

CZECH UNIVERSITY OF LIFE SCIENCES PRAGUE

**Faculty of Environmental Sciences
Department of Environmental Geosciences**



**Metal sorption efficiency of biochar modified by manganese
oxides**

BACHELOR THESIS

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FINAL THESIS ASSIGNMENT

Andreu Piqueras Barceló

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Thesis title

Metal sorption efficiency of biochar modified by manganese oxides

Objectives of thesis

Aim of this study is to compare removal rate of newly modified biochar (by amorphous manganese oxide) on different metal(loid)s. Laboratory pH-stat experiments will be implemented in order to assess metal(loid) sorption efficiency of the biochar.

Methodology

Biochar prepared previously by Trakal et al. (2014) will be here utilized. Biochar will then be modified by amorphous manganese oxide (AMO) and birnessite, respectively. Additionally, the AMO by itself will also be utilized.

First, all tested sorbents will be analysed for their initial characteristics (pH, PZC, CEC and presence of Mn oxides in the structure of biochar). Next, laboratory batch experiment with synthetic metal or metalloid solution will then be implemented in order to establish a sorption efficiency of all tested sorbents. More specifically, pH-stat experiment with synthetic solution of Cd(II), Pb(II) and As(V) will be realized under pH = 5.00 and pH = 7.00 until equilibrium state. Sorption efficiency (in time) of current metal or metalloid will then be counted for each sorbent individually and the efficiency will then be compared/evaluated.

The proposed extent of the thesis

40-50

Keywords

biosorption, biochar, amorphous manganese oxide, metals and metalloids

Recommended information sources

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DECLARATION

I declare that this thesis developed independently under the supervision of Mgr. Lukás Trakal, Ph. D and Maria Isabel Villaescusa, Ph. D and I stated all literature and publications, from which I drew.

In Prague on

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ABSTRACT

The main aim of this bachelor thesis is to test and compare the newly modified biochars efficiency in removing metal(loid)s from water of by using amorphous manganese oxide (AMO). The studied metal(loid)s were arsenic, cadmium and lead in its dissolved form As(V), Cd(II) and Pb(II). The sorption was measured by solving 1mM of the metal(loid) in an aqueous solution. The experiments were analysed in batch. The modified biochars resulted to be highly efficient, especially synthesized together composites because were produced using the same procedure than non-purified AMO which means without the purification. The purification of AMO synthesis is a wash with milling water got demonstrated that decreases the sorption potential of the manganese modified biochar and also the AMO. The non-purification enhanced the sorption 80% better in arsenic, 40% more in cadmium and 25% better in lead removal compared to the original biochar. Kinetics were also studied for all the metal(loid)s that reveal again a better removal curve for synthesized together and non-purified AMO. The high efficiency of lead sorption and the fast kinetics presented by both AMOs suggests technological applications in lead removal from wastewaters.

Keywords: biosorption, biochar, amorphous manganese oxide (AMO), metals, metalloids, AMO-biochar composites.

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1 HYPOTHESIS AND AIM OF THE STUDY

The aim of this study was to increase the performance of the biochar and the AMO by creating modified biochar (by amorphous manganese oxide). Specially, the aim of this study was to improve the adsorption efficiency of manganese oxide modified biochar combining the affinities for the adsorption of AMO and biochar separately.

AMO-modification of biochar will be suitable improvement for metal(loid)s sorption from aqueous solution.

For this purpose laboratory pH-stat experiments will be implemented in order to assess metal(loid) sorption efficiency of the biochar.

2 REVIEW

2.1 METAL(LOID)S HAZARD IN ENVIRONMENT

The main problem of the heavy metals such arsenic, cadmium and lead is that have a strong affinity to bioaccumulation. It means that once an animal or plant absorbs these metals it belongs a long time in the trophic chain causing several health problems.

In the case of arsenic a variety of adverse health effects, e.g. skin and internal cancers, cardiovascular, and neurological effects mainly from drinking water (Abernathy et al. 1999)¹.

Arsenic tends to reduce from As(V) to As(III), when the As(V) is reduced into As(III) it is reacting and producing methylarsonic acid and dimethylarsinic acid. These acids can perturb the mitochondrial respiration and as a consequence of this the production of ATP (adenosine triphosphate) can decrease (Abernathy et al. 1999)¹.

For these reasons arsenic has become a worldwide public health issue, being controlled around the world.

The more problematic regions are located in the east of China, Bangladesh and the southeast of Asia and in the south of South America.

The main sources of arsenic are the rocks and minerals that contain it. To consider water is not contaminated by arsenic the concentration of the metal must be between 0.0005-0.001 mg/L (Wang et al. 2005)⁵³.

Another important source of arsenic is the erosion of the rocks, but there are other ways of arsenic pollution, e.g. the pesticides. Arsenic is present in many pesticides, in wood preservatives and thermal and coal-fired power generation.

As the others heavy metals when they start being part of environment it is very complicated to remove them.

As all the heavy metals, As remains in the food chain for a long time if it's not removed.

Figure 1 is a simple representation of the main sources of arsenic and the different ways of arsenic fate and transport in the environment, water, atmosphere and soil.

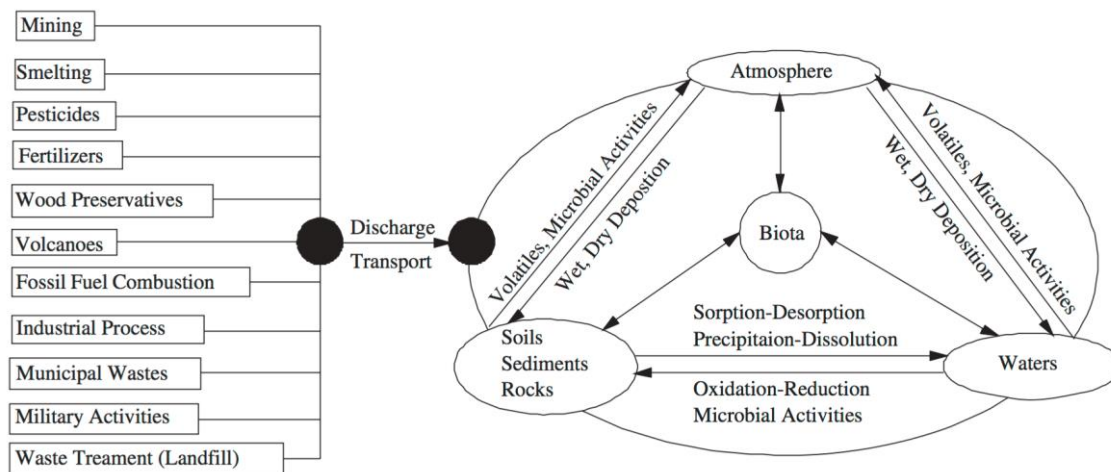


Figure 1. Simple diagram of arsenic cycle (Wang et al. 2005)⁵³.

According to cadmium is classified among substances with high toxicity, persistence and tendency towards bioaccumulation (Quinn et al., 2011)⁴⁰.

This metal have been associated with various forms of cancer, nephrotoxicity (toxicity of the kidneys), central nervous system effects and cardiovascular disease in humans in short-term exposure (Barry Ryan et al., 2000)¹³.

According to WHO's recommendation the limit concentration in drinking water of Cd(II) is 0.005 mg/L (Rao et al., 2010)⁴¹.

Finally, lead is the oldest known toxic metal and exposure to this metal can majorly occur through drinking water, smoking or even due to various industrial processes like smelting, through battery recycling, and paints. Lead exerts its toxicity basically by replacing the monovalent and bivalent ions like Na⁺, Ca⁺ and Mg⁺. This disturb metabolism and affect directly to processes like cell adhesion, cell signalling, apoptosis and release of neurotransmitters (Iyer et al., 2015)²⁷.

2.2 METAL(LOID)S IN AQUEOUS SOLUTIONS

2.2.1 Arsenic

Arsenic is a metalloid; it means that its behaviour is in between the metallic and the non-metallic elements. Arsenic has four oxidation states (-3, 0, +3, +5) being the two first oxidation states organic forms of arsenic. (As(-III) is very difficult to find because it is only found in extremely reduced environments) (Wang et al. 2005)⁵³. The most common states are: As (III) and As (V), being both easy to find in the environment. As (III) is considered more toxic and you can find it in reduced environment conditions. Nevertheless As (V) remove it is more common in oxidized environment conditions.

As said before, arsenic in water is found as As(III) and As(V) which are the two oxidation states of inorganic arsenic. Whereas it's very uncommon to find organic arsenic in the water because it can't be dissolved so it is negligible.

It is more common to find inorganic arsenic in waters. That's like this because the organic arsenic requires being produced by biological activity; it's common to find it when the water is significantly polluted from industries.

Most of toxic trace metals occur in solution as cations (e.g. Pb^{2+} , Cu^{2+} , Ni^{2+} , Cd^{2+} , Co^{2+} , Zn^{2+}), which generally become increasingly insoluble as the pH increases. It is common to find these metal(loid)s in ground waters but their solubility is limited by precipitation or co-precipitation. In fact most oxyanions including arsenate tend to become more weakly sorbed as the pH increases (Dzombak D A and Morel F M M, 1990)²⁰.

Sorption of arsenite on amorphous Fe hydroxide and activated alumina increased at low pH, peaked between pH 7 and 8, and decreased at high pH. (Adriano 2001)³. Arsenic has more affinity to get adsorbed by oxides. The oxides that are more common are iron oxide and manganese oxide.

In general, As(III) is more weakly sorbed than As(V); it is generally more mobile in the +3 oxidation state than in the +5 oxidation state (Adriano 2001)³.

Major Cycle (Inorganic As)

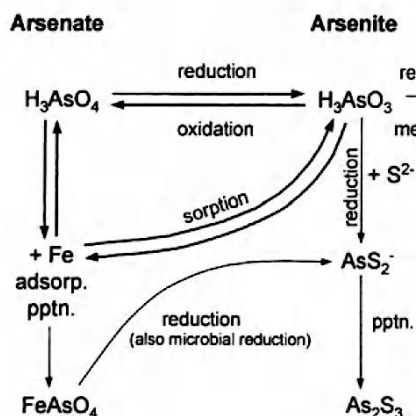


Figure 2. Cycle of inorganic arsenic during a sorption and its speciation in water (Adriano 2001)³.

In figure 2 the mechanism of adsorption is to oxidise As(III) to As(V) and adsorb it using a Fe oxide which also has a strong affinity towards As. In this study, the oxide used is Mn oxide. According to this information, Mn oxides have the ability to remove As from the water because As(III) tends to react with the oxide and gets oxidized to As(V) which is more easy to adsorb (Adriano 2001)³.

The manganese oxide reacts with arsonite (As(III)) in a acid environment producing arsenic acid (As(V)) and the manganese cation.

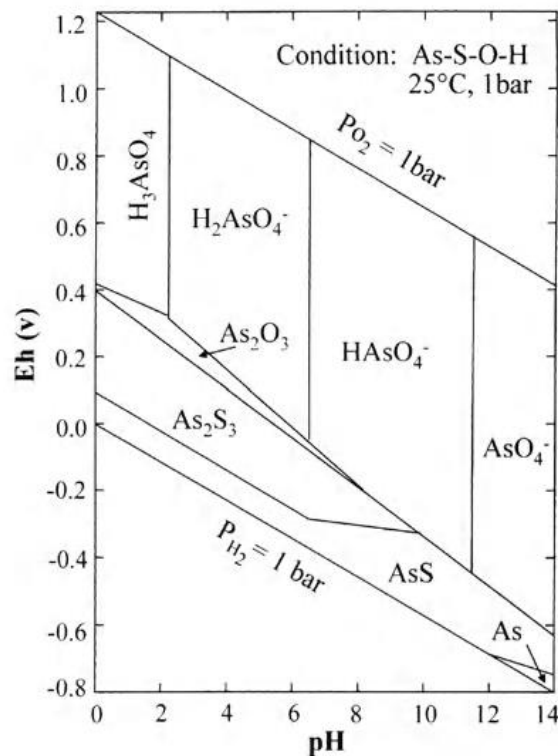
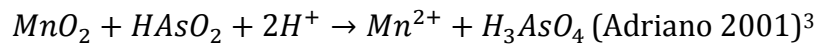


Figure 3. Predicted Eh-pH stability field for arsenic (Adriano 2001)³.

The speciation of arsenic that we can find in ground waters is explained in this graphic. Also is possible to see that the pH is directly related with the reduction potential and it means that the ideal pH to work is the one that is easy to find As(V) because as said before it is easy to be adsorbed. When looking at figure 3 we can conclude that this pH is around 6-8 because according to the reduction potential is an spontaneous pH for As(V) to be formed.

