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CARRERA PROFESIONAL DE INGENIERÍA AMBIENTAL

“DEVELANDO LOS FACTORES QUÍMICOS Y FÍSICOS QUE  
EXPLICAN LA CAPACIDAD DE ADSORCIÓN DE METALES  
CONTAMINANTES POR EL BIOCHAR”

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**DEVELANDO LOS FACTORES QUÍMICOS Y FÍSICOS QUE EXPLICAN LA CAPACIDAD DE ADSORCIÓN DE METALES CONTAMINANTES POR EL BIOCHAR**

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Luego de haber evaluado el informe final de tesis y evaluado el desempeño del estudiante de la carrera de Ingeniería Ambiental en la sustentación, concluyen de manera unánime ( X ) por mayoría simple ( ) calificar a:

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## DEDICATORIA

A Patricia, mi madre, y Jenny, mi tía, por impulsar mi desarrollo profesional y motivarme a crecer como persona.

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## RESUMEN

Se evaluó la capacidad del biochar de adsorber metales y se verificó, específicamente, la hipótesis de que la capacidad de adsorción depende de las propiedades del biochar, los atributos del metal y por las condiciones experimentales, en ese orden. Para ello, se analizaron 559 isothermas de adsorción de Langmuir individuales extraídas de 133 estudios y se cubrió la capacidad de adsorción del biochar elaborado por seis diferentes clases de materia prima, tres tipos distintos de pretratamientos a la materia prima, cinco tipos de tratamiento post-pirólisis al biochar, y por 17 metales diferentes. La capacidad del biochar de adsorber metales dependió significativamente de la materia prima usada para elaborar el biochar, por la composición elemental del biochar y por el tratamiento post-pirólisis del biochar respectivamente. Este análisis mostró que la materia prima usada para producir el biochar es esencial. Al analizar las variables con el valor de importancia más alto, el biochar elaborado con materia prima rica en nutrientes, pareció ser más efectivo para inmovilizar metales. Los resultados también demostraron la efectividad de los tratamientos químicos post-pirólisis, los cuales acidifican u oxidan el biochar para adsorber los metales. La capacidad del biochar de inmovilizar metales mostró mejores resultados que otros tratamientos de suelos utilizados en la actualidad, y esto, adicionado al hecho de que el biochar puede elaborarse con residuos orgánicos, enfatizó el importante rol que el biochar podría tener en un modelo de economía circular donde los residuos de los procesos de la industria alimentaria podrían ser usados para remediar los suelos y potenciarlos.

## ABSTRACT

The capacity for biochars to sorb metal contaminants was assessed, and the hypothesis that the sorption capacity would be affected by biochar properties, attributes of the metal and by the experimental conditions in that order was tested. 559 individual Langmuir adsorption isotherms were extracted from 133 studies and the adsorption capacity of biochar elaborated from six different feedstock classes, three different types of feedstock pretreatment, five types of post pyrolysis treatments of biochar, and for 17 different metals was covered. The ability of biochars to sorb metals was most significantly affected by the feedstock used to make the biochar, the biochars elemental composition and by post pyrolysis treatment of biochar respectively. In this analysis it was showed that the feedstock used to produce biochar is critical. When analyzing the variables with the highest importance value, Biochar elaborated from nutrient dense feedstocks appeared most effective at immobilizing metals. The results also demonstrated the effectiveness of post pyrolysis chemical treatments which acidify or oxidize the biochar for metal sequestration. Biochars capacity to immobilize metals showed better results than currently used soil remediation amendments, and this, together with the fact that biochar can be made from organic waste highlights the important role that biochar could play in a more circular economy were the residues from the food industry processes could be used to remediate and improve soils.

**I. ARTÍCULO ENVIADO A PUBLICAR**

Unravelling the chemical and physical factors that explain biochars sorption capacity for metal contaminants

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## Abstract

The capacity for biochars to sorb metal contaminants was assessed, and the hypothesis that the sorption capacity would be affected by biochar properties, attributes of the metal and by the experimental conditions in that order was tested. 559 individual Langmuir adsorption isotherms were extracted from 133 studies and the adsorption capacity of biochar elaborated from six different feedstock classes, three different types of feedstock pretreatment, five types of post pyrolysis treatments of biochar, and for 17 different metals was covered. The ability of biochars to sorb metals was most significantly affected by the feedstock used to make the biochar, the biochars elemental composition and by post pyrolysis treatment of biochar respectively. In this analysis it was showed that the feedstock used to produce biochar is critical. When analyzing the variables with the highest importance value, Biochar elaborated from nutrient dense feedstocks appeared most effective at immobilizing metals. The results also demonstrated the effectiveness of post pyrolysis chemical treatments which acidify or oxidize the biochar for metal sequestration. Biochars capacity to immobilize metals showed better results than currently used soil remediation amendments, and this, together with the fact that biochar can be made from organic waste highlights the important role that biochar could play in a more circular economy were the residues from the food industry processes could be used to remediate and improve soils.

**Article Highlights:**

- The predictor variables of  $C_{\max}$  with the highest important value were feedstock, contaminant type, the hydrogen/carbon ratio of biochar and the nitrogen content of the biochar.
- The predictor variables of  $K_L$  with the highest important value were the hydrogen/carbon ratio of the biochar, the background solution used in the sorption experiment, post-treatment of the biochar, and feedstock.
- The best performing biochars were made from animal biowaste, this result correlates with the fact that we found a positive relationship between biochar sorption capacity and nitrogen, meaning that nutrient dense biochars may immobilize contaminants more effectively due to their effects on solute chemistry.

**Keywords:** Biochar, Sorption affinity, Maximum sorption capacity, Metal, Aluminum, Arsenic, Langmuir absorption coefficients.

## Introduction

Contamination of soils with heavy metals and other inorganic pollutants is a global concern (FAO and ITPS 2015; Friberg and Vahter 1983; Selin et al. 2018), seriously threatening human health and our ability to reach the sustainable development goals. According to FAO's global assessment of the main threats to soil, contamination is the third worst threat for Europe, north Asian, central Asian and western Asian; and the fourth most significant threat in north Africa (Montanarella et al. 2016). Soil contamination from inorganic pollutants has received attention through the Minamata convention on mercury which aims to "protect human health and the environment from anthropogenic emissions and releases of mercury and mercury compounds" focusing on policies to regulate mercury emissions into the environment (Selin et al. 2018). However, remediation of already contaminated soils is an equally important challenge. One of the most promising strategies among the array of proposed solutions is the use of organic matter (Alloway 2013; Bradl 2004; Wuana and Okieimen 2014) and especially biochars (Ahmad et al. 2014; Dieguez-Alonso et al. 2019; Vithanage et al. 2017). Biochar has been gaining attention as a potential organic soil amendment for contaminant immobilization owing to specific properties that may be more effective in comparison to non-poly-aromatic carbon sources (Ahmad et al. 2013; Borchard et al. 2012; S. D. Joseph et al. 2010). Furthermore tailored or bespoke biochar formulations could prove even more effective for contaminant immobilization across various soil types (Ahmad et al. 2014; Borchard et al. 2012).

Biochar is produced by applying heat to biological material under oxygen-limited conditions to form a product with a poly-aromatic and porous structure accompanied by volatile compounds and ash, also referred to as  $\text{PYR}_C$  (Pyrogenic Carbon) (Bird et al. 2015). Experimental results suggest that biochar may affect contaminant availability in soil due to its effect on soil pH and/or due to associated ash compounds in biochar that may change soil solution chemistry (Banerjee et al. 2016). Bioavailability may also vary with the contaminant being studied (Chen et al. 2011). Biochar has also attracted attention due to the fact that soil organic matter provides sorption sites (Ahmad et al. 2014; Beesley and Marmiroli 2011; Vithanage et al. 2017), which may change in quantity and quality due to the natural degradation of biochar (e.g. oxidation and formation of functional groups) and due to the occupation of biochar sorption sites by non-pyrogenic organic matter and/or soil nutrients (Nguyen et al. 2010; Prost et al. 2012; Uchimiya, Lima, et al. 2010).

Four main mechanisms have been proposed to explain the ability of biochar to immobilize contaminants (Ahmad et al. 2013; Borchard et al. 2012; S. D. Joseph et al. 2010): 1) electrostatic interactions between contaminant ions and the charged biochar surface, 2) complexation or ionic exchange between ionizable protons on the surface of biochar and contaminant ions, 3) sorptive interactions involving delocalized  $\pi$ -electrons of biochar, and 4) the porous nature of biochar which may favor sorption of contaminants (Borchard et al. 2012; Xiaoling Dong et al. 2014; Vithanage et al. 2017). These mechanisms have been investigated using batch experiments that measure the Langmuir adsorption constant ( $K_L$ ) and the maximum adsorption capacity ( $C_{max}$ ) (Volesky and Holan 1995). The results show a wide range of capacities: some biochars show little to no adsorption capacity for contaminants (Zhou et al. 2013), while others studies/biochars appear very effective for contaminant immobilization (Xudong Dong et al. 2014).

