242		500	6.26	4.64	83.09	3.07	0.21	13.63	0.42	0.44	0.22	5.5	238.6 ± 36.4
BC237		350	5.83	1.44	71.88	4.33	0.15	23.63	0.36	0.72	0.44	22.6	61.3 ± 20.1
BC215	Apple	700	8.59	380.59	84.27	1.18	0.18	14.37	0.35	0.16	0.23	6.8	546.2 ± 76.8
BC220		500	7.11	8.48	81.19	3.09	0.15	15.57	0.32	0.46	0.26	9.3	70.9 ± 18.8
BC225		350	6.44	*-	69.23	4.31	0.07	26.39	0.17	0.75	0.51	18.3	28.2 ± 19.9
BC218	Cherry	700	8.32	252.11	87.98	1.18	0.14	10.70	0.26	0.16	0.16	4.4	209.6 ± 62.5
BC219		500	6.33	118.88	77.52	3.22	0.33	18.93	0.71	0.50	0.33	5.2	97.1 ± 18.6
BC241		350	5.55	0.72	70.10	4.04	0.06	25.81	0.13	0.69	0.49	13.1	205.4 ± 66.4
BC214	Hickory	700	9.86	229.67	81.07	1.09	0.07	17.76	0.15	0.16	0.29	4.6	473.63 ± 94.4
BC222		500	7.40	14.41	75.99	2.88	0.38	20.74	0.84	0.46	0.36	6.9	104.7 ± 12.6
BC233		350	6.50	0.84	69.40	3.91	0.24	26.45	0.58	0.68	0.51	25.3	14.4 ± 8.6
BC213	Mesquite	700	7.17	178.27	79.81	1.64	0.84	17.71	1.77	0.25	0.29	5.8	276.6 ± 61.4
BC221		500	6.68	1.66	71.67	3.25	0.62	24.45	1.46	0.54	0.45	9.7	13.5 ± 14.1
BC231		350	6.18	0.79	66.80	7.08	0.61	28.51	1.52	0.73	0.57	14.3	15.3 ± 10.2
BC217	Oak	700	7.75	269.44	86.08	1.80	0.19	11.93	0.38	0.25	0.18	8.0	116.5 ± 19.1
BC232		500	6.43	1.04	70.11	4.23	0.23	25.43	0.55	0.72	0.48	21.2	26.7 ± 7.1
BC224		350	6.66	2.52	73.87	2.89	0.26	22.98	0.59	0.47	0.41	66.1	15.0±3.0
BC216	Pecan	700	6.86	280.87	83.69	1.50	0.21	14.61	0.42	0.22	0.23	10.8	76.5 ± 9.5
BC223		500	6.42	7.52	81.56	3.53	0.40	14.51	0.82	0.52	0.24	8.6	13.8 ± 6.8
BC226		350	6.03	0.56	70.18	5.05	0.23	24.54	0.55	0.86	0.47	17.9	41.2 ± 11.8
Inorganic sorbents													
SW-Fe			4.94	36 ^a									149.0 ± 6.00
CTI-Fe				81.39									63.2 ± 7.0
Goe			5.23	51.24 ^b									14.0 ± 5.1
Ferri			4.99	346 ^c									154.7 ± 10.5

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646 ^a Cox et al. (2000)

647 ^b Wei et al. (2014)

648 ^c Cruz-Guzmán et al. (2003)

649 *Stabilisation problems.

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655 **Table 2.** Freundlich sorption parameters for azimsulfuron for Alder wood biochars (BC228 and
 656 BC242), Apple wood biochars (BC215 and BC220), SW-Fe, CTI Fe, Goethite and Ferrihydrite.

	K_f	$1/n_f$	R^2	K_{fd}	$1/n_{fd}$	R^2	H	K_d (1ppm)
ALDER WOOD (700°C)	(10.62 – 3.30)	3.46 ± 0.21	0.822	(0.98 – 0.98)	3.31 ± 0.00	0.964	1.0	5672.73 ± 156.10
ALDER WOOD (500°C)	(356.45 - 50.35)	1.06 ± 0.16	0.926	(1.48 – 1.16)	2.52 ± 0.02	0.705	2.4	238.59 ± 36.35
APPLE WOOD (700°C)	(16.63 – 3.41)	2.52 ± 0.11	0.764	(1.03 – 0.83)	3.05 ± 0.01	0.201	1.2	546.17 ± 76.79
APPLE WOOD (500°C)	(304.09 – 30.13)	1.21 ± 0.18	0.886	(0.82 – 0.52)	2.77 ± 0.04	0.633	2.3	70.96 ± 18.78
SW-Fe	(58210.32 – 464.52)	2.37 ± 0.12	0.862	(25.06 – 6.65)	2.99 ± 0.04	0.882	1.3	149.01 ± 5.96
CTI-Fe	(214.78 – 42.46)	1.80 ± 0.10	0.940	(1.42 – 1.14)	2.89 ± 0.01	0.707	1.6	63.19 ± 6.96
Goe	(1555.96 – 111.69)	1.03 ± 0.20	0.913	(0.93 – 0.79)	2.82 ± 0.01	0.780	2.7	14.03 ± 5.09
Ferri	(65.77 – 1.06)	2.23 ± 0.05	0.970	(1.06 – 0.96)	3.02 ± 0.01	0.010	1.4	154.69 ± 10.51

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Graphical abstract