Arsenic mobilisation sensitivity at ground waters frequent pH (pH 6.5–8.5) and under oxidising and reducing conditions (Smedley and Kinniburgh, 2001)⁴⁵. One of the more common oxyanion-forming elements in ground waters is the As oxyanion. Arsenic is the most problematic oxyanion-forming elements because of its relative mobility over a wide range of redox conditions (Smedley and Kinniburgh 2002)⁴⁶.

2.2.2 Cadmium

Cadmium is a transition metal; it has two oxidation states, Cd(I) and Cd(II) nevertheless in most of cadmium compounds this metal is found as Cd(II). That's because Cd(I) is not stable in water and it directly changes into the Cd(II) form.

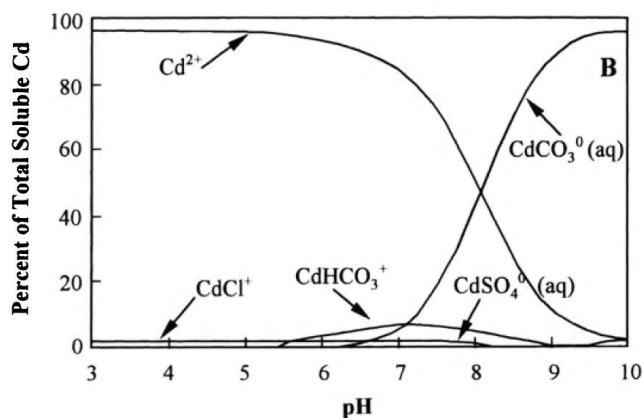


Figure 4. Speciation of cadmium depending on the pH in water (Adriano 2001)³.

Cadmium is an element that can appear in many stable complexes in aqueous solution. There may be 10 to 20 different metal cations (including trace metals) that can react with many different inorganic and organic ligands to form 300 to 400 soluble complexes and up to 80 solid phases. Under pH 6 almost all the Cd dissolved exist in the form Cd^{2+} usually associated with carbonates. Under reduced conditions, the amount of sulphide and organic matter becomes dominant (Vink 2010)⁵¹. At pH between 6 and 8.2, Cd carbonate species ($CdHCO_3^+$ and $CdCO_3^0$) become more important. Between pH 8.2 and 10, almost all the cadmium soluted is a neutral carbonate, $CdCO_3^0$. Other species like $CdHCO_3^+$, $CdSO_4^0$, $CdCl^+$ and $CdOH^-$ are also present but at lower concentrations. (Adriano 2001)³.

It is not usual to find organic Cd because its behaviour is similar to Ca once and the concentration of calcium is very high in all the waters. So the organic complexes are preferably made with calcium.

The pH plays an important role in the solubility of cadmium in water; solubility is increased at low pH. In spite of this Cd at high pH (7.0-8.4) can precipitate as phosphate or carbonate.

Several factors may influence the degree by which Cd is adsorbed. In addition to pH, ionic strength and exchangeable cations also influence Cd adsorption. Ionic strength of various salt solutions (NaClO_4 , NaCl , and Na_2SO_4) affected the amount of Cd sorbed on montmorillonite surfaces. The adsorption of Cd^{2+} from Cl^- solutions decreased while salt concentration was increasing, and formed some uncharged and negatively charged complexes of Cd with Cl^- ligands. (Adriano 2001)³. The main problem of the chloro species of Cd is that are less strongly adsorbed than Cd^{2+} .

The adsorption of cadmium is also perturbed by other cations present in water. Calcium is a huge competitor of cadmium just for the fact explained before about the precipitation. Zinc is also a truly competitor. When both metals are present in solution the adsorption level of both decreases; adsorption is ineffective at pH between 4 and 8. At higher pH the Zn is more likely to get adsorbed.

2.2.3 Lead

Lead is also considered a heavy metal. Its oxidation states are: Pb(II) and Pb(IV). The most important lead oxides are: lead monoxide, PbO , in which lead is in the +2 state; lead dioxide, PbO_2 , in which lead is in the +4 state; and tri lead tetroxide, Pb_3O_4 .

Most of the lead in an aqueous solution is adsorbed due to cation exchange. The surface of biochar contains many functional groups, having some of them a cation in the end of the chain being most of them Na, Ca, K... The point is that lead has more affinity with oxygen because of the electrostatic force. Therefore lead exchanges the position with these cations and is adsorbed by the biochar.

Lead has strong affinity to be sorbed by organic composites, so it's easy to find lead in soils because of the organic matter present in soils. (Adriano 2001)³.

That means that it is easy for lead to reach ground waters when it rains.

The speciation of Pb in soils and waters is: exchangeable, sorbed, organic, carbonate and sulphide fractions of lead. The predominant species is carbonate

fraction, although the less common is exchangeable and sorbed fractions of lead in water what indicate low bioavailability.

The solubility of lead is 100 times less than cadmium in the pH range of 5 to 9.

The adsorption of lead in aqueous solutions conformed to either the Langmuir or Freundlich isotherm over a wide range of concentrations.

In other situations, the oxides of Mn and Fe may exert a predominant role on Pb adsorption by soils. When measuring the adsorption of several trace elements by synthetic Mn and Fe oxides, it was found that Pb adsorption by Mn oxides was up to 40 times greater than that by the Fe oxides, and that Pb was adsorbed more strongly than any other metal (Co, Cu, Mn, Ni, and Zn) studied.

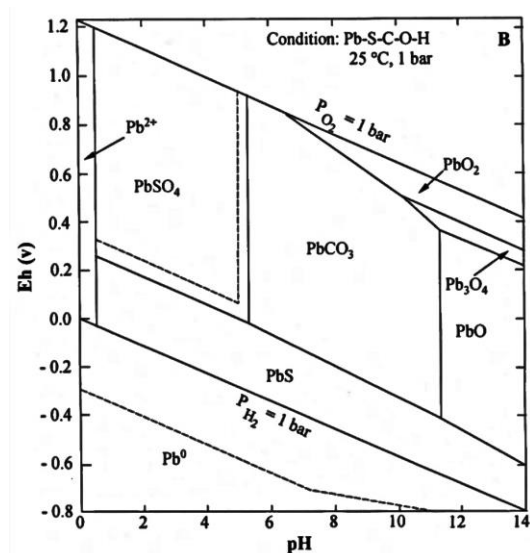


Figure 5. Aqueous speciation of lead as a function of pH (Adriano 2001)³.

2.3 Removal of metal(loid)s from waste waters

2.3.1 Principal methods

The metal(loid)s removal from water is composed of many different ways and their effectivity depends on the metal and the purpose of removal. Being some of these techniques cheaper than others but the main reason to choose one of them is the affinity or the efficiency with the metal you pretend to remove.

METHOD	SUMMARY	METAL REMOVED	REFERENCE	
Chemical precipitation	Molecule or element that reacts with the metal producing a molecule that precipitates.	Pb	(Matlock et al. 2002) ³³	
		As		
Flotation	Add a substance that reacts with the metal creating a complex molecule and forming a colloid where the solid phase is less dense and it floats.	Fe	(Gonzalez-Muñoz et al., 2006) ²⁴	
		Cu	(Rubio and Tessele 1997) ⁴³	
		Ni		
Sorption	Adsorption	Pb	(Cao et al. 2009) ¹⁵	
		Cd		
	Absorption	The metal is sorbed inside the molecule, can be physical or chemical process.		—
		Ion exchange	Chemical process that works with the affinity of the metals to separate them from the water.	(Dabrowski et al., 2004) ¹⁷
Electrochemical deposition	Uses electricity to pass a current through an aqueous metal-bearing solution containing a cathode plate and an insoluble anode. Positively charged metallic ions cling to the negatively charged cathodes	Pb	(Agarwal et al., 1984) ⁴	
		Cu		
		Ni	(Yang, 2003) ⁵⁵	
		Cd		

	leaving behind a metal deposit that is strippable and recoverable.		
Membrane filtration	Uses the pressure to make the water pass through a membrane with small pores. The pores are able to separate the metal from the water.	Cu Ni Zn	(Blöcher et al., 2003) ¹²
Electrodialysis	Membrane separation in which ionized species in the solution are passed through an ion exchange membrane by applying an electric potential. The membranes are thin sheets of plastic materials with either anionic or cationic characteristics. When a solution containing ionic species passes through the cell compartments, the anions migrate toward the anode and the cations toward the cathode, crossing the anion exchange and cation exchange membranes.	Pb Zn Cd Cu	(Pedersen et al., 2003) ³⁸ (Ferreira et al., 2005) ²²
Photocatalysis	Acceleration of a photoreaction in the presence of a catalyst. In catalysed photolysis, light is absorbed by an adsorbed substrate. In photo-generated catalysis, the photo-catalytic activity (PCA) depends on the ability of the catalyst to create electron-hole pairs, which generate free radicals (e.g. hydroxyl radicals (OH) able to undergo secondary reactions.	Cr Pb Co	(Ku and Jung, 1999) ³⁰ (Harraz et al., 2013) ²⁶

Table 1. Summary of sorption methods for metal(loid)s removal.

2.3.2 Sorption methods

Sorption is any removal of a compound from solution to a solid phase. It can be a physical process, or a chemical and physical process, it depends on if there is or there is not a chemical reaction.

Sorption is a general concept, so the best way to understand it is explaining the types of sorption.

Absorption is a physical or chemical phenomenon in which a molecule or atom (sorbate) reacts with the sorbent and gets inside the volume of the sorbent. It's different than adsorption, in which the sorbate remains in the surface after the reaction.

There are two types of absorption, the chemical absorption and the physical absorption. As said before, the chemical absorption includes a chemical reaction between the sorbent and the sorbate. And the physical reaction is only a physical process without any reaction.⁶⁶

Adsorption capacity of all solid substances to attract to their surfaces molecules of gases or solutions they are in contact with. Solids that are used to adsorb gases or dissolved substances are called adsorbents; the adsorbed molecules are usually referred to adsorbate. An example of an excellent adsorbent is the charcoal used in gas masks to remove poisons or impurities from a stream of air.

Adsorption can be also a chemical process or a physical process, the same as absorption.⁶⁷

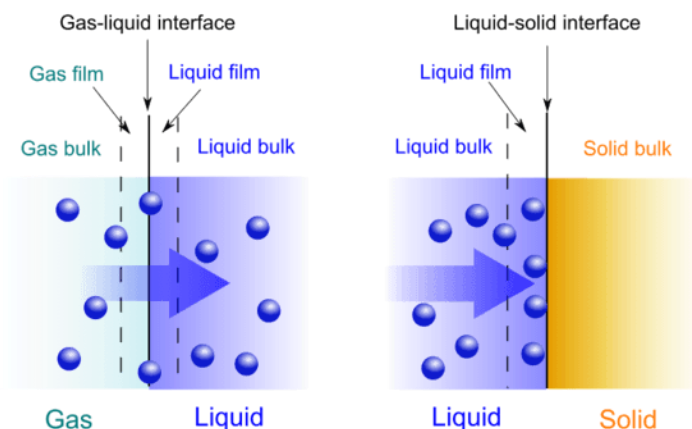


Figure 7. The main differences of absorption and adsorption. On the left side absorption between gas-liquid. On the right adsorption between liquid-solid ⁶⁹.

Adsorption is the preferred technique for heavy metals removing from polluted waters. That's why there are a lot of materials able to adsorb the ions of these metals. The following table summarize the most used adsorbents in metal removal.

MATERIAL	METAL REMOVED	REFERENCE
Activated carbon (agricultural solid waste)	Cu, Ni, Pb	(Kadirvelu et al., 2001) ²⁸
Manganese and iron oxides	Cu, Cd, Pb, Zn	(Della Puppa et al., 2013) ³⁹
Clays (Na-montmorillonite)	Cd, Cr, Mn, Pb	(Abollino et al., 2003) ²
Submerged aquatic plants (<i>Ceratophyllum demersum</i>)	Cu, Pb, Zn	(Keskinan et al., 2004) ²⁹
Biochar	- Nut shells - Plum stones - Wheat straws - Grape stalks	(Trakal et al., 2014) ⁵⁰

Table 2. Compilation of studies related with sorption in metal removal.

Ion exchange is the only method that involves chemical reaction. The reaction consists between two substances, one positively charged and the other negatively charged.

Ions are atoms or groups of atoms that can be negatively or positively charged. When ionic substance is dissolved in the water the ions are freed. It means that are not more retained in the crystal form of the substance. Therefore is easily for them to react with a negatively charged substance not dissolved in the water replacing the negatively charged ions from the surface. This method is widely used in the scientific laboratory. Some of the applications are to purify water and medically to act as artificial kidneys.⁶⁸

2.3.3 Biosorption as heavy metals removal from water

In the recent years there appeared a new kind of sorption, in which the sorbent is biologic. The discovery of the **biosorption** was a revolution. Biosorption represents a very effective tool to remove or separate metals from water. The word biosorption comes from the microbial, alive or dead, which has cells where the metals can be placed and in consequence, removed from the solution. That's the simple explanation of biosorption. There are many different ways of biosorption and they depend directly on the metabolism of the cells.