There are many variables involved in biochar production that have been the topic of previous studies. Feedstock has been found to influence the elemental and ash content and the CEC of biochar (Zhao et al. 2013). Pyrolysis temperature can affect carbon content, thermal stability, and the presence of surface functional groups on biochar (Sun et al. 2014; Uchimiya et al. 2011), whereas the duration of this process may affect surface area, ash content and yield of biochar (Wang et al. 2013). Pre- and post-pyrolysis modifications have also been used to enhance the sorption properties of biochar by changing surface properties including surface area, surface charge, functional groups, pore volume and distribution (Rajapaksha et al. 2016; Sizmur et al. 2017).

Approaches used thus far to modify the surface of biochar to increase the sorption efficiency of biochars, include: 1) washing with water (e.g. Inyang et al. 2011) and acids (J. H. Park et al. 2013; Xu et al. 2014), 2) chemical and physical activation (Angin, Altintig, and Köse 2013; Ippolito et al. 2012; S. J. Park et al. 2003), 3) chemical modifications (Betts et al. 2013; Qian, Zhao, and Xu 2013), and 4) magnetic polarization (e.g. M. Zhang et al. 2013). However, the effectiveness of such modifications in comparison to non-modified biochars and traditional technologies (e.g. activated carbon) requires further research (S. Joseph et al. 2013; Ng et al. 2003; Novak et al. 2014).

In order for biochar to become a reliable tool in the remediation of contaminated soils, there is a need to better understand how the modifications mentioned above change biochars sorption ability. This in turn will allow for tailoring of biochar production for specific purposes. To achieve this, the mechanistic processes controlling interactions between inorganic contaminants and biochars need to be addressed systematically. Here we synthesize existing experimental data, extracted from 133 studies, on the ability of biochar to sorb inorganic contaminants. We hypothesize that the capacity for biochars to sorb contaminants is determined by the characteristics of the biochar, the characteristics of the pollutant, and by the experimental conditions in decreasing order of importance.

### Material and methods

An exhaustive literature search was conducted focused on peer-reviewed articles published between January 1 in 2010 and December 31 in 2018 using the Web of Science database (Thomson Reuters) using the term “biochar” in the “topic” field. Of the articles retained, only those that presented the results from batch experiments conducted to assess adsorption capacity and affinity of contaminants on biochar were selected (n=133). These articles reported on a total of 559 individual Langmuir adsorption isotherms. The biochars were categorized into one of six types based on the feedstock used (see Table 1), and studies were grouped by metal contaminant (n=17) (see Appendix 1).

The dependent variables in our analysis were the Langmuir adsorption constant ( $K_L$ ) and the maximum adsorption capacity ( $C_{max}$ ) of the tested biochars.  $K_L$  is a measure of affinity or how strongly the relevant biochars attract the contaminants studied ( $L\ g^{-1}$ ) and  $C_{max}$  is the maximum adsorption capacity of the biochars for the contaminants ( $g\ Kg^{-1}$ ).  $C_{max}$  and  $K_L$  were logarithmically transformed prior to analysis to reduce the influence of outliers in the data set/analysis (Reid 2003). Because our objective was to predict adsorption of contaminants on biochars we collated the information shown in Table 1 for use as independent variables.

Random forest (RF) models were developed by means of the *cforest* function in *party* package for R (Strobl et al. 2007) to assess relationships between  $C_{max}$  and  $K_L$  as response variables and the explanatory variables shown in Table 1, and calculated variable importance values with the *varimp* function. To quantify variability in variable importance scores we developed 20 RF models based on random

selections of 80% of cases. Importance values were based on the mean decrease in model accuracy and were standardized across runs by dividing by the value of the most important variable. A RF model was also generated based on all available data points to evaluate how well the model was able to predict observed values. RF models were run for all contaminants combined, and for individual contaminants when enough numbers of measurements were obtainable from the literature for meaningful statistical analyses (i.e. for Cd, Pb, Cu).

## Results

### *Analysis across all contaminants*

The most important predictor variables of  $C_{\max}$  (RF model with  $R^2=0.63$ ; Figure 1a) were: (i) feedstock, (ii) contaminant type, (iii) the hydrogen/carbon ratio of biochar and (iv) the nitrogen content of the biochar (Figure 1b). The RF model for  $K_L$  produced an  $R^2$  of 0.67 (Figure 1c), the most important predictor variables for it were: (i) the hydrogen/carbon ratio of the biochar, (ii) the background solution used in the sorption experiment, (iii) post-treatment of the biochar, and (iv) feedstock (Figure 1d).

One of the striking aspects of the data was the variability of results obtained by the different studies when  $C_{\max}$  and  $K_L$  values were plotted against individual predictor variables identified as important in the random forest analysis (Figures 2 and 3). Nevertheless, it was possible to unveil some general trends: i) Biochar made from animal biowaste and manure seems to sequester contaminants more effectively than biochar made from woody plant residues, ii) Biochar showed better adsorption capacity for Pb(II) and Cr(VI) than for As(V) and Zn(II), iii)  $C_{\max}$  values decreased as the hydrogen/carbon ratio of the biochar increased, iv)  $C_{\max}$  values increased as the nitrogen content of biochar increased, v)  $K_L$  values increased as the hydrogen/carbon ratio of the biochar increased, vi)  $K_L$  values were higher in experiments that use a di-valent background solution than in experiments that use a mono-valent background solution or deionized water, vii)  $K_L$  values were higher for biochars that were chemically modified, i.e. washed or magnetized following pyrolysis, and viii)  $K_L$  values were higher when biochars made with sludge or manure, and lower when biochars made with woody plant residues or from plant-based food industry waste.

### *Analysis of individual contaminants*

*Cadmium (Cd (II))*: For Cd (II), the random forest analysis for  $C_{\max}$  had an  $R^2$  of 0.53 (Figure 4a). The most important predictor variables were: maximum temperature of pyrolysis, post-treatment and surface area of the biochar and feedstock (Figure 4d). The random forest analysis for  $K_L$  had an  $R^2$  of 0.46 (Figure 5a). The most important predictor variables were: background solution, feedstock, post treatment and the hydrogen/carbon ratio (Figure 5d).

*Lead (Pb (II))*: For Pb (II), the random forest analysis for  $C_{\max}$  had an  $R^2$  of 0.74 (Figure 4b). The most important predictor variables were: the hydrogen/ carbon ratio, feedstock, pretreatment and the percentage carbon of the biochar (Figure 4e). The random forest analysis for  $K_L$  had an  $R^2$  of 0.64. The most important predictor variables were: the hydrogen/carbon ratio, the feedstock, the percent carbon, and post treatment (Figure 5e).

*Copper (Cu (II))*: For Cu (II), the random forest analysis for  $C_{\max}$  had a  $R^2$  of 0.56 (Figure 4c). The most important predictor variables were: feedstock, pyrolysis duration, percent nitrogen and the carbon/nitrogen ratio (Figure 4f). The random forest analysis for the K value had a  $R^2$  of 0.64 (Figure 5c). The most important predictor variables were: post treatment, feedstock, duration and maximum temperature of pyrolysis (Figure 5f).

## Discussion

### *Section 1: How do biochars made of various feedstock compare to other commonly used soil amendments?*

Our results demonstrate that the sorption capacity of biochar is in the range of other commonly used organic soil amendments used to immobilize contaminants that are, however, usually more expensive than biochar (e.g. activated carbon; Table 2) (Ng et al. 2003). However,  $C_{\max}$  values for biochar were extremely variable, and to a large degree, determined by the feedstock used. Even when we only consider a small range of biochars made from the same raw materials the ability to sorb contaminants may span orders of magnitude clearly highlighting the need for more research. The best performing biochars were made from nutrient-dense feedstocks (animal biowaste). However, the number of studies that used this feedstock was limited (n=23), so this result needs to be interpreted with caution. On the other hand, we also found a positive relationship between biochar sorption capacity and nitrogen content which also hints

at the fact that nutrient dense biochars may immobilize contaminants more effectively due to their effects on solute chemistry, as further discussed below. The worst performing biochars were made from wood and these had a lower  $C_{\max}$  than compost.