The biosorption process needs a solid phase, which will be the adsorbent where the metal will be retained, and a liquid phase where the metal will be solved before being adsorbed.

Biosorption of heavy metal is a passive non-metabolically mediated process of metal binding by biosorbent. Biosorbents are usually agricultural waste and industrial by-products, bacteria, fungi or algae. Biosorption is considered to be a fast physical/chemical process, and the type of the process governs its rate. During the biosorption other processes may be present like ion exchange, coordination, complexation, chelation, adsorption and microprecipitation (Febrianto et al., 2014)²¹

According to the reference (Sun et al., 2014)⁴⁸, a wide range of biosorbents were tested in heavy metals removal as crab shell particles, dried activated sludge, tea waste, wool, coconut copra meal, baker's yeast, for example. And there are plenty of theorems that predict the biosorption equilibrium (Langmuir, Freundlich, Brunauer-Emmett-Teller (BET), Sips...) but Langmuir and Freundlich models are the most popular ones because can define almost all the equilibriums in biosorption as concludes (Sun et al., 2014)⁴⁸.

The range of biosorbents studied is getting wider the recent years because as said before, the discovery of biosorption was a revolution in heavy metal removing from waters.

According to (Annadurai et al., 2003)⁷ every biosorbent must have a large surface area in order to improve the performance. This last study named was working with banana and orange peel because of that trying the efficiency removing copper,

zinc, lead, cobalt and nickel. The results showed that orange and banana peel has strong affinity with lead but in general it worked well with all the metals studied.

The biosorption basically has a solid phase (the sorbent, in our case amorphous manganese oxide, AMO, and biochar), which is the material that retains the metal. And a liquid phase which is a solution that contains the metals dissolved.

When a biosorption process starts it takes some time (depends directly to the metal that has to be adsorbed, the pH, the solution...) to reach the equilibrium between the amount of metal sorbed on the sorbent and the concentration of the metal in solution.

The behaviour of a substance being biosorbed in an aqueous solution is similar for all the processes. For this reason we can conclude that there is one isotherm model for all the substances. The isotherms tend to increase the sorption very fast at the beginning of the experiment until reaching the equilibrium, which depends on the material sorbed and also on the sorbent.

As said before, many materials have been tested as biosorbents in order to remove heavy metals from waters. Including algae, fruit peel, fungi, and many others. But one of the most common biosorbents, and also one that these last years is being more important is the **biochar**.

2.3.4 Biochar as biosorbent

Biochar is a very useful biosorbent. That means that biochar is a natural product able to remove contaminants from the environment, mainly from the water. It is natural because it comes from the pyrolysis or carbonization of plant and animal based biomass.

In the past biochar was connected to the ancient Amerindian known as Terra Preta de Indio (Ahmad et al. 2013)⁵.

Biochar was first used as a soil amendment for soil fertility and sustainability. The different applications of biochar are: soil improvement, waste management, climate change mitigation, energy production. All of this can be explained because of its high organic C content.

Biochar works as an sorbent and the specific properties of biochar are large specific surface area, porous structure, enriched surface functional groups and mineral components, and they make biochar a perfect adsorbent working in

contaminated waters for removing pollutants. Most of these properties can be found in activated carbon, which is known as very good adsorbent already. The main differences between biochar and activated carbon is that biochar is simply cheaper to produce, because the temperature to synthesize is lower than activated carbon (Tan et al., 2014)⁴⁹. The distribution of the chemicals on the surface of the biochar plays an important role on the biochar efficiency. These chemicals are different for different types of biochar made of; the pyrolysis temperature also has an important role. When the pyrolysis temperature is increased most of the chemicals groups are decreasing (Tan et al., 2014)⁴⁹. Another characteristic related to the amount of functional groups in the surface is the O/C ratio is: a higher ratio means that the surface will be rich of chemicals and functional groups such as hydroxyl, carboxylate and carbonyl. And this means a higher cation exchange capacity of the biochar, which means a high efficiency of the adsorbent.

The surface of the biochar is the most important point of it. It define how it works. Basically the structure is composed by carbon and oxygen, the relation between the volume and the surface is very big so that makes biochar a good sorbent. In the Figure 8 it is shown the composition of the surface.

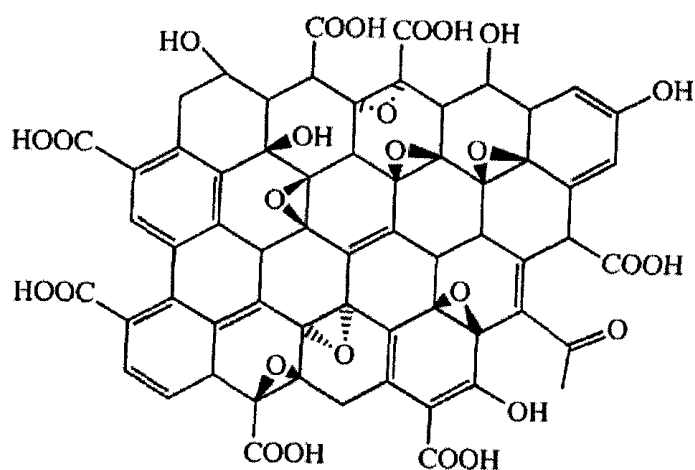


Figure 8. Distribution of the functional groups in the surface of biochar. (Lehmann and Joseph 2009)³¹.

Biochar has been studied in the last years as an important sorbent for its properties and because it is economic to produce. And it has been studied removing a big quantity of heavy metal(loid)s. The following table show some examples.

BIOCHAR	METAL REMOVED	REFERENCE
Biochar, orchance prune residues	As	(Beesley et al., 2013) ¹⁰
Biochar, sewage sludge	Cu, Ni, Pb, Zn	(Beesley et al., 2010) ¹¹
Biochar, green waste compost	As, Cd, Cu, Zn	(Méndez et al., 2012) ³⁴
Biochar, oak wood and oak bark	Cd, Pb	(Mohan et al., 2014) ³⁶
Magnetic biochar, pine bark	Cd, Pb	(Harikishore and Lee, 2014) ²⁵
Biochar, crop straws	Cd	(Sun et al., 2014) ⁴⁸

Table 3. Biochar compilation in metal(loid)s removal.

A high degree of pyrolysis means less functional groups on the surface and also less exchange of cations. Therefore, the best biochar is produced at low temperature. On the other hand high temperature means that cellulose and hemicellulose will escape due to volatilization and the adsorbent surface area will increase. Also the quantity of pores will increase too. The structure of the biochar will change and some porous structures will be placed inside of the biochar.

Another important issue about biochar is the pH. It can be alkaline or acid, depending on the pyrolysis temperature and the feedstock that has been used for producing the biochar.

The following figure shows the exchangeable cations that biochar has. Being Ca, K and Na the cations that can exchange with lead and get adsorbed.

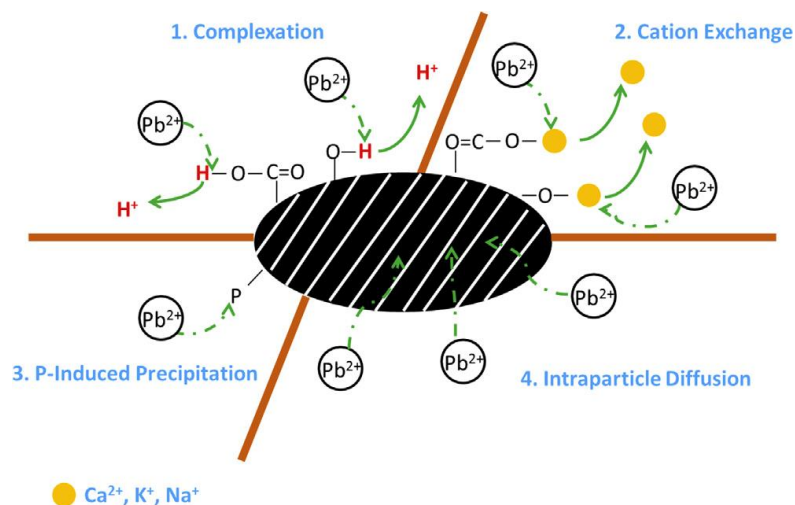


Figure 6. Four more common methods to remove lead from water (Iyer et al., 2015)²⁷.

Adsorption isotherm is essential in optimizing the use of adsorbents because it describes how adsorbates interact with adsorbents. A number of empirical models have been employed to analyse experimental data and describe the equilibrium of heavy metals adsorption onto biochars. As evidenced by the collected data, both Langmuir and Freundlich model fit the data better than other equations when used to describe the equilibrium adsorption of heavy metals by biochars. (Tan et al., 2015)⁴⁹.

2.3.5 Biochar modifications to improve its adsorption

Biochar has a very wide range of affinities in removing metals from the water. The main characteristic is how the biochar is made with, because as commented before it is made of organic waste. It's for that reason that biochar has been mixed many times with other compounds so as to improve the efficiency at adsorbing heavy metals.

There are some studies that modified biochar by another composite. Amino modification of the biochar is a promising method for enhancing the adsorption efficiency of metal ions on biochar. Therefore, amino modification made biochar very useful to selectively adsorb metal ions (Yang and Jiang, 2014)⁵⁶.

According to the study (Liu et al., 2012)³² biochar was modified with acid or alkali in order to change the surface areas as well as the amount of functional groups of the biochar surface. Changing these two factors the adsorption potential was affected. They concluded that the modified biochar had a stronger potential at removing metals from water.

Biochar modified with chitosan was tested in the study (Zhang et al., 2015)⁵⁷ and (Zhou et al., 2013)⁵⁸. This combination was combining the adsorption potential of the biochar and the chemical affinity of chitosan. Was demonstrated that that chitosan-modified biochar not only effectively removed heavy metals from aqueous solutions, but also greatly reduced the toxicity of heavy metals to plants. Another treatment that was tried with the biochar was with hydrodioxide. That increased the oxygen-containing groups on the biochar surface and so enhances its ability to remove heavy metals from water (Xue et al., 2012)⁵⁴

One of the compounds that have been studied mixing it with biochar is the manganese oxide in this study will be tested the efficiency of the biochar combined with this manganese oxide.

The modification of biochar by using iron oxides is called magnetic biochar, (Micháلكova et al., 2014)³⁵ evaluated the potential of Fe-oxides for the stabilization of Cd, Pb and Cu.

2.3.6 Biochar modification by using manganese oxides

Iron and manganese oxides have both the affinity to immobilize metals in aqueous solutions. Particularly manganese oxide has a strong power with As.

Biochar has been mixed with AMO: amorphous manganese oxide. It is a very efficient compound and also really cheap to produce.

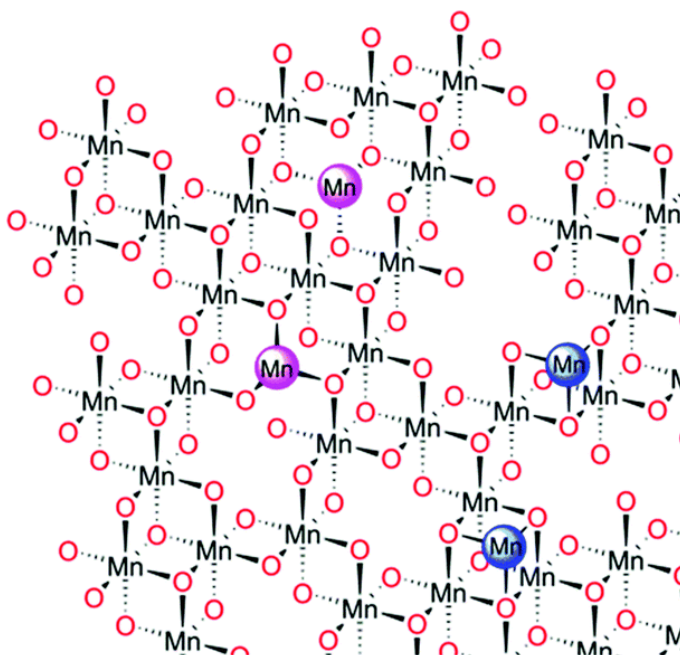


Figure 9. Structure of a molecule of manganese oxide (AMO) (Shevchenko et al., 2014)⁴⁴.