### *Section II: post-pyrolysis modifications and sorption properties of biochars*

According to the importance values obtained in the random forest projections for both  $C_{\max}$  and  $K_L$ , feedstock, post pyrolysis treatment, and the contaminant in question all played a part in the ability of biochar to sorb contaminants. Washing biochar post pyrolysis was often done to neutralize pH and remove alkaline elements such as ash and soluble salts (Uchimiya, Wartelle, et al. 2010; Yang et al. 2004; P. Zhang et al. 2013). Our results indicated that such washing significantly increased biochars ability to sorb contaminants. This could be related to the augmentation of the effective surface area after washing or reactions inducing formation of oxygen-containing functional groups on biochar surfaces, but further study is needed to unravel the mechanistic basis of the correlation (Leon y Leon et al. 1992). Activation was the post treatment category that resulted in the lowest  $K_L$  values. Most of the studies considered here that reported activation used steam activation to increase surface area and pore volume. However, with steam activation formation of oxygen-containing groups that favor sorption of metals could be low due to the low oxidation value of steam in comparison with the oxidants most commonly used to chemically activate biochar (Shen, Li, and Liu 2012).

In the Random forest models post treatment of biochar had importance scores of  $\sim 0.8$  and  $\sim 0.3$  in the case of  $K_L$  and  $C_{\max}$  respectively. This suggested that chemical modification post pyrolysis could be an important area for future research where the aim is to develop biochar formulations with the capacity to sequester contaminants in soils where contaminant concentrations are low: high affinity may be beneficial in this context.

The use of  $H_2O_2$  was one of the more effective post pyrolysis modifications and this may be due to the transformation of hydroxyl (R-OH) and aldehyde groups (R-CHO) into carboxylic groups (R-COOH) (Xue et al. 2012). This change in functional groups was also an effect that occurred with  $HNO_3$  activation (Hadjittofi, Prodromou, and Pashalidis 2014). Chitosan also appeared to be an effective chemical modifier of biochar that may increase pore volume and surface area (Deng et al. 2017). The use of KOH on the other hand may increase pore volume by removing organic matter and ash (Jin et al. 2016). Finally,



magnetization was a common modification and it emerged as an important determinant of  $K_L$  values in this analysis. Magnetization was normally achieved by Fe-treatment, which increased surface area and may favor the formation of iron oxides on biochar surfaces that may cause co precipitation of contaminants (Bakshi et al. 2018; Son et al. 2018). Magnetization appeared more effective for biochars with well-developed structure and for metals with high mobility (Trakal et al. 2016).

### ***Section III: Recommendations for practitioners and researchers***

The results of this synthesis showed that very simple attributes of biochar can have a very big impact on the potential to immobilize contaminants (Dieguez-Alonso et al. 2019). The implications of this result for the nascent efforts to develop standards for biochar production are important. It showed that the feedstock used to produce the biochar, the H/C ratio, and the N content, determined, to a large degree, how effective a biochar is likely to be at sorbing contaminants. Being confident that a specific biochar formulation tailored for a specific purpose such as contaminant sequestration will be fit for purpose should be a boon in the nascent efforts to develop certification systems for biochar.

The rapid growth in biochar research and funding witnessed over the last decade is a clear indication that both scientists and natural resource managers see potential in biochar. Perhaps the most attractive thing about biochar is its potential to offset significant amounts of anthropogenic greenhouse gases emissions (Werner et al. 2018; Woolf et al. 2010). However, for biochar to achieve this type of climate relevant impact and contribute to the resolution of environmental problems in the real-world, people actually need to use it at scale. The economic value proposition of biochar needs to be clear. This hasn't been the case to date (Bach, Wilske, and Breuer 2017). Developing and demonstrating that biochar can immobilize contaminants hints at an economically viable pathway for getting biochar into the soil. Our results showed that biochar isn't magic, that it worked better for some contaminants than others. Further, even when we consider biochars manufactured from a single feedstock variance was significant, i.e.  $C_{max}$  values from 0.0143 to 980.39 milligrams per gram for biochars made from non-wood plant residues (Tong et al. 2011). This demonstrated that we still need additional study to be able to make clear recommendations about biochar manufacture for specific purposes (Shackley and Sohi 2010). Although theoretical studies are also providing clues to the question of how we can best optimize biochar

manufacture so that biochar is fit for purpose (Dieguez-Alonso et al. 2019; Hagemann et al. 2017; Stephen Joseph et al. 2018). It should also be noted that the results synthesized here are from lab studies. Experiences gained in the lab need to be tested in the field where variations in water availability, temperatures, soil mineralogy etc. may influence the effectiveness of biochar in addressing different challenges. To conclude, the collective progress inherent in the data compiled here demonstrated that biochar has the potential to play an important role in remediation of contaminated soils, and also in the move toward a more circular economy.

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Effects.” *Chemical Engineering Journal* 231: 512–18.

**Table 1:** Metadata of variables used in the analyses.

	VARIABLE	DESCRIPTION
Independent /response Variables	Cmax g Kg <sup>-1</sup>	The maximum adsorbate consumed in the given conditions (Volesky and Holan 1995).
	K-value L g <sup>-1</sup>	The coefficient related to the affinity between the adsorbent and adsorbate (Volesky and Holan 1995). This is a measure of the strength with which a biochar may sequester a contaminant, stickiness is less technical language.
Biochar properties used as dependent variables in the analysis	Feedstock	We used 6 categories (animal bio waste, plant based food industry waste, non woody plant residues, woody plant residues, manure, and sludge). a) Woody plant residues: Plant residues with high C:N ratios and high lignin content. b) Non-woody plant residues: Plant residues with low C:N ratio, and lignin content. c) Plant based food industry waste: Waste from food processing plants, i.e. peels, seeds, etc. d) Animal-bio waste: bone, meat, blood, etc. e) Manure: Any type of manure. f) Sludge: Any sludge, usually obtained from sedimentation ponds linked to waste water treatment but also including brewery sludge.
	Max Temp °C	The maximum temperature during the pyrolysis process.
	Duration hours	The duration of the pyrolysis process.
	Pre treatment	Any treatment applied to the feedstock before pyrolysis: <ul style="list-style-type: none"> <li>Chemical modification (The feedstock was modified by adding: KMnO<sub>4</sub>, AlCl<sub>3</sub>, anaerobically digested, KOH, NaOH, Fe<sub>2</sub>O<sub>3</sub>, flocculating agent, composted, graphene, Na<sub>3</sub>PO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> or H<sub>2</sub>O<sub>2</sub>)</li> <li>H<sub>2</sub>O washed (washed with water or deionized water)</li> <li>None (If there was no treatment mentioned)</li> </ul>
	Post treatment	Any treatment applied to the biochar after pyrolysis: <ul style="list-style-type: none"> <li>Activation (The biochar was activated with KOH, H<sub>2</sub>O<sub>2</sub>, HNO<sub>3</sub>, NH<sub>3</sub>, steam, sonication, or other physical or chemical activators)</li> <li>Chemical modification (The biochar was modified by acidification, oxidation, Al, Br, Ca, P, Mg, Mn, Na, N, Zn, chitosan, gelatin, H<sub>2</sub>O<sub>2</sub>, KOH, NaOH, HNO<sub>3</sub>, KMnO<sub>4</sub>)</li> <li>Magnetization (The biochar was magnetized with a treatment of Fe or Ni/Mn)</li> <li>Washing (The biochar was washed with water, deionized water, HCl, CH<sub>2</sub>Cl<sub>2</sub>)</li> <li>None (If there was no treatment mentioned)</li> </ul>
	Ash content (%)	The percentage ash of the biochar.
	C (%)	The percentage carbon of the biochar.
	H (%)	The percentage hydrogen of the biochar.
	N (%)	The percentage nitrogen of the biochar.
	O (%)	The percentage oxygen of the biochar.
O/C	The atomic ratio between oxygen and carbon found in the biochar.	
H/C	The atomic ratio between hydrogen and carbon found in the biochar.	