Manganese oxides with different phases or its composition have been extensively used as adsorbents for heavy metals. Furthermore, manganese oxides were reported to have stronger binding with heavy metals than iron oxides with similar surface area (Song et al., 2014)⁴⁷

Chemical stabilization is the way in which manganese oxides works. The main immobilization processes include adsorption, surface precipitation and complexation. The parameters that have more relevance are the pH and the speciation of the metals. Despite their high immobilization potential, Mn oxides have been examined to a much lesser extent for chemical stabilization than Fe oxides.

Metal stabilization resulted from combined specific adsorption onto the AMO surface together with an increase in soil pH promoting the adsorption of metallic cations (Michálkova et al., 2014)³⁵. This study concluded that adsorption tests proved that the AMO was the most effective treatment for the stabilization of metals.

Manganese oxides can become a reasonable alternative in chemical stabilization (Della Puppa et al., 2013)³⁹.

Manganese oxide minerals occur in soils. Birnessite is usually found in soils showed a very good adsorption capacity, the metal(loid)s that showed more affinity were Pb(II) > Cu(II) > Zn(II) > Co(II) > Cd(II). Manganese (IV) oxides are known to specifically adsorb Pb.

There is another compound about manganese also with a high adsorption capacity named birnessite (Bolan et al., 2014)¹⁴

In the study of (Song et al., 2014)⁴⁷ biochar made of corn straws was modified with manganese oxide and tested in order to remove copper ion. The conclusion of the study was that the unique nanostructure makes the MnO-loaded biochar has much stronger adsorption capacity for copper ion than original biochar. The increased adsorption of copper on the MnO-loaded biochar was mainly due to the formation of surface complexes with manganese oxides and O-containing groups.

In the study (Wang et al., 2015)⁵² and biochar/birnessite (i.e., BPB) composites were synthesized. In comparison to the pristine biochar, BPB showed enhanced sorption of As(V) and Pb(II). The enhanced As(V) and Pb(II) sorption by BPB was mainly due to the presences of birnessite particles, which showed strong affinity with both heavy metals.

3 MATERIALS AND METHODS

3.1 Sorbents preparation and characteristics

3.1.1 Biochar preparation and characterization

The biochar was produced from grape stalks. The material was homogenised, air dried overnight and analysed to determine the bulk density, moisture, ash content and material composition according to TAPPI T264 (1997) and TAPPI T211 (1993). Then the pH was measured with a pH-meter; also the content of C, H, N, O and S was determined using the Flash EA 1112 apparatus in the CHNS/O configuration. And also was performed to identify the chemical groups of feedstock (Trakal et al., 2014)⁵⁰.

The grape stalks were then pyrolysed at 600 °C in a muffle furnace under 16.7 mL min⁻¹ nitrogen flow rate at atmospheric pressure and retention time of 30 min. Additionally, the yield of biochar (in %) was calculated as the quotient between the weight of biochar and weight of agro-waste. The resulting biochars were then cooled overnight under the same nitrogen flow rate as before. Pyrolysed products prepared in this way were then ground, homogenised, sieved (all used biochar particles were 0.25–0.50 mm in size), washed by ultra-clean water Milli-Q Integral and dried at 60 °C for 24 h until constant weight (Trakal et al., 2014)⁵⁰.

Point of zero charge was defined as the pH at which the sorbent surface charge is equal to zero. At this pH, the charge of the positive surface sites is equal to those of negative one (Fiol et al., 2008)²³. When pH is higher than pH_{pzc} the surface interacts with positive metal species, and when is lower it interacts with negative ones.

The point of zero charge was analysed for all the mixtures of AMOchar showed in the table before. This method was analysed by mixing a solution of 0.1M of BaCl₂ with the mixture making a 25g/L solution. Once prepared every mixture has to be adjusted between pH 6 and 8, four samples for each one. After preparing and adjusting the correct pH, the samples must be agitated during 24 hours in a shaker at 250 rpm (GFL Shaker 3006). Once passed the 24 hours, the pH of the solutions was analysed again. The samples were measured using pH-meter until constant pH value. The change of pH (Δ pH) during equilibrium was calculated and the pH_{pzc} was identified as the initial pH with minimum Δ pH.

The cation exchange capacity (CEC) was also measured for all the mixtures as well. Specifically 0,2 g of biochar were mixed with 10 mL of BaCl₂ solution at 0,1 M of concentration. Two duplicates for each mixture, and afterwards the preparation were agitated in a GFL Shaker 3006 at 300 rpm. After that the samples were put in the centrifuge at 10000 rpm during 15 minutes in order to be filtrated correctly. Then the liquid filtrated was analysed using the ICP-OES (ICP-OES, Agilent 730, Agilent Technologies, USA).

3.1.2 AMO and birnessite preparation

The amorphous manganese oxide (AMO) was prepared according to a modified sol-gel procedure (advised for the preparation of birnessite), consisting of adding 0.5 L of a 1.4 M glucose solution to 0.5 L of a 0.4 M KMnO₄ solution. After gel formation, the solution was filtered and washed with 2 L of pure water in order to remove the excess of reactants. The gel was subsequently dried at room temperature. The protocol modification omitted the heating step (at 400 °C) after gel drying. Pure birnessite was prepared, which consists of adding dropwise 1 L of a 1 M HCl solution to 1.25 L of a 0.5 M boiling KMnO₄ solution (Wang et al., 2015)⁵². The solution was then left to cool at room temperature, filtered and washed with pure water (Della Puppa et al, 2013)³⁹. Anyway, two prepared AMOs were synthesized AMO purified and non-purified. The only difference in the preparation procedure between these two compounds was that purified AMO was rinsed several times with deionized water to remove synthesis by-products. Although, non-purified AMO was used right after milling as it is.

Point of zero charge and CEC were analysed as well for AMO and birnessite following the same procedure than the biochar characterization.

3.1.3 Manganese oxide modified biochar synthesis

The AMOchar (biochar mixed with AMO) used in the study has different composition and also different ways to produce it. We can distinguish two principal ways to produce it, synthesized together and separately. It means that the mixture between AMO and biochar has been done before the synthesis of both, in

the case of synthesized together. On the other hand, synthesized separately means that first we produce both and then we mix them.

The aim of studying these mixtures is to increase the performance of the biochar and the AMO also. There are some metals that have affinity to one of these compounds. For example lead, as explained before, has strong affinity with the AMO but not with the biochar. Happen the same for arsenic but not so strong as for lead. That's the aim of this study; try to improve the adsorption efficiency of AMOchar combining the affinities for the adsorption of AMO and biochar separately.

So, for this study many combinations of AMO and biochar has been prepared, they are shown in the Table 4. All the combinations have been tested for the adsorption properties.

This is the aim of the study; try to perform both capacities to adsorb mixing biochar and AMO.

Preparation	Composition	Proportion
Synthesized together	AMO-Biochar	1:1
	AMO-Biochar	1:2
	AMO-Biochar	2:1
Synthesized separately	AMO-Biochar	1:1
	AMO-Biochar	1:2
	AMO-Biochar	2:1
	Pure AMO	-
	Pure Biochar	-
	Biochar+Birnessite	1:1

Table 4. Manganese modified biochars studied.

The two different ways of mixing biochar and AMO are synthesizing together or separately. Modified biochars whose synthesis was together were prepared using the same method than non-purified AMO, without the final wash of the product. And biochars whose synthesis was separately were prepared in the same way than original AMO, without the last wash to purify it.

AMO-modified biochars were prepared in two different ways at three AMO/BC ratios: 1/2, 1/1, 2/1 (w/w). In the first approach, biochar was added directly into the reaction mixture for the synthesis of AMO. Biochar was mixed with KMnO_4 solution and subsequently glucose solution was added. Originated gel was then washed several times with deionized water, dried at laboratory temperature and milled in agar mortar. In the second approach, already prepared AMO and biochar were mixed together under specific pH conditions at three AMO/BC ratios: 1/2, 1/1, 2/1 (w/w) and agitated together in deionized water (20/1 L/S) for 24 hours at pH 9. The pH was controlled using KOH.

3.2 Kinetic batch sorption experiments

The batch solutions were prepared with the metal and a solution 0.01M NaNO_3 used as a background electrolyte in order to measure the concentration due to a kinetic reaction. The reagents used for reach the 1mM concentration for each metal was: for arsenic $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ for lead $\text{Pb}(\text{NO}_3)_2$ and for cadmium $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. The solution was 600mL with 0.01M of NaNO_3 , 1mM the concentration of the metal and mixed with 1.2g of the AMOchar mixture in a beaker. The solution must be removed to help the adsorption and the pH was controlled at the value of 5 for lead and cadmium, and at pH 7 for arsenic to avoid precipitation. The adjustment of pH was done using 0,1M NaOH and HNO_3 solutions.

The solution was agitated during all the batch, that in the case of lead and cadmium it last 3 hours and the sample's time was: 3', 5', 10', 20', 40', 60', 90', 120' and 180'. As arsenic had a different behaviour to reach the equilibrium, being slower to get it, so the arsenic batch sorption last 7 hours and a half. The sample timing was the same during the first 3 hours (3', 5', 10', 20', 40', 60', 90', 120' and 180') and afterwards sampling every 90 minutes (270', 360' and 450').

The samples were taken from the solution and directly filtered in order to separate the biochar from the solution and stop the sorption. The filter used was 0.45 μm the size of the pores.

The solutions filtered were diluted 1:10 so as to analyse it in the ICP-OES (inductively coupled plasma optical emission spectroscopy, ICP-OES, Agilent 730, Agilent Technologies, USA) and also diluted to analyse the total content of carbon with TOC-L CPH (Shimadzu, Japan).

To calculate the % metal removal was calculated using the following equation (1):

$$\% \text{ metal removal} = \frac{C_i - C_{teq}}{C_i} \times 100 \quad (1)$$

Where C_i (mg/L) is initial metal concentration and C_t (mg/L) metal concentration at equilibrium time t .

4 RESULTS

4.1 SORBENTS CHARACTERIZATION

4.1.1 Biochar, AMO and birnessite

All the properties obtained from the biochar of grape stalks are showed in Table 5. All the data has been calculated and some obtained directly from other recently articles.

Chemical characteristics	BET: 72 m ² /g
	pH _{H2O} : 10±0,1
	pH _{zpc} : 9,92±0,10
	CEC: 402±3 mmol/kg
Elemental composition (%)	N: 1,45±0,02
	C: 70,2±0,56
	H: 1,70±0,03
	O: 12,5±0,08

Table 5. Characterization of grape stalks biochar. (Trakal et al., 2014)⁵⁰

The data was obtained from the article (Trakal et al., 2014)⁵⁰ so all the charactersitics values in the table come from there.

The pH of biochar is high. Therefore, biochar has a basic pH.

The surface of the biochar was negatively charged because pH is higher than the pH of zero charge.

The CEC of the biochar is a high value as well as the carbon content is more than 70%.

	pH	pH _{ZPC}	CEC (mmol/kg)
Birnessite	3.3 ± 0,1	2,7 ± 0,3	2470 ± 29
AMO non-purified	6,98 ± 0,3*	7,13 ± 0,1*	**
AMO original	8,1 ± 0,3	8,3 ± 0,1	340 ± 1

The values with (*) were obtained from own data.

** data in progress

Table 6. Birnessite and AMO characterization. (Puppa et al., 2013)³⁹

The values from Table 6 were obtained from the article (Della Puppa et al., 2013)³⁹. Birnessite has an acidic pH compared to the others. It can be considered as an acid sorbent as indicated by its point of zero charge. The point of zero charge of the birnessite is so low compared with others both AMO original and non-purified as well as the cation exchange capacity. Same comments must be due for birnessite cation exchange capacity. AMO original has a higher pH of zero charge compared to non-purified AMO.

4.1.2 Manganese oxide modified biochars characterization

Evidences of the presence of manganese in the modified biochars are shown in the Figure 10 obtained from a XPS analyser.