	C/N	The mass ratio between carbon and nitrogen found in the biochar.
	Pore diameter (nm)	The diameter of the pores found in the biochar.
	Total pore volume (cm <sup>3</sup> /g or m <sup>3</sup> /t)	The volume of pores found in the biochar.
	CEC (cmol/Kg)	Cation exchange capacity - capacity to sorb cations.
	Surface area m <sup>2</sup> /g N <sub>2</sub>	The surface area of the biochar, this is characterized by the Brunauer-Emmett-Teller (BET) method (Brunauer, Emmett, and Teller 1938).
	pH (biochar)	The pH of the biochar.
Attributes of the contaminant contaminants used as dependent variables in the analysis across all contaminant types	Contaminant	The species of contaminant used in the adsorption experiment (Ag, Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, U, Zn).
	Anion/Cation	Shows if the metal used has a positive (cations) or negative charge (anions).
	Goldschmidt Classification	The geochemical behavior (of the contaminant studied) separates the chemical nature of the contaminant according to the classification of Goldschmidt. This classification is based on the formation of oxides and sulfides and provides a view of the affinities / associations between elements. It also allows us to know which cations are more likely to enter to spaces in the particles of mineral structures. This is determined based on the ionic radius and the ionic charge (Goldschmidt 1954; Scott and Pain 2019).
	Geochemical availability	This variable (geochemical availability) is a measure of the pH which causes a dissolution or maximum mobility of the contaminant being considered (Sarkar and Taylor 2010).
	Ionic radius Angström	The ionic radius is the distance between the nucleus and the electron in the outermost shell of an ion.
	Ionic charge	The electrical charge of an ion, created by the gain (negative charge) or loss (positive charge) of one or more electrons from an atom or group of atoms.
	Ionic potential	Relation between ionic radius and its charge. This measure allows us to know how strong or weak the ion will be electrostatically attracted to ions of opposite charge (Railsback and Georgia 2015).
	Molar mass	A physical property defined as the mass of a given substance divided by the amount of substance.
Experimental Conditions used as dependent variables in the analyses	Normality	The normality of a solution is the gram equivalent weight of a solute per liter of solution.
	Background solution	Solution where the adsorption experiment takes place. The solutions were categorized as deionized water (DI), mono-valent (e.g. NaNO <sub>3</sub> ), di-valent (e.g. CaCl <sub>2</sub> ).
	pH (solution)	The pH of the solution is a categorical variable related to the solution used for the adsorption experiment. The solutions were CaCl <sub>2</sub> , H <sub>2</sub> O, or KCl.
	Contact time (h)	The time in which the biochar was in contact with the contaminant for the adsorption process.

Table 2: a)  $C_{max}$  values of biochar and compost obtained by synthesizing the peer reviewed literature, and  
 b)  $C_{max}$  values of three commonly used amendments soil remediation taken from empirical studies.

Amendment	$C_{max}$ (g/Kg)	Standard Deviation	Metal	Source
<i>a) estimates of absorption capacity of soil amendments obtained from literature syntheses</i>				
Biochar	65.1 (mean value)	120.01		This study (appendix S1)
Biochar (animal biowaste)	317 (mean value)	189.62		This study
Biochar (wood)	33 (mean value)	55.77		This study
Compost	43.27 (mean value)	133.76		Anastopoulos & Kyzas, 2015
<i>b) estimates of absorption capacity of soil amendments from individual empirical studies</i>				
Activated carbon (heated with $H_2S$ )	230		Hg(II)	Gomez-Serrano, MacÍas-García, Espinosa-Mansilla, & Valenzuela-Calahorra, 1998
Activated carbon (modified with tetrabutyl ammonium)	9.9		Cu(II)	Monser & Adhoum, 2002
Granular activated carbon	20		Zn(II)	Álvarez-Merino, López-Ramón, & Moreno-Castilla, 2005
Chitosan	815		Hg(II)	Mckay & Blair, 1989
Chitosan	273		Cr(VI)	Udaybhaskar, Iyengar, & Rao, 1990
Sludge	560		Hg(II)	Srivastava, Tyagi, & Pant, 1989
Sludge	95		Zn(II)	Srivastava, Singh, & Sharma, 1994
Sludge	1865		Pb(II)	Srivastava, Singh, & Sharma, 1994

Legend to Figures:

Figure 1: A) The correlation between predictions of  $C_{\max}$  derived from the Random Forest model vs. values reported in the peer reviewed literature ( $R^2 = 0.63$ ). B) The correlation between Random Forest  $K_L$  predictions and measured values ( $R^2 = 0.67$ ), C) The most important independent variables for  $C_{\max}$  prediction, D) The most important variables for  $K_L$  prediction. See Table 1 for detailed description of the independent variables used in the analyses, and appendix S1 for raw data.

Figure 2: Univariate plots of the 4 most important variables for  $C_{\max}$  prediction across all contaminant species.

Figure 3: Univariate plots of the 4 most important variables for  $K_L$  prediction across all contaminant species.

Figure 4: Observed vs. predicted values for individual metals + variable importance plots for  $C_{\max}$  for the three most studied individual contaminants. A & D) Cadmium, B & E) Lead, C & F) Copper.

Figure 5: Observed vs. predicted values for individual metals and variable importance plots for  $K_L$  for the three most studied individual contaminants. A & D) Cadmium, B & E) Lead, C & F) Copper.

Figure 1:

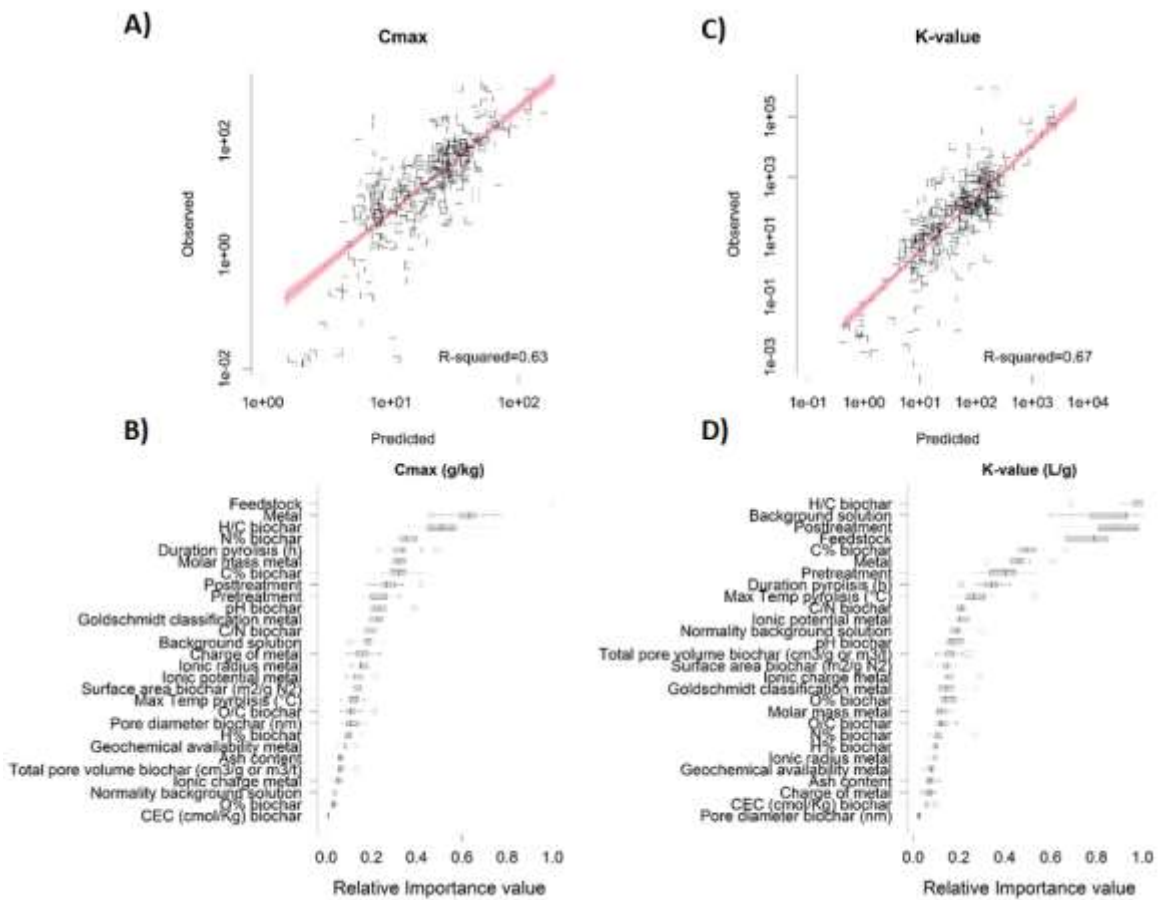


Figure 2:

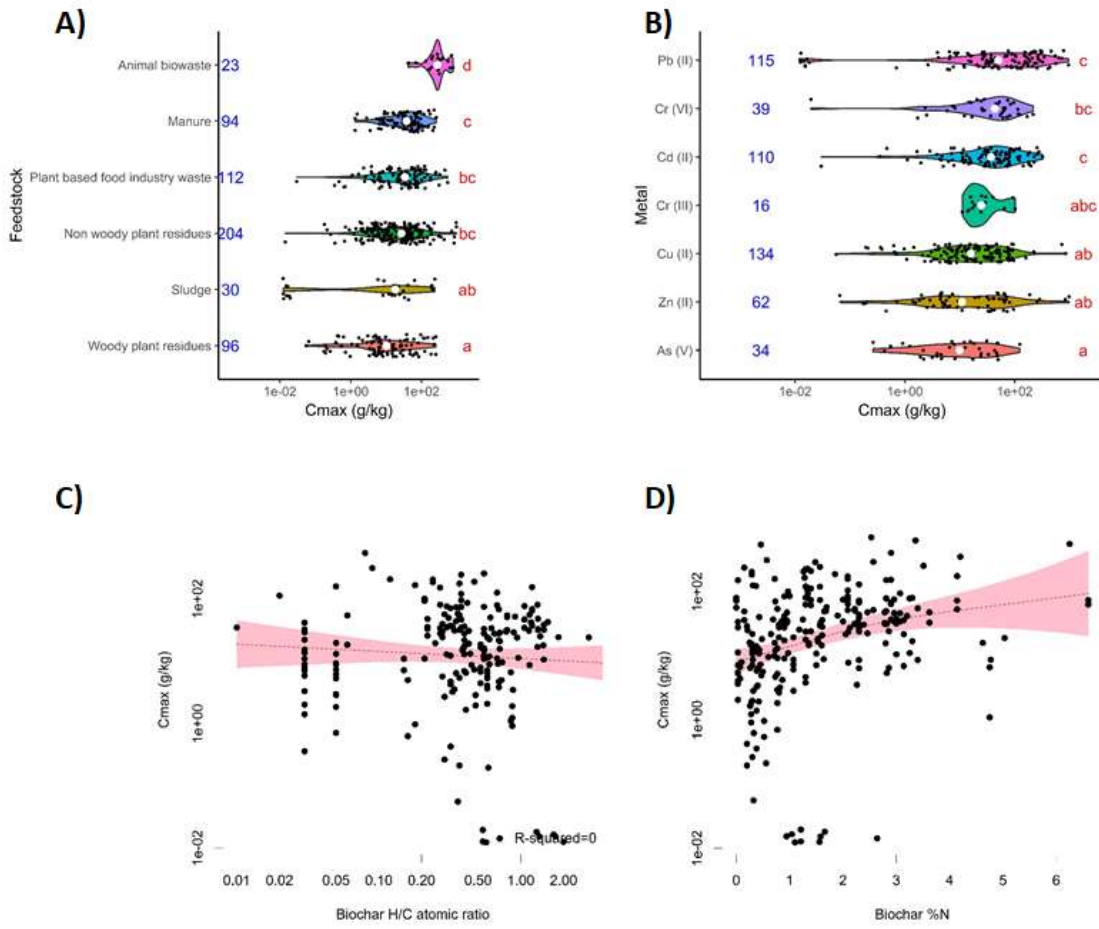




Figure 3:

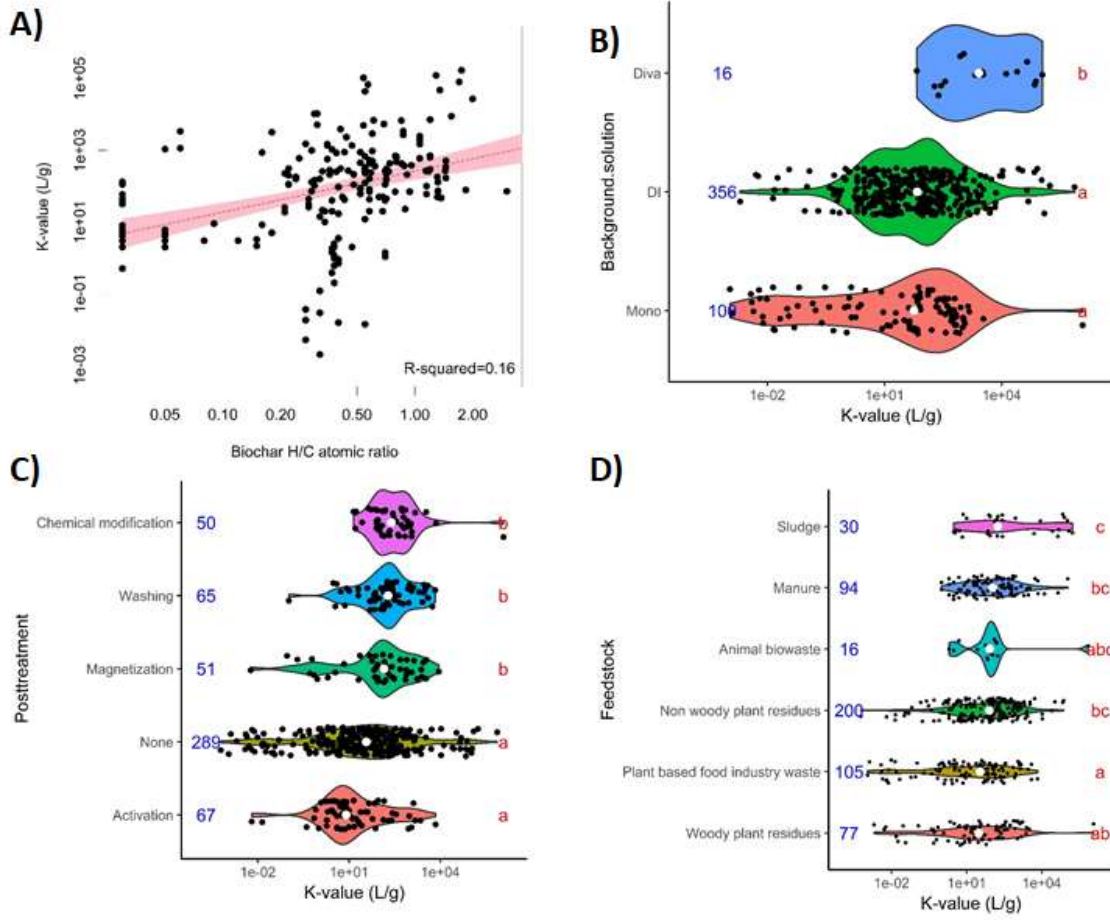


Figure 4:

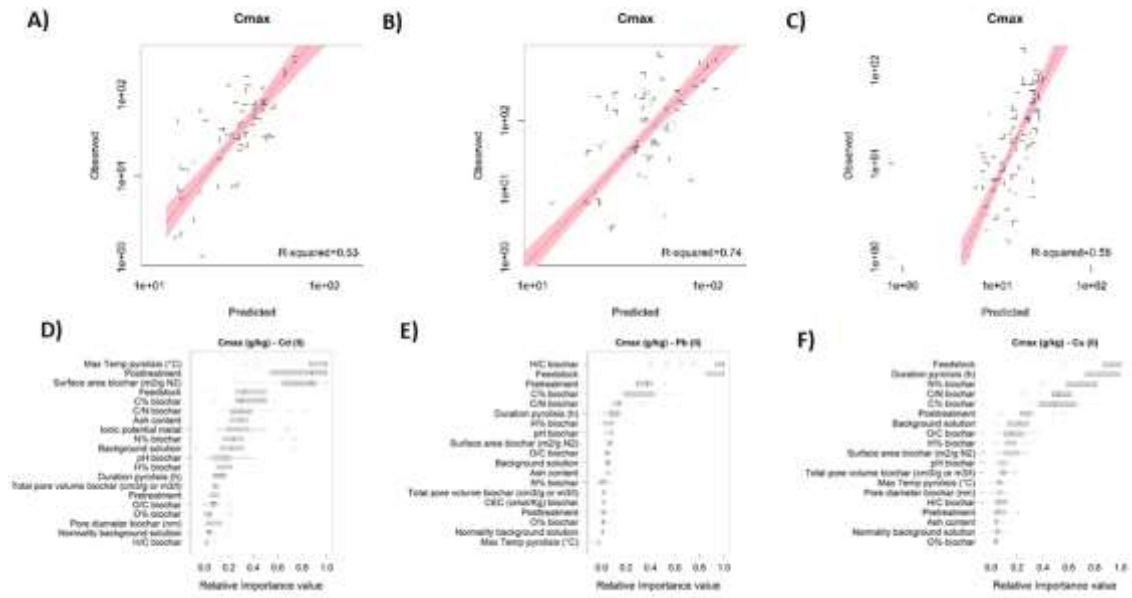
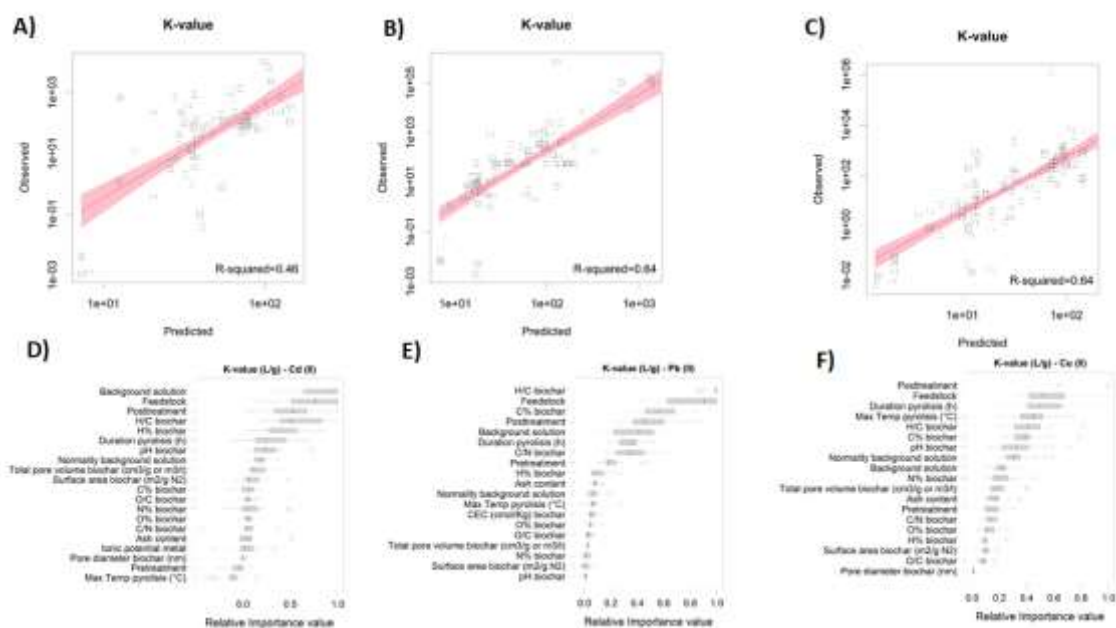