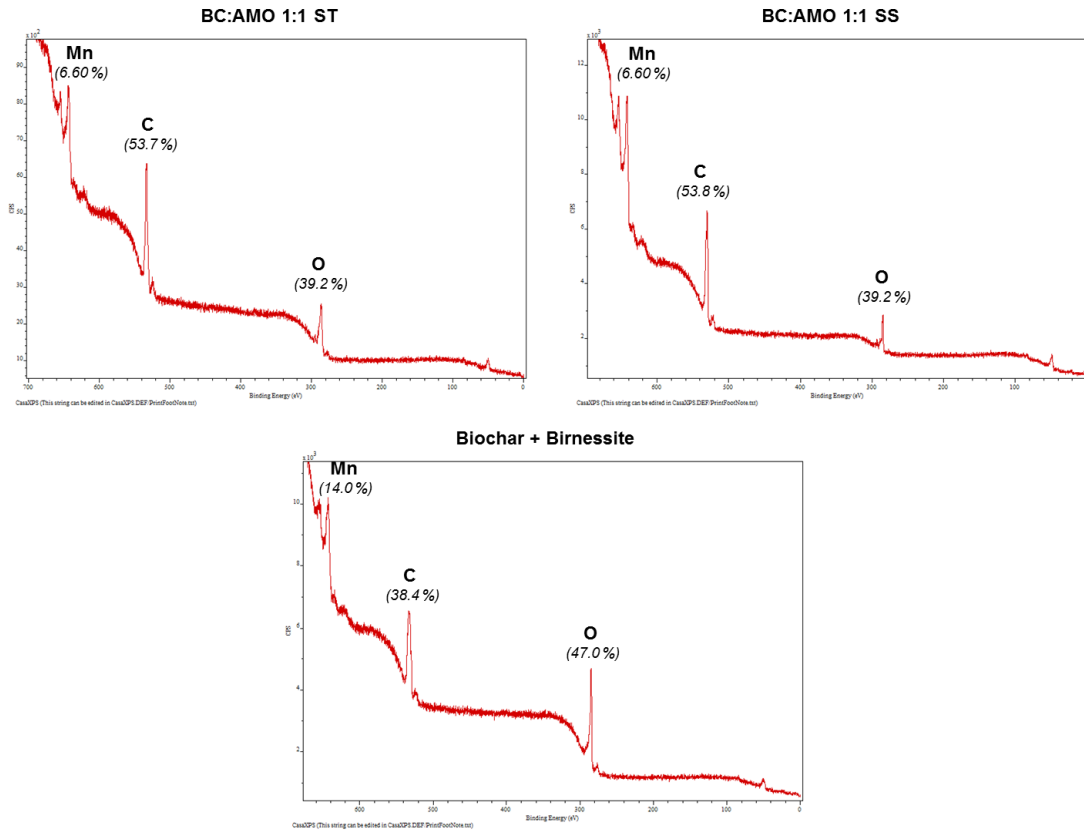


Figure 10. XPS results showing the presence of Mn in modified biochars.

Same proportion of manganese was found in the synthesized together and separately mixtures (6,60%). And in the case of biochar+birnessite was found the double proportion than the other manganese modified biochars.

The pH of aqueous solutions, point of zero charge and CEC of all the biochar managanese oxide mixtures and biochar+birnessite were analysed. The obtained results are shown in Table 7.

	pH	pH _{pzc}	CEC (mmol/kg)
AMO:BC 1:1 SS	7,56	6,97 ± 0,1	274,2
AMO:BC 1:2 SS	7,07	7,37 ± 0,1	257,8
AMO:BC 2:1 SS	6,68	6,94 ± 0,1	289,2
AMO:BC 2:1 ST	8,47	7,88 ± 0,1	*
AMO:BC 1:1 ST	8,34	7,99 ± 0,1	*
AMO:BC 1:2 ST	8,39	7,94 ± 0,1	*
Birnessite+Biochar	6,97	6,39 ± 0,1	298,7

* data in progress

Table 7. Characterization of the manganese modified biochars studied.

Significant differences in pH are found between synthesized together and separately mixtures, the last ones presented a basic pH and the former a neutral pH. In spite of the fact that birnessite is acid the mixture birnessite+biochar exhibited an unexpected neutral pH. pH in comparison with original biochar is very low in biochar+birnessite and AMO:BC SS composites.

Points of zero charge pH values are expected because they are in accordance of the found pH of the mixtures in aqueous solution. From the pH values the only composites positively charged are AMO:BC 1:2 SS and AMO:BC 2:1 SS.

All the CEC results are similar to each other for all the modified biochars. Birnessite+biochar has the most unexpected CEC value because original birnessite has a really high CEC compared to biochar.

4.2 SOPRTION EXPERIMENTS

First, maximum sorption efficiency was compared through the all sorbents and studied metal(loid)s, respectively.

Next, the effect of time on arsenic, lead and cadmium sorption was studied using all the combinations of biochar mentioned before. The initial pH of the metal solutions was between 6.5 and 7.

4.2.1 Arsenic sorption batch experiments

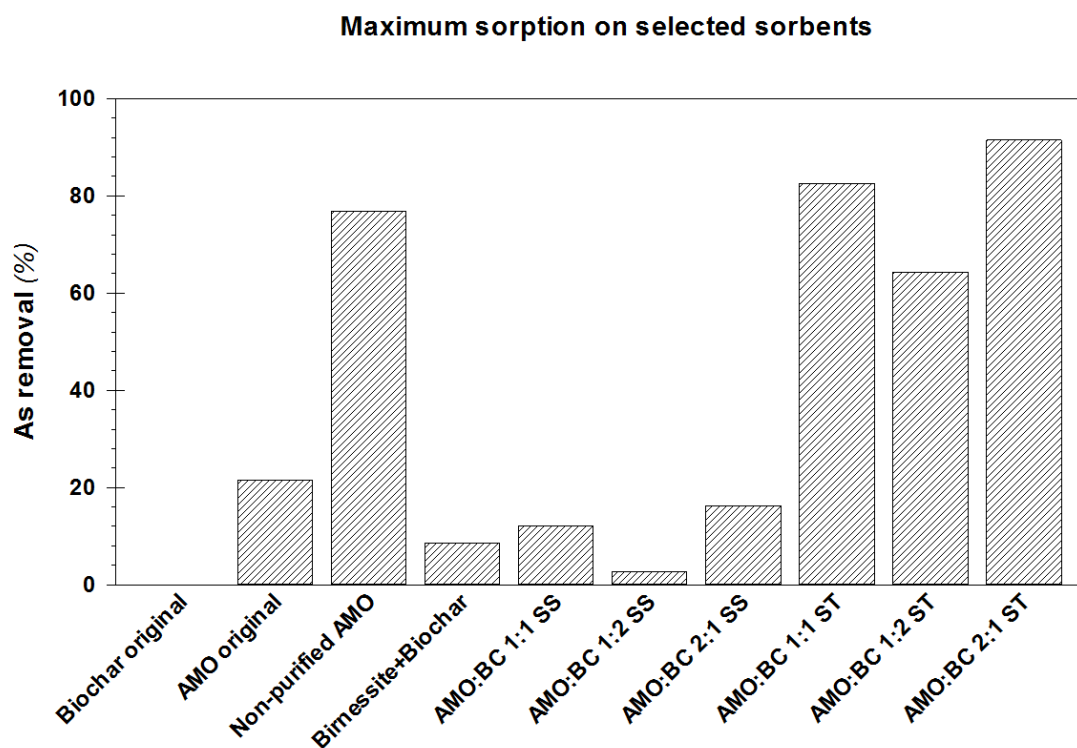


Figure 11. Sorption results for arsenic.

From Figure 11 we can see that in arsenic case there are a lot of differences between all the mixtures.

This graphic only represents the maximum sorption reached after or during the batch sorption experiments. We can see the difference between mixtures synthesized separately and mixtures synthesized together. Second ones are significantly more efficient.

Concerning to the original sorbents, AMO non-purified has a around 80% of maximum adsorption, comparable to the synthesized together mixtures, more than AMO purified.

Original biochar maximum sorption value is equal to 0, the same that Biochar+Birnessite and for synthesized separately mixtures <20%.

Observing the maximum sorption results, we can expect a similar behaviour for all the synthesized together and separately mixtures, so the kinetics only on sample of that ratio is showed because no dramatical changes wasn't observed.

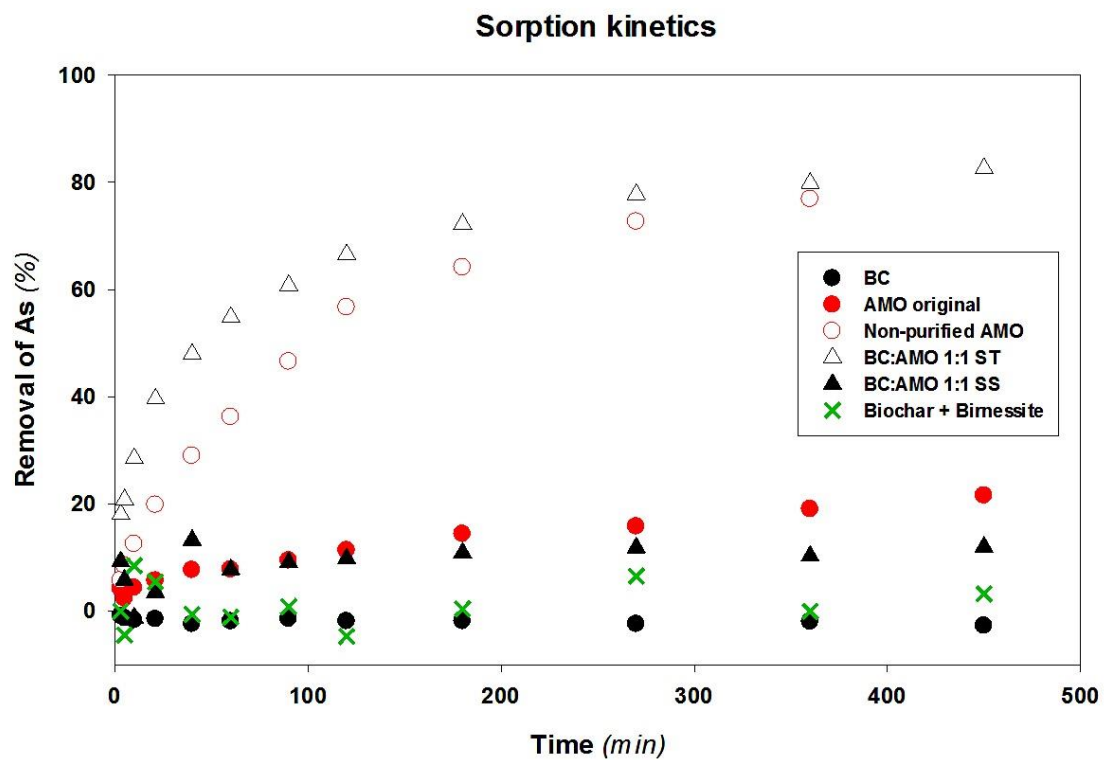


Figure 12. Kinetics results for arsenic.

It is obvious from the kinetics graph that biochar+Birnessite and BC:AMO 1:1 SS sorption reaches almost the maximum value between half and one hour of process. Conversely, it can also be noticed that the original biochar exhibits the lesser affinity for arsenic with a negligible sorption percentage.

Non-purified AMO and BC:AMO 1:1 ST have similar kinetics during the first two hours and present an progressively increase of sorption until almost maximum sorption is achieved. At the end of the process AMO original reaches a higher sorption efficiency than BC:AMO 1:1 ST.

Biochar+birnessite mixture had a very strange behaviour. It increased with time during the first 30 minutes and start decreases to reach a fixed low sorption value (<5%) similar to the one of BC:AMO 1:1 SS.

4.2.2 Cadmium and lead sorption batch experiments

For cadmium and lead experiments the procedure of the batch were exactly the same, because the behaviour against pH of these metals was similar.

According to (Trakal et al., 2014)⁵⁰ the pH for the grape stalk's biochar, the optimum pH for the adsorption of lead and cadmium is 5.

In Figure 13 results of maximum sorption for cadmium are shown.

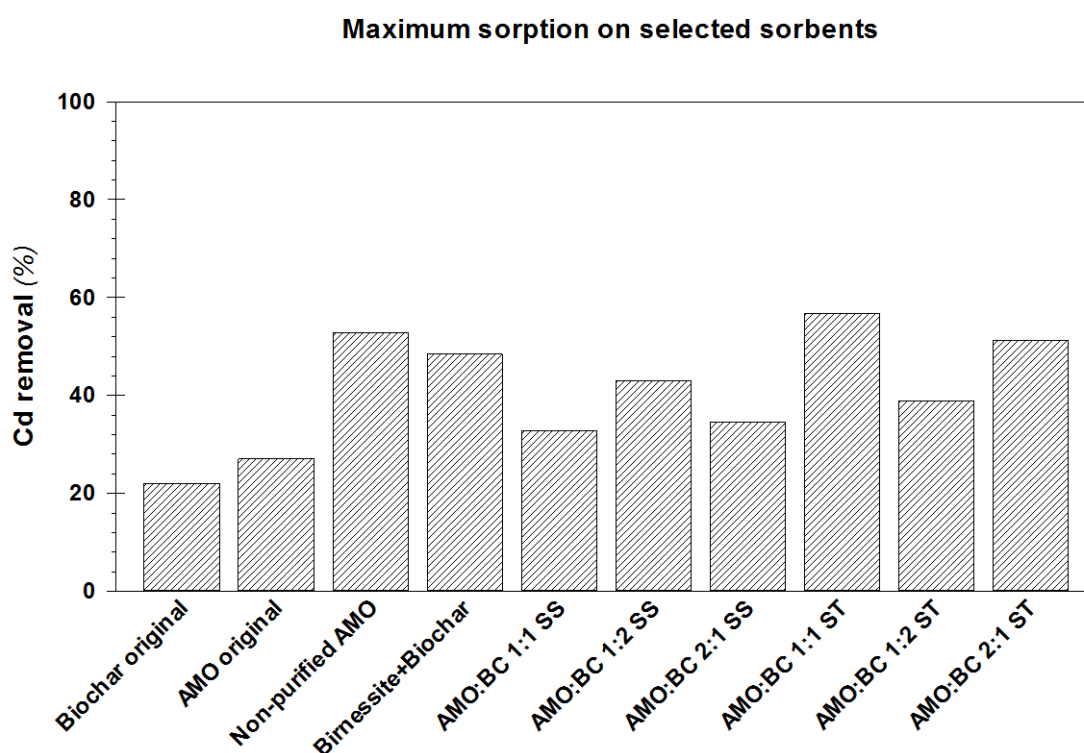


Figure 13. Sorption results for cadmium

More specifically, the differences between the maximum sorption of cadmium and arsenic are that in cadmium case there are fewer differences in the quantity adsorbed in the equilibrium. In general, the maximum of adsorption are not that higher like in arsenic case, being the top one AMO:BC 1:1 ST with a value of 57%.

But mainly the result is so similar to arsenic. Synthesized together mixtures have a higher value of maximum sorption compared to synthesized separately mixtures. AMO:BC 1:1 ST mixture has the higher sorption of cadmium.

Non-purified AMO also is able to adsorb almost the double of cadmium than original AMO, which has the same sorption efficiency than original biochar.

And the mixture of Biochar+Birnessite is able to adsorb almost the same quantity than non-purified AMO.

What is easy to see about synthesized together mixtures is shown in Figure 14 for cadmium.

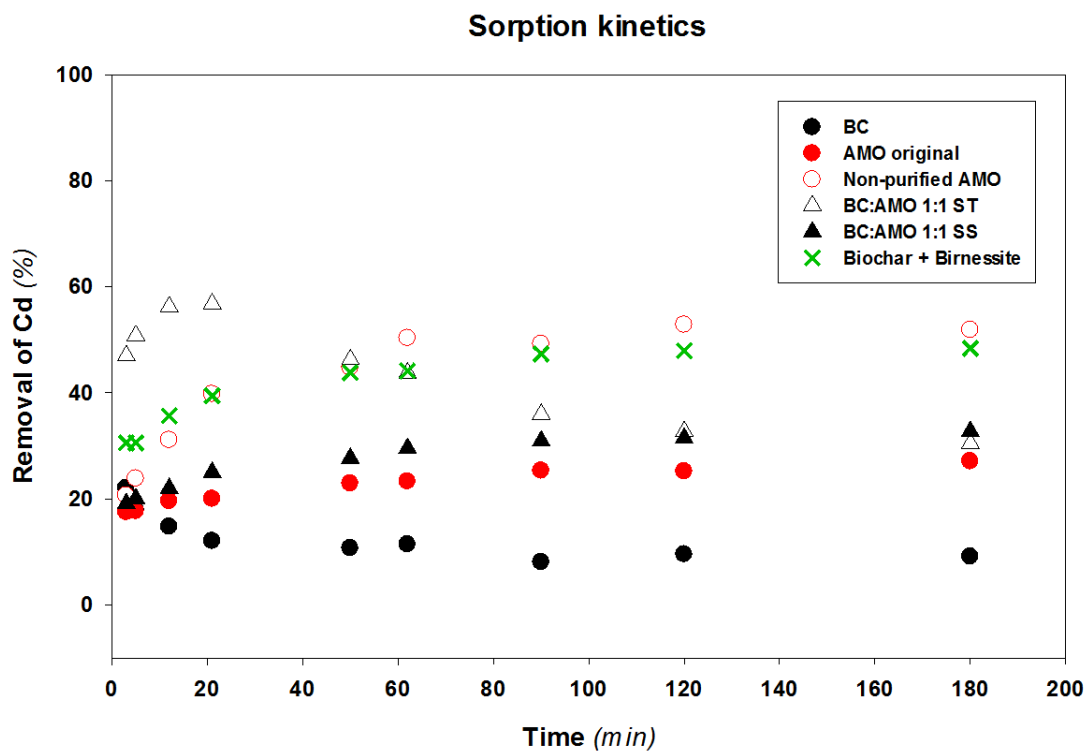


Figure 14. Kinetics results for cadmium

All the mixtures have the same behaviour and the maximum peak of sorption is at the end. All except of original biochar and BC:AMO 1:1 ST, which have the maximum sorption at the beginning of the experiment and its equilibrium was represented by less sorption efficiency than the beginning of the batch.

BC:AMO 1:1 SS and BC:AMO 1:1 ST reach the equilibrium with the same sorption value but in case of the synthesized separately mixture the maximum sorption was reached at the equilibrium. On the other hand, in the case of the synthesized

together mixture the peak of maximum sorption is reached in the minute 20 and then decreasing slowly until the equilibrium.

AMO original behaviour is almost equal to synthesized separately mixture but lower sorption than non-purified AMO as well. Non-purified AMO as well as biochar+birnessite reach the maximum sorption at the equilibrium after increasing the sorption during all the batch experiment.

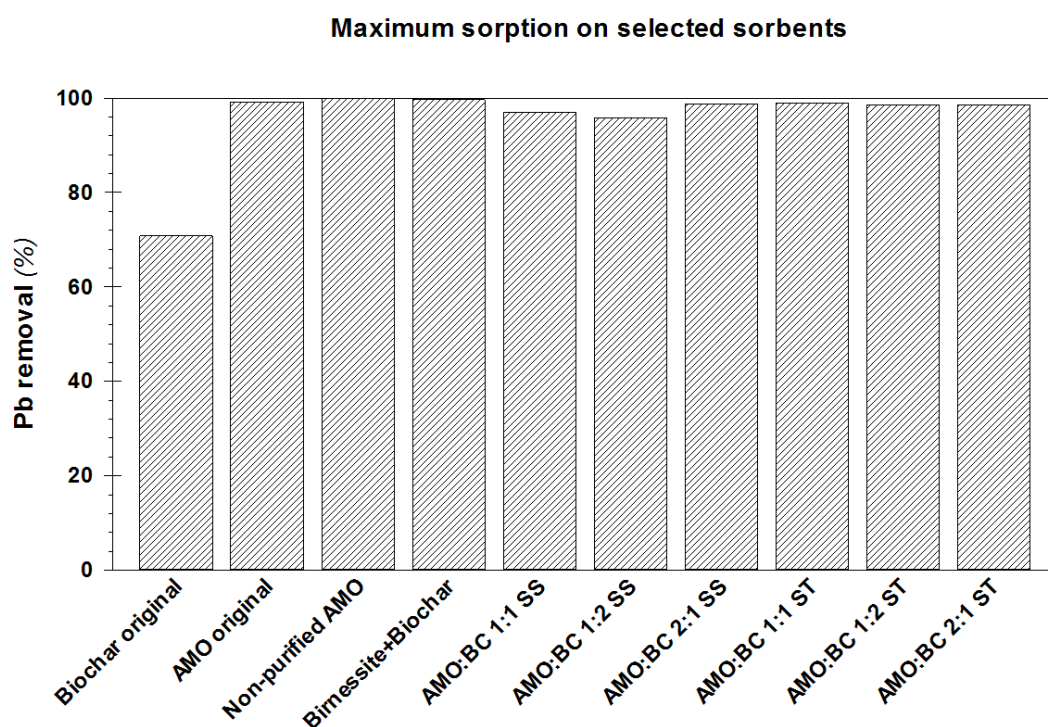


Figure 15. Sorption results for lead.

Original biochar has less affinity with lead than all the other mixtures, as we can see that almost half of the initial lead hasn't been adsorbed. All the others mixtures have almost the same affinity with lead because all the maximum adsorptions are between 96-99%.

A little difference was observed between synthesized together and separately mixtures because in general the average of ST mixtures is higher than SS mixtures. Nevertheless, this difference (<5%) was negligible.

It is obvious to expect a good kinetics after seeing the efficiency in lead removal, so the Figure 16 shows the sorption kinetics.

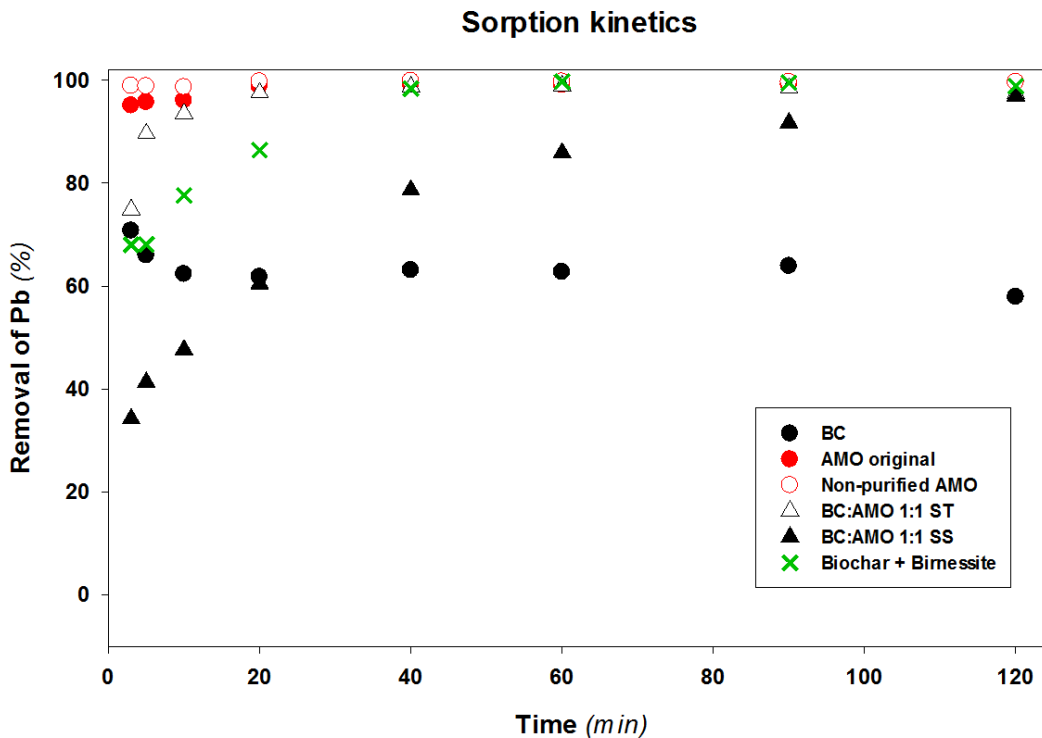


Figure 16. Kinetics results for lead.

Biochar stills with the peak of maximum sorption at the beginning. The rest mixtures reach the maximum sorption at the equilibrium.

See that BC:AMO 1:1 SS is the mixture with last more to reach the equilibrium because the kinetics show that is increasing the sorption power during all the batch. Whereas, the opposite behaviour is seen in both of AMO's (original AMO and non-purified AMO) that in lead case has similar shape of the kinetics curve. Both sorption at the beginning of the batch is close to maximum and they are maintaining that sorption during all the kinetics.

Biochar+Birnessite and BC:AMO 1:1 ST have a similar shape but the second one has a more pronounced pending at the beginning so it arrives at the equilibrium at 30 minutes, though Biochar+Birnessite mixture reaches it at 50 minutes.

All the mixtures showed in the graphic reach the equilibrium at the same sorption except biochar, which reaches the equilibrium with a lower sorption.

4.2.3 Leaching of selected elements

There are three selected elements that are measured during the sorption process: K, Mn and DOC (dissolved organic carbon). These elements reveal the behaviour of the biochar and all the mixtures with AMO.