Figure 5:



## II. VERSIÓN EN CASTELLANO

### Resumen

Se evaluó la capacidad del biochar de adsorber metales y se verificó, específicamente, la hipótesis de que la capacidad de adsorción depende de las propiedades del biochar, los atributos del metal y por las condiciones experimentales, en ese orden. Para ello, se analizaron 559 isothermas de adsorción de Langmuir individuales extraídas de 133 estudios y se cubrió la capacidad de adsorción del biochar elaborado por seis diferentes clases de materia prima, tres tipos distintos de pretratamientos a la materia prima, cinco tipos de tratamiento post-pirólisis al biochar, y por 17 metales diferentes. La capacidad del biochar de adsorber metales dependió significativamente de la materia prima usada para elaborar el biochar, por la composición elemental del biochar y por el tratamiento post-pirólisis del biochar respectivamente. Este análisis mostró que la materia prima usada para producir el biochar es esencial. Al analizar las variables con el valor de importancia más alto, el biochar elaborado con materia prima rica en nutrientes, pareció ser más efectivo para inmovilizar metales. Los resultados también demostraron la efectividad de los tratamientos químicos post-pirólisis, los cuales acidifican u oxidan el biochar para adsorber los metales. La capacidad del biochar de inmovilizar metales mostró mejores resultados que otros tratamientos de suelos utilizados en la actualidad, y esto, adicionado al hecho de que el biochar puede elaborarse con residuos orgánicos, enfatizó el importante rol que el biochar podría tener en un modelo de economía circular donde los residuos de los procesos de la industria alimentaria podrían ser usados para remediar los suelos y potenciarlos.

**Puntos destacados:**

- Las variables predictivas del  $C_{max}$  con el mayor valor de importancia fueron la materia prima, el tipo de contaminante, la relación hidrógeno/carbono del biochar y el contenido de nitrógeno del biochar.
- Las variables predictivas del  $K_L$  con el mayor valor de importancia fueron la relación hidrógeno/carbono del biochar, la solución base utilizada en el experimento de adsorción, el tratamiento posterior del biochar y la materia prima.
- Los biochars con mejor desempeño fueron hechos de residuos animales, este resultado se correlaciona con el hecho de que se encontró una relación positiva entre la capacidad de adsorción del biochar y el contenido de nitrógeno, esto significaría que los biochars más densos en nutrientes podrían inmovilizar contaminantes de forma más eficiente debido a sus efectos en la química del soluto.

**Palabras clave:** Biochar, Afinidad de adsorción, Capacidad máxima de adsorción, Metal, Contaminantes, Aluminio, Arsénico, Coeficiente de adsorción de Langmuir.

## Introducción:

La contaminación del suelo con metales pesados y otros contaminantes inorgánicos es un problema global que amenaza seriamente la salud humana, así como nuestra habilidad de alcanzar metas de desarrollo sostenible (FAO y ITPS 2015; Friberg y Vahter 1983; Selin et al. 2018). De acuerdo con la evaluación global de la FAO (*Food & Agriculture Organization*) respecto a las principales amenazas del suelo, la contaminación es la tercera mayor amenaza en Europa, Norteamérica, Asia central y Asia occidental; y es la cuarta amenaza significativa en el norte de África (Montanarella et al. 2016). La contaminación del suelo debido a contaminantes inorgánicos ha recibido atención a través de la convención de Minamata sobre el mercurio, cuya meta es proteger a la salud humana y al ambiente, de emisiones antropogénicas y liberaciones de este elemento y sus derivados, enfocándose en políticas para regular dichas emisiones al ambiente (Selin et al. 2018). Sin embargo, la remediación de suelos ya contaminados es un desafío igualmente importante. Una de las estrategias más prometedoras entre el grupo de soluciones propuestas, es el uso de materia orgánica (Alloway 2013; Bradl 2004; Wuana y Okieimen 2014), especialmente de biochar (Ahmad et al. 2014; Dieguez-Alonso et al. 2019; Vithanage et al. 2017). El biochar ha ido ganando atención como potencial enmienda orgánica del suelo a través de la inmovilización de contaminantes debido a sus propiedades específicas, las cuales podrían ser más efectivas comparadas con fuentes de carbono no poli aromáticas (Ahmad et al. 2013; Borchard et al. 2012; S. D. Joseph et al. 2010). Además, la formulación hecha a la medida de un biochar podría probar ser aún más efectiva para la inmovilización de contaminantes en distintos tipos de suelos (Ahmad et al. 2014; Borchard et al. 2012).

EL biochar se produce al aplicar calor a material biológico en condiciones con oxígeno limitado para formar un producto con una estructura poli aromática y porosa, acompañada de compuestos volátiles y ceniza, también conocidos como PYRc (*Pyrogenic Carbon*) (Bird et al. 2015). Resultados experimentales sugieren que el biochar podría afectar la disponibilidad del contaminante en el suelo debido a su efecto en el pH, y/o debido a los compuestos asociados a las cenizas del biochar las cuales podrían cambiar la composición química del suelo (Banerjee et al. 2016). La biodisponibilidad podría variar de acuerdo al contaminante estudiado (Chen et al. 2011). El uso de biochar también ha llamado la atención debido a que la materia orgánica del suelo proporciona sitios de adsorción (Ahmad et al. 2014; Beesley and Marmiroli 2011; Vithanage et al. 2017), los cuales pueden variar en cantidad y calidad por la degradación natural del biochar (ejemplo: oxidación y formación de grupos funcionales), y debido a la ocupación de los sitios de adsorción del biochar por materia orgánica no pirogénica y/o nutrientes del suelo (Nguyen et al. 2010; Prost et al. 2012; Uchimiya, Lima, et al. 2010).

Se han planteado cuatro mecanismos principales para explicar la habilidad del biochar para inmovilizar contaminantes (Ahmad et al. 2013; Borchard et al. 2012; S. D. Joseph et al. 2010): 1) interacciones electrostáticas entre los iones de los contaminantes y la superficie cargada del biochar; 2) complejación o intercambio iónico entre protones ionizables en la superficie del biochar y los iones del contaminante; 3) interacciones de adsorción que involucran a los electrones  $\pi$  deslocalizados del biochar; y 4) la naturaleza porosa del biochar, la cual puede favorecer la adsorción de contaminantes (Borchard et al. 2012; Xiaoling Dong et al. 2014; Vithanage et al. 2017). Estos mecanismos han sido investigados usando experimentos por pilas que miden la constante de afinidad de adsorción de Langmuir ( $K_L$ ) y la capacidad máxima de adsorción ( $C_{max}$ ) (Volesky y Holan

1995). Los resultados mostraron un amplio rango de capacidades: algunos biochars mostraron poca o ninguna capacidad de adsorción de contaminantes (Zhou et al. 2013), mientras que otros estudios/biochars parecieron muy efectivos en la inmovilización de contaminantes (Xudong Dong et al. 2014).