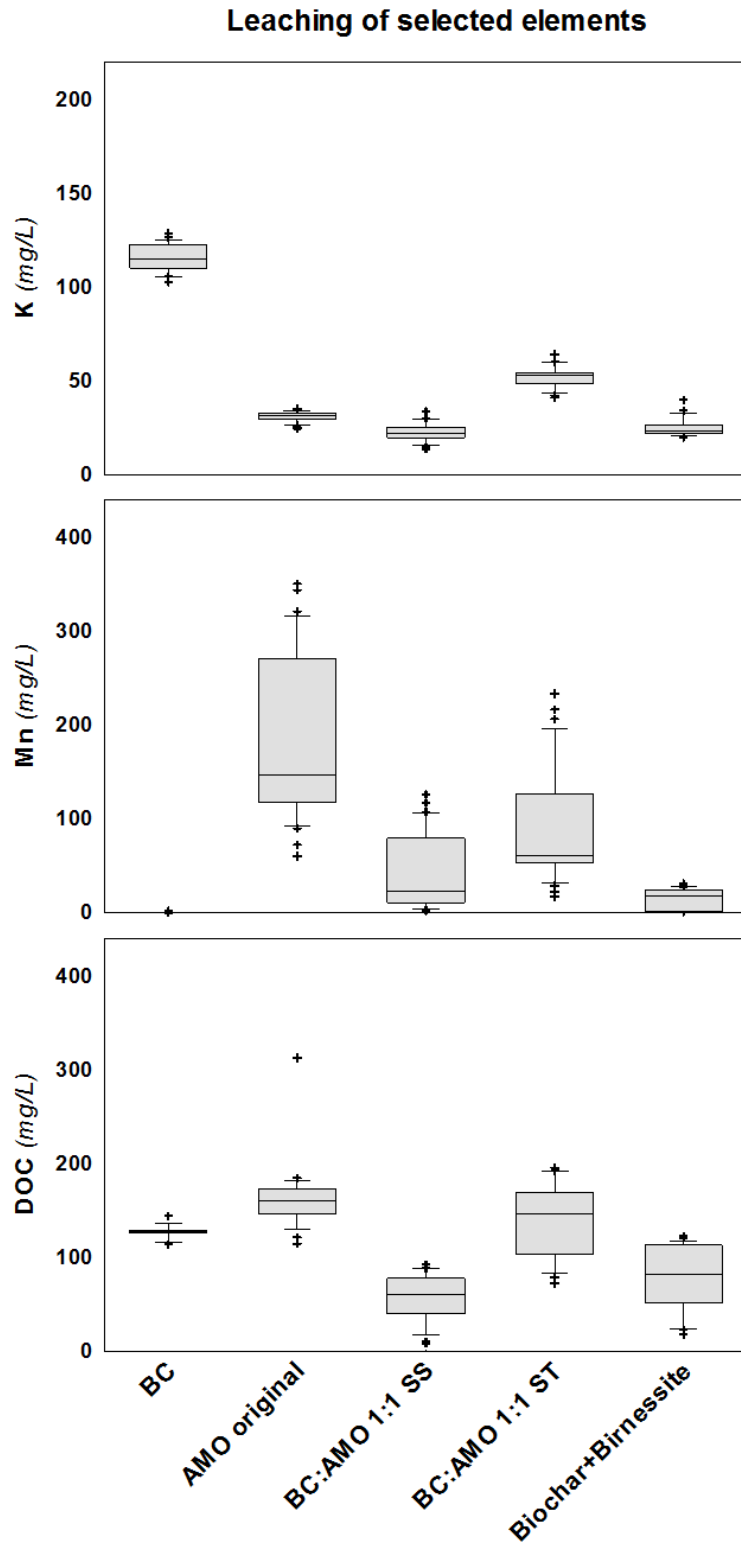


Figure 17. Leaching of selected elements graph.

First of all potassium (K), it has to be mention that our biochar is made from grape stalks, so it means it is full of potassium. Basically potassium defines the CEC because mainly potassium is exchanged for the metal we need to remove and so as that potassium takes part in the solution.

The highest concentration of potassium is in the original biochar (more than the double of the others mixtures).

Concerning to the others mixtures we can see that original AMO, biochar+birnessite and AMO:BC 1:1 SS have more or less the same leached potassium in the solution and finally AMO:BC 1:1 ST was bit higher than those ones.

Concerning manganese (Mn) its come is negligible in the biochar, but still some Mn leached. But AMO original has a very strong leaching, because increases during all the kinetics, so the highest concentration at the end will be with original AMO. There is no significant difference between AMO:BC 1:1 SS and AMO:BC 1:1 ST being a little bit higher the second one but both are increasing the leaching of Mn in the same way during the process. Concerning the Biochar+Birnessite has the lower value of leached Mn and the smallest pending during the batch.

Finally DOC leaching, showed the lowest amount carbon from the biochar which has similar concentrations of C during all experiment. AMO original concentration is a little bit higher at the beginning compared to biochar. AMO:BC 1:1 ST mixtures has approximately the same final value as AMO original but leached more C during the batch and is also the one that leached more C compared to the others.

The lowest value is AMO:BC 1:1 SS but anyway leached more C during the batch than biochar.

5 DISCUSSION

5.1 Characterization of the modified biochars

Biochar characteristics show a high value for CEC and a normal value for BET. Having a big surface CEC makes increase the sorption potential. This parameter can significantly affect the final metal sorption efficiency, as reported on (Ahmad et al., 2014)⁵. Also a high value of cation exchange capacity deals perfectly with a good sorbent because a lot of cations can be exchanged in order to adsorb the metal(loid)s we want to. The pH of the biochar is a basic pH, higher than the others original compounds.

AMO original has similar but lower CEC compared to biochar, is that low because original AMO was purified and during this last wash some cation exchange capacity was lost. On the other hand, birnessite CEC is enormous and it makes the surface of the birnessite a greater potential sorbent. That happens because the acid pH of the birnessite can interfere with the CEC making it higher. Anyway, according to (Della Puppa et al., 2013)³⁹ the effectiveness of AMO and birnessite is not directly correlated with their physicochemical properties.

Proof of the presence of manganese into modified biochars is shown by XPS analyses. This analysis is used to know the stoichiometry of a substance that needs to be analysed. The Figure 10 shows that all the mixtures (synthesized together and separately) have the same amount of manganese, about 6,60%. Concerning biochar+birnessite amount of manganese was shown, this mixtures has the double amount of manganese because was synthesized in different conditions and the manganese binding on biochar+birnessite was stronger than in AMO case.

Concerning the pH, pH of zero charge and CEC values shown in the table, the differences between synthesized together and separately in pH have no clear explanation, because both AMOs have similar pHs. Additionally biochar+birnessite has an unusual neutral pH not expected because birnessite is a very acid sorbent by itself.

The CEC values are really similar for all the reagents, and lower than the original compounds are made off. The loss of this potential happened during the last wash, some cations in the surface were lost because of the milling water wash. And some

other part of the potential during the batch sorption experiments because of the stirring, it creates leaching of potassium and other cations.

5.2 Sorption of the metal(loid)s

Concerning to batch experiments first of all is important to conclude that pH is a driven factor because it takes part on the speciation of the metals as explained in the review part. According to (Trakal et al., 2014)⁵⁰ is important to control pH in any sorption processes.

The first metalloid of the study was arsenic. Clearly there is an important difference between the synthesized together mixtures and separately in the sorption efficiency.

Synthesized together mixtures are the ones that have more efficiency removing arsenic. That happens because when synthesizing together some characteristics get changed and it makes them having a strong removal potential. Comparing now AMO original and non-purified AMO we can see that the difference of efficiency is remarkable having 3 times more sorption potential non-purified AMO against original. Synthesized together mixtures are synthesized using the same method than non-purified AMO, without the final wash. That could be the reason why their results are so similar, because that last wash doesn't eliminate from the surface some citrates found in the surface (Micháلكova et al., 2014)³⁵ that could interfere with the sorption of arsenic, increasing it.

Comparing biochar to AMO. The efficiency of AMO original is higher because biochar efficiency is negligible, biochar cannot remove arsenic. Biochar only removes a few milligrams of arsenic per gram of biochar in waters, according to (Mohan and Pittman, 2007)³⁷ because pH is basic in biochar and it may cause arsenic form change being more difficult to adsorb it.

Biochar+birnessite has a higher efficiency in removing arsenic compared to the pristine biochar but, anyway, the efficiency is not comparable to non-purified AMO. So in terms of efficiency, synthesized together mixtures and AMO non-purified are good solutions for removing arsenic because their sorption is between 70% and 90%.

Kinetics are confirming the affinity of synthesized together mixtures and non-purified AMO having the maximum sorption at the equilibrium of the batch and increasing during all the process what makes these compounds more stable and predictable in the removal of arsenic from waste waters.

In the case of cadmium, the average of efficiencies is lower in general than arsenic. That may happen because cadmium is the most mobile metal(loid) studied according to (Rolka 2015)⁴², any it can interfere in the sorption process. The difference in maximum sorption between synthesized together and separately mixtures is very similar, synthesized together mixtures are a bit higher, specially AMO:BC 1:1 ST which has the maximum sorption potential.

Non-purified AMO has the double maximum sorption than original AMO what means again that is better not to purify the AMO with milling water because its sorption properties get punished.

Original biochar has the lowest sorption efficiency, which means that all the mixtures have improved the sorption potential compared to the original biochar. But biochar is almost at the same level than original AMO and biochar+birnessite, all these three compounds have less efficiency than all the others mixtures.

Kinetics shape for synthesized together mixtures are completely different than in arsenic case. Synthesized together mixture's equilibrium is reached with a lower sorption than expected. It is because synthesized together mixtures are prepared without the final wash so the reason why the maximum sorption is so early and then decreases, could be due to a weak cadmium sorption with the surface and then during the stirring there is a loss of cadmium.

The two mixtures that fit perfectly for lead removing are biochar+birnessite and non-purified AMO; their maximum sorption is respectable and it is reached at the equilibrium. All the others mixtures have a good kinetics shape but not enough sorption potential. Biochar is the exception because the maximum sorption is at the early beginning of the kinetics and this may happen because at the beginning the pH rises faster and the adjustment isn't strictly time-dependent. So there is arsenic that precipitate and that's the initial peak of biochar. It makes biochar the less effective sorbent, again.

The maximum sorption in the case of lead shows a strong affinity taking part in all the mixtures analysed, also biochar. Almost 100% of efficiency was observed in synthesized together, AMO original, non-purified AMO and biochar+birnessite. Synthesized separately mixtures still not at the same level than synthesized together mixtures but lead shows the less differences between these two ratios, practically negligible.

Again biochar has lower maximum sorption than the others so the sorption potential has been increased in all the mixtures studied. It could be explained lead is easily sorbed to organic compounds, so that's one of the reasons why modified biochars were all able to be efficient in lead removal as explained in (Adriano 2001)³.

Kinetics reveals that there are more differences than maximum sorption graphic was showing. Synthesized together mixtures are better sorbents than synthesized separately mixtures they reach almost the same maximum sorption but synthesized together mixtures reach the equilibrium faster.

Biochar+birnessite is a better sorbent than synthesized separately mixtures. AMO compounds have strong affinity with lead because both purified and non-purified have almost the same shape and they reach the equilibrium at the early beginning, so we can conclude that in the lead case the fact to wash AMO (purify it) has no relevancy. But both AMOs showed a really fast sorption time and were capable to remove all the lead with short time, according to (Dong et al., 2007)¹⁹ metal oxides were very important sorbents for all kinds of metal ions, especially for Pb and As. That's a good improvement in technology terms. For example to wash a waste water contaminated with lead using AMO, in about 3-4 minutes is able to remove 1mM of lead in the water without decreasing the flow.

In all the cases, biochar has the same behaviour, having the peak of maximum sorption too early and then decreasing the sorption and reaching the equilibrium. The final conclusion is that all the combinations have more sorption potential than original biochar and AMO but synthesized together mixtures show the best behaviour for every metal or metalloid and the maximum sorption as well. Although non-purified AMO has similar global efficiency than synthesized together mixtures, in lead case more obvious.

AMO original has always less potential than non-purified AMO so it means that for every metal(loid) non-purified AMO removal potential is higher. So washing the AMO is not a good idea, because it loses several sorption potential.

And in general, AMO suits better with biochar than birnessite though biochar+birnessite is more constant in depend on the metal we are talking about.

5.3 Leaching of selected elements

Biochar is the one that leached more potassium, that's completely normal because it is full of potassium as it's made of grape stalks and a lot of pesticides are used in that plant, so K is one of the most used pesticides and fertilizers. That potassium is leached because of the cation exchange during the sorption; the potassium gets replaced for the metal or metalloid to remove.

AMO is a manganese oxide and potassium that contains comes from the preparation because it is prepared using a KMnO_4 solution, so the leaching of potassium comes from the preparation. The other three compounds show a leaching of potassium similar than AMO but with more pending.

Biochar is leaching a negligible amount of manganese during the process. Original AMO has the highest manganese leaching because has the highest manganese concentration as is not mixed with any other compound, only manganese oxide. The XPS analyses show that biochar+birnessite has more manganese than all the others mixtures between AMO and biochar but the leaching of manganese is the lowest. The reason of that happens in the last step of the preparation, some cations are eliminated, or removed from the surface in the purification. In the case of biochar+birnessite the binding of manganese is stronger than the other mixtures as explained before.

The DOC leaching reveals that the compounds with higher leaching are the synthesized together mixtures. The explanation is again that these ST mixtures didn't lose all the citrates in the purification step of the preparation. So that citrates are organic carbons (Michálkova et al., 2014)³⁵.