Existen muchas variables involucradas en la producción de biochar que han sido materia de estudios anteriores. Se ha descubierto que la materia prima influye en el contenido elemental y las cenizas así como en la CIC (capacidad de intercambio catiónico) del biochar (Zhao et al. 2013). La temperatura del proceso de pirólisis pudo afectar el contenido de carbono, la estabilidad térmica y la presencia de grupos funcionales en la superficie del biochar (Sun et al. 2014; Uchimiya et al. 2011), mientras que la duración de dicho proceso pudo afectar el área de la superficie, el contenido de ceniza y la producción del biochar (Wang et al. 2013). Las modificaciones pre y post pirólisis también han sido usadas para mejorar las propiedades de adsorción del biochar al cambiar las propiedades de su superficie incluyendo área, carga, grupos funcionales, volumen de los poros y distribución (Rajapaksha et al. 2016; Sizmur et al. 2017).

Los métodos usados hasta el momento para modificar la superficie del biochar e incrementar su eficiencia de adsorción incluyen: 1) lavado con agua (e.g. Inyang et al. 2011) y ácidos (J. H. Park et al. 2013; Xu et al. 2014); 2) activación química y física (Angin, Altintig, y Köse 2013; Ippolito et al. 2012; S. J. Park et al. 2003); 3) modificaciones químicas (Betts et al. 2013; Qian, Zhao, y Xu 2013); y 4) polarización magnética (e.g. M. Zhang et al. 2013). No obstante, la efectividad de dichas modificaciones en comparación con biochars no modificados y tecnologías no tradicionales (ejemplo: carbono activado) requiere mayor investigación (S. Joseph et al. 2013; Ng et al. 2003; Novak et al. 2014).



Para que los biochars se conviertan en una herramienta confiable en la remediación de suelos contaminados necesitamos tener un mejor entendimiento respecto a cómo las modificaciones antes mencionadas cambian la habilidad de adsorción del biochar. Esto permitirá la producción de biochar para propósitos específicos. Para lograr ello, los procesos mecanizados que controlan las interacciones entre los contaminantes inorgánicos y el biochar deben ser atendidos sistemáticamente. Aquí hemos sintetizado la data experimental existente, extraída de 133 estudios sobre la habilidad del biochar de adsorber contaminantes inorgánicos. Nosotros hipotetizamos que la capacidad del biochar de adsorber contaminantes inorgánicos está determinada, en orden de importancia descendiente, por las características del propio biochar, las características del contaminante y por las condiciones experimentales.

### **Material y métodos:**

Se realizó una búsqueda exhaustiva enfocándonos en artículos publicados y revisados entre el 01 de enero del 2010 y el 31 de diciembre del 2018 usando la base de datos *Web of Science (Thomson Reuters)* e ingresando el término “biochar” en el campo de “*topic*”. De los artículos encontrados, solo fueron seleccionados aquellos que mostraron resultados de experimentos por pilas, realizados para determinar la capacidad de adsorción y la afinidad de los contaminantes por el biochar (n=133). Estos artículos reportaron un total de 559 isoterms individuales de absorción de Langmuir. Los biochars fueron clasificados en uno de seis tipos en base a la materia prima utilizada (ver Tabla 1), y los estudios fueron agrupados por el metal contaminante (n=17) (ver Anexo 1).

Las variables dependientes en nuestro análisis fueron la constante de adsorción de Langmuir ( $K_L$ ) y la capacidad máxima de adsorción ( $C_{max}$ ) de los biochars evaluados. La  $K_L$  es una medida de afinidad o cuán fuerte es la atracción de los biochars hacia los contaminantes estudiados ( $L\ g^{-1}$ ) y el  $C_{max}$  es la capacidad máxima de adsorción de contaminantes por el biochar ( $g\ Kg^{-1}$ ).  $C_{max}$  and  $K_L$  fueron transformados logarítmicamente antes del análisis para reducir la influencia de valores atípicos en la base de datos/análisis de la data (Reid 2003). Debido a que nuestro objetivo era predecir la adsorción de contaminantes por el biochar, recolectamos la información mostrada en la Tabla 1 a ser usada como variables independientes.

Desarrollamos modelos *random forest* (RF) por el promedio de la función *cforest* del paquete *party* para R (Strobl et al. 2007) para evaluar la relación entre el  $C_{max}$  y  $K_L$  como variables de respuesta y las variables explicativas mostradas en Tabla 1, y se calculó la variable de importancia con la función *varimp*. Para cuantificar la variabilidad en la variable de los valores de importancia, desarrollamos 20 modelos RF basados en la selección aleatoria del 80% de los casos. Los valores de importancia estuvieron basados en la disminución promedio en el modelo de exactitud y fueron estandarizados a través de corridas al dividirlos por el valor de la variable más importante. También generamos un modelo RF basado en todos los puntos de la data disponible para evaluar qué tan bien el modelo fue capaz de predecir los valores observados. Los modelos RF fueron corridos para todos los contaminantes combinados, y para cada contaminante de forma individual en los casos en los cuales se obtuvieron suficientes mediciones para un análisis estadístico significativo (ejemplo: para Cd, Pb, Cu).

## Resultados

### ***Análisis de todos los contaminantes***

Las variables de predicción más importantes de  $C_{max}$  (modelo RF con  $R^2=0.63$ ; Figura 1a) fueron: (i) materia prima, (ii) tipo de contaminante, (iii) la proporción hidrógeno/carbono del biochar y (iv) el contenido de nitrógeno del biochar (Figura 1b). El modelo RF para  $K_L$  produjo  $R^2=0.67$  (Figura 1c). Las variables de predicción más importantes fueron: (i) la proporción hidrógeno/carbono del biochar, (ii) la solución base del experimento de adsorción, (iii) el tratamiento posterior del biochar, y (iv) la materia prima (Figura 1d).

Uno de los aspectos sorprendentes de la data fue la variabilidad de resultados obtenidos de los diferentes estudios cuando los valores de  $C_{max}$  y  $K_L$  fueron correlacionados con variables de predicción individuales determinadas importantes en el análisis RF (Figuras 2 y 3). Sin embargo, fue posible descifrar algunas tendencias generales: i) El biochar hecho de residuo biológico animal y estiércol parece adsorber contaminantes de manera más efectiva que uno hecho de residuos de vegetal leñoso, ii) El biochar mostró mejor capacidad de adsorción para  $Pb(II)$  y  $Cr(VI)$  que para  $As(V)$  y  $Zn(II)$ , iii) Los valores de  $C_{max}$  disminuyeron a medida que la proporción hidrógeno/carbono aumenta en el biochar, iv) Los valores de  $C_{max}$  aumentaron a medida que el contenido de nitrógeno aumenta en el biochar, v) Los valores de  $K_L$  aumentaron a medida que la proporción hidrógeno/carbono aumenta en el biochar, vi) Los valores de  $K_L$  fueron más elevados en experimentos que usaron una solución divalente que en aquellos que usaron una solución monovalente o agua desionizada, vii) Los valores de  $K_L$  fueron más elevados en biochars que fueron químicamente modificados, por ejemplo lavados o magnetizados después de la pirólisis, y viii) Los valores de  $K_L$  fueron más elevados cuando los biochars

son hechos de lodos o estiércol, y menos elevados cuando están hechos de residuos vegetales leñosos o desechos de fábricas de alimentos provenientes de una fuente vegetal.

### **Análisis de contaminantes individuales**

*Cadmio (Cd (II))*: Para el Cd (II), el análisis RF para  $C_{max}$  tuvo un  $R^2$  de 0.53 (Figure 4a). Las variables de predicción más importantes fueron: temperatura máxima de pirólisis, tratamiento posterior, el área superficial del biochar y la materia prima (Figura 4d). El análisis RF para  $K_L$  dio un  $R^2$  de 0.46 (Figura 5a). Las variables de predicción más importantes fueron: La solución base, la materia prima, el tratamiento posterior y la relación hidrógeno/carbono (Figura 5d)

*Plomo (Pb (II))*: Para el Pb (II), el análisis RF para  $C_{max}$  tuvo un  $R^2$  de 0.74 (Figura 4b). Las variables de predicción más importantes fueron: la proporción hidrógeno/carbono, la materia prima, el tratamiento previo y el porcentaje de carbono del biochar (Figura 4e). El análisis RF para  $K_L$  tuvo un  $R^2$  de 0.64. Las variables de predicción más importantes fueron: la relación hidrógeno/carbono, la materia prima, el porcentaje de carbono y el tratamiento posterior (Figura 5e).

*Cobre (Cu (II))*: Para el Cu (II), el análisis RF para  $C_{max}$  dio un  $R^2$  de 0.56 (Figura 4c). Las variables de predicción más importantes fueron: la materia prima, la duración de la pirólisis, el porcentaje de nitrógeno y la relación carbono/nitrógeno (Figura 4f). El análisis RF para el valor de  $K_L$  dio un  $R^2$  de 0.64 (Figura 5c). Las variables de predicción más importantes fueron: el tratamiento posterior, la materia prima, la duración de la pirólisis y la temperatura máxima de la pirólisis (Figura 5f).

### **Discusión:**

***Sección 1: ¿Cómo se comparan los biochars hechos de diferentes materias primas con otros tratamientos comúnmente usados para el suelo?***

Nuestros resultados demostraron que la capacidad de adsorción del biochar está dentro del rango de otros tratamientos orgánicos del suelo usados comúnmente que, no obstante, normalmente son más caros que un biochar (por ejemplo el carbón activado; Tabla 2) (Ng et al. 2003). Sin embargo, los valores de  $C_{max}$  para el biochar fueron extremadamente variantes, y en gran medida, debido a la materia prima utilizada. Inclusive cuando solo se consideraron un pequeño rango de biochars hechos con los mismos materiales, la capacidad de adsorber contaminantes pudo abarcar órdenes de magnitud evidenciando claramente la necesidad de mayor investigación. Los biochars de mejor rendimiento fueron hechos con materia prima rica en nutrientes (residuo orgánico animal). Pero el número de estudios que utilizaron este tipo de materia prima fue limitado ( $n=23$ ), así que el resultado debe ser interpretado con cuidado. Por otro lado, también encontramos una relación positiva entre la capacidad de adsorción del biochar y el contenido de nitrógeno lo cual sugiere que los biochars ricos en nutrientes podrían inmovilizar los contaminantes debido a su efecto en la química del suelo, como se analiza con mayor detalle abajo. Los biochars de peor rendimiento fueron hechos de materia vegetal leñosa y estos tenían un  $C_{max}$  menor que el compost.

***Sección II: modificaciones post-pirólisis y propiedades de adsorción del biochar***

De acuerdo con los valores de importancia obtenidos en las proyecciones de RF tanto para  $C_{max}$  como  $K_L$ ; la materia prima, el tratamiento post-pirólisis, y el contaminante en sí, jugaron un papel importante en la habilidad del biochar de adsorber contaminantes.

El lavado post-pirólisis de los biochars se realizó frecuentemente para neutralizar el pH y remover elementos alcalinos como las cenizas y las sales solubles (Uchimiya, Wartelle, et al. 2010; Yang et al. 2004; P. Zhang et al. 2013). Nuestros resultados indicaron que dicho lavado aumenta significativamente la habilidad del biochar de adsorber contaminantes. Esto pudo estar relacionado con el aumento del área superficial efectiva luego del lavado o las reacciones que conllevan a la formación de grupos funcionales que contienen oxígeno en la superficie del biochar; sin embargo, es necesario un estudio más profundo para develar la base mecánica de esta correlación (Leon y Leon et al. 1992). La activación fue la categoría de tratamiento posterior que tuvo los menores valores de  $K_L$ . La mayoría de los estudios considerados aquí que emplearon activación usaron una activación a vapor para aumentar el área superficial y el volumen de poros. No obstante, con la activación a vapor la formación de grupos con contenido de oxígeno que favorecen la adsorción de metales pudo ser baja debido al bajo valor de oxidación del vapor en comparación con los oxidantes comúnmente utilizados en la activación química de los biochars (Shen, Li, and Liu 2012).

En los modelos RF para tratamientos posteriores del biochar, se dio puntaje de importancia de 0.8 y 0.3 para el caso de  $K_L$  y  $C_{max}$  respectivamente. Esto sugiere que la modificación química post-pirólisis podría ser un área importante de futuras investigaciones donde el objetivo sea desarrollar formulaciones de biochar con la capacidad de atrapar contaminantes en suelos donde la concentración de contaminantes sea baja, ya que una mayor afinidad podría ser beneficiosa en ese contexto.

El uso de  $H_2O_2$  fue una de las modificaciones post-pirólisis más efectivas y esto puede deberse a la transformación de grupos hidroxilo (R-OH) y grupos aldehídos (R-CHO) en grupos carboxílicos (R-COOH) (Xue et al. 2012). Este cambio en los grupos funcionales es también un efecto de la activación con ácido nítrico ( $HNO_3$ ) (Hadjittofi, Prodromou, and Pashalidis 2014). El quitosano también parece ser un efectivo modificador químico del biochar que podría incrementar el volumen de poros y el área superficial (Deng et al. 2017). Por otro lado, el uso de hidróxido de potasio (KOH) podría incrementar el volumen de poros removiendo material orgánico y cenizas (Jin et al. 2016). Por último, la magnetización es una modificación común y apareció como un importante determinante de los valores  $K_L$  de este análisis. La magnetización se logra comúnmente mediante tratamiento con hierro, el cual aumenta el área superficial y podría favorecer la formación de óxidos de hierro en la superficie del biochar, lo cual a su vez podría causar la coprecipitación de los contaminantes. La magnetización parece más efectiva para los biochars con estructuras bien desarrolladas y para metales de mayor movilidad (Trakal et al. 2016).

### ***Sección III: Recomendaciones para profesionales e investigadores***

Los resultados de esta síntesis mostraron que atributos muy simples de un biochar pueden tener un gran impacto en su potencial para adsorber contaminantes (Dieguez-Alonso et al. 2019). Las implicancias del resultado de esfuerzos incipientes de desarrollar estándares para la producción de biochars son importantes. Esto muestra que la materia prima usada para producir biochar, la relación hidrógeno/carbono, y el contenido del Nitrógeno determinan, en gran medida, cuán efectivo es un biochar en adsorber

contaminantes. Tener la confianza de que una formulación a la medida para un propósito en específico como el secuestro de un contaminante debería ser una ventaja en los nacientes esfuerzos de desarrollar sistemas certificados de producción de biochar.

El rápido crecimiento en la investigación y financiamiento del biochar observado en la última década es una clara señal de que tanto los gestores de recursos científicos como lo de recursos naturales ven potencial en este. Tal vez, lo más atractivo sobre el biochar es su potencial para compensar cantidades significantes de emisiones de gases de invernadero antropogénico (Werner et al. 2018; Woolf et al. 2010). Sin embargo, para que el biochar logre esta relevancia en el impacto climático y puedan contribuir a la resolución de problemas ambientales en el mundo real, las personas tienen que empezar a utilizarlo a escala. El valor económico de la propuesta del uso de biochar debe estar claro, y a la fecha, este no ha sido el caso (Bach, Wilske, y Breuer 2017). El desarrollo y demostración de que los biochars pueden inmovilizar contaminantes, representaría un camino económicamente viable para llevar los biochars a los suelos. Nuestros resultados mostraron que el uso de biochar no es magia, que funcionó mejor para algunos contaminantes que otros. Inclusive, cuando consideramos biochars desarrollados de una misma materia prima, la varianza fue significativa, por ejemplo, los valores de  $C_{max}$  varían entre 0.0143 a 980.39 miligramos por gramo para los biochars hechos con residuos vegetales no leñosos (Tong et al. 2011). Esto demuestra que se necesitan estudios adicionales para poder dar recomendaciones claras sobre la fabricación de biochars para propósitos específicos (Shackley y Sohi 2010). Aunque algunos estudios teóricos también han brindado respuestas a la interrogante de cómo optimizar la manufactura del biochar para que sirva su propósito (Dieguez-Alonso et al. 2019; Hagemann et al. 2017; Stephen Joseph et al. 2018), también se debe destacar que



los resultados obtenidos aquí son de estudios en laboratorio. Las experiencias obtenidas en los laboratorios deben ser evaluadas en el campo donde las variaciones de disponibilidad del agua, temperaturas, mineralogía del suelo, etc. influenciarían la efectividad del biochar planteando diferentes desafíos. En conclusión, el progreso colectivo inherente en la data recolectada aquí demuestra, más allá de la duda, que los biochars tienen el potencial de jugar un rol importante en la remediación de la contaminación de suelos, y para dirigirnos hacia una economía más circular.

III. **ANEXOS (OBLIGATORIO SI LOS TIENES)**  
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