Synthesized separately mixtures have the lowest DOC leaching and the reason is the explained just before, they lost all the citrates in the purification step.

6 CONCLUSION

In arsenic case, original biochar shows a very weak sorption potential compared to the others modified biochars. So we can conclude that manganese modified biochars have improved the metal(loid) removal efficiency, specially for arsenic removal. According to that original biochar has no affinity in removing arsenic; modified biochars improved the efficiency very significantly.

Cadmium is the most mobile metal(loid) studied, but again synthesized together are definitely more efficient. But in cadmium case biochar+birnessite and non-purified AMO are more predictable and stable during the kinetics, because the stirring caused the synthesized together mixtures a loss of sorption during the process.

All the mixtures revealed strong efficiency in removing lead from water. That's why lead has affinity with organic sorbents. But the top of efficient was both purified and non-purified AMOs followed by synthesized together mixtures. Both AMOs were able to remove all the lead in 3-4 minutes which is a very important improvement in technology.

Important to see is that the last purification step of the AMO eliminate from the surface important citrates and carbon compounds that are significantly important during the sorption. Those modified biochars with more sorption potential are the synthesized together mixtures and non-purified AMO.

The leaching of potassium is predictable, and biochar has the highest rate because it is full of fertilizers and pesticides from the grape stalks. That was confirmed by the XPS analysis.

Manganese leaching has the lowest rate in biochar+birnessite although has more manganese than others modified biochars but the binding is stronger.

DOC leaching confirms that synthesized together mixtures didn't have the final wash (purification) and that means that the leaching of citrates during the sorption process was higher than the other modified biochars.

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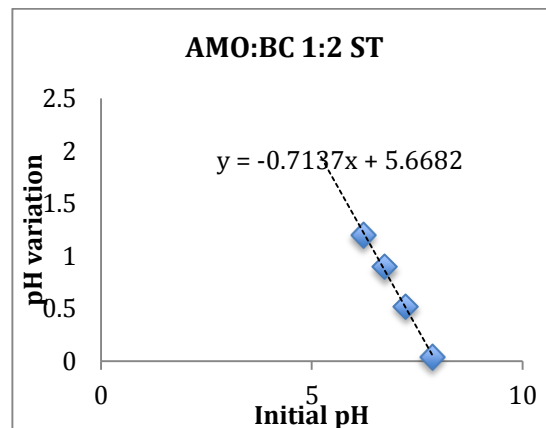
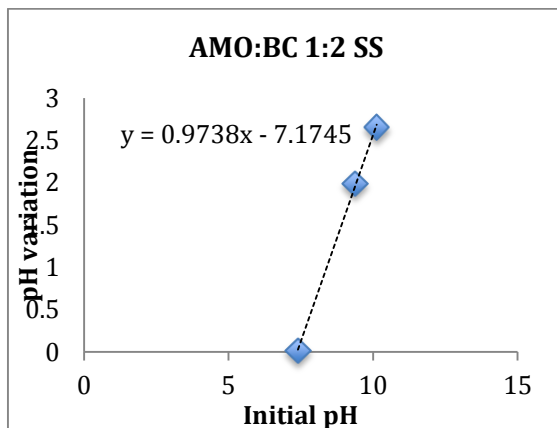
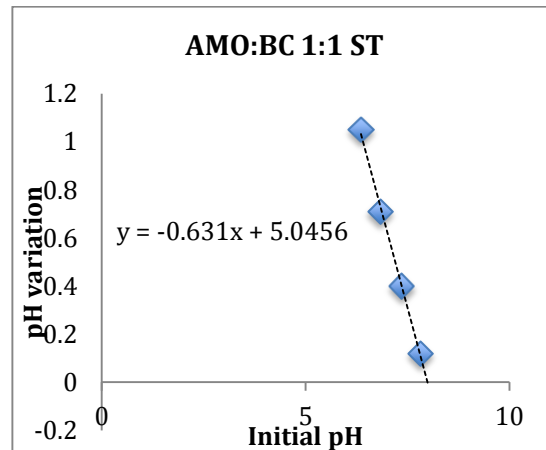
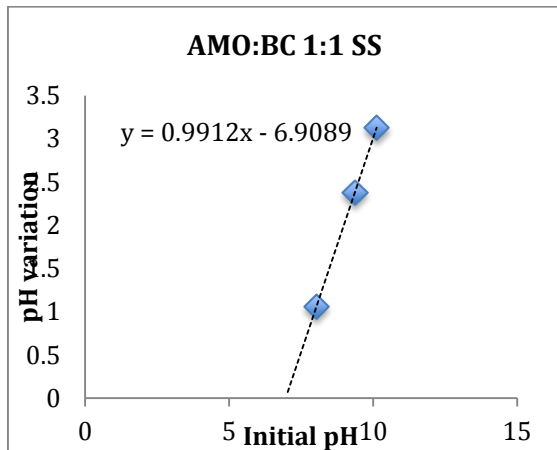
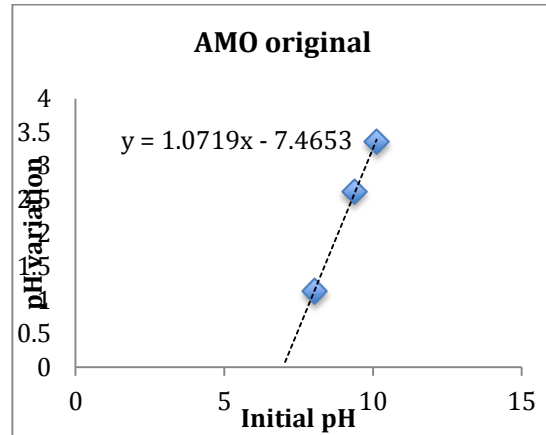
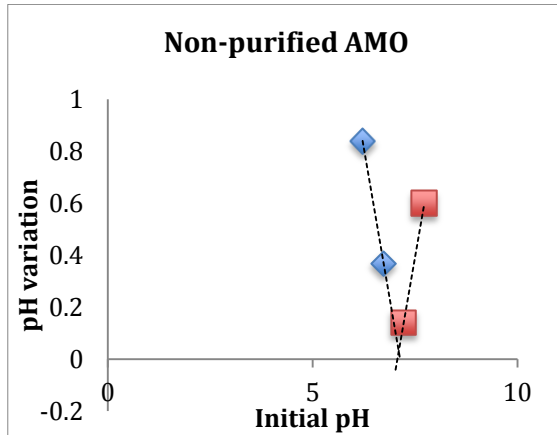
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8 ANNEX

8.1 POINT OF ZERO CHARGE GRAPHIC METHOD RESULTS

Results of the pH of zero charge calculation of all the modified biochars and original sorbents.



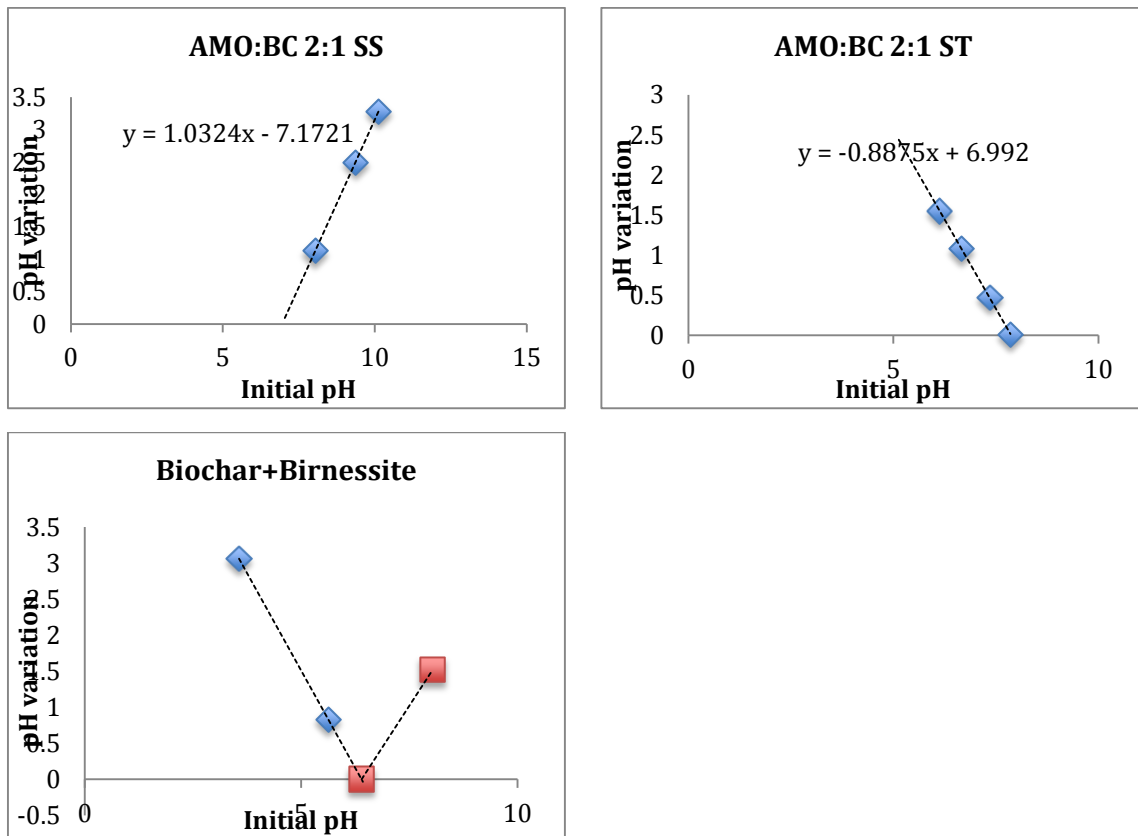


Figure A1. Results of pH of zero charge for all modified biochars.

8.2 STRUCTURES OF INITIAL SORBENTS

8.2.1 Biochar

SEM (Scanning Electron Microscope) image from the surface of the biochar⁷⁰.

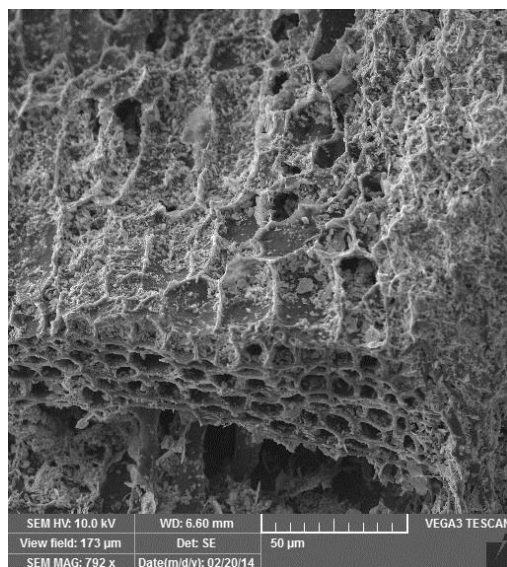
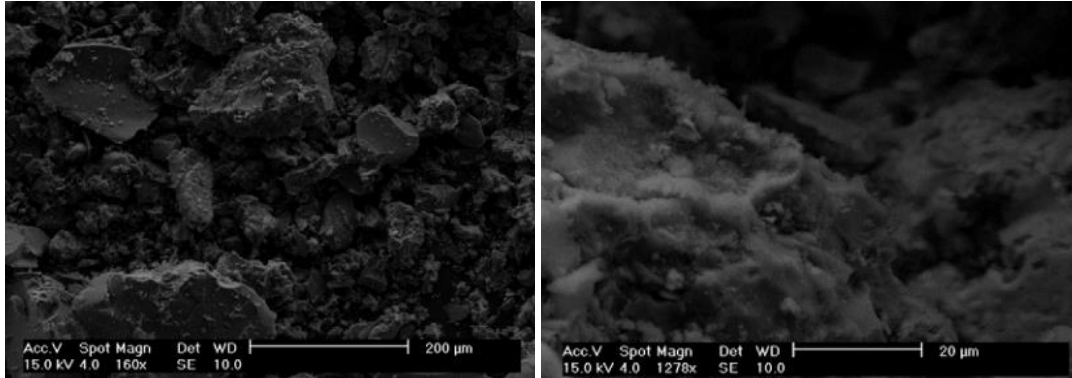


Figure A2. SEM from the biochar surface.

8.2.2 AMO

SEM images obtained from (Della Puppa et al., 2013)³⁹ from the AMO surface.



Figures A3 (left) and A4 (right). SEM from the AMO surface. Figure A3 at normal temperature, Figure A4 at 140°C.

8.3 LEACHING OF SELECTED ELEMENTS IN TIME

In results part leaching of selected elements were shown in Figure 17. The next figure, Figure , is showing the leaching results for these selected elements in time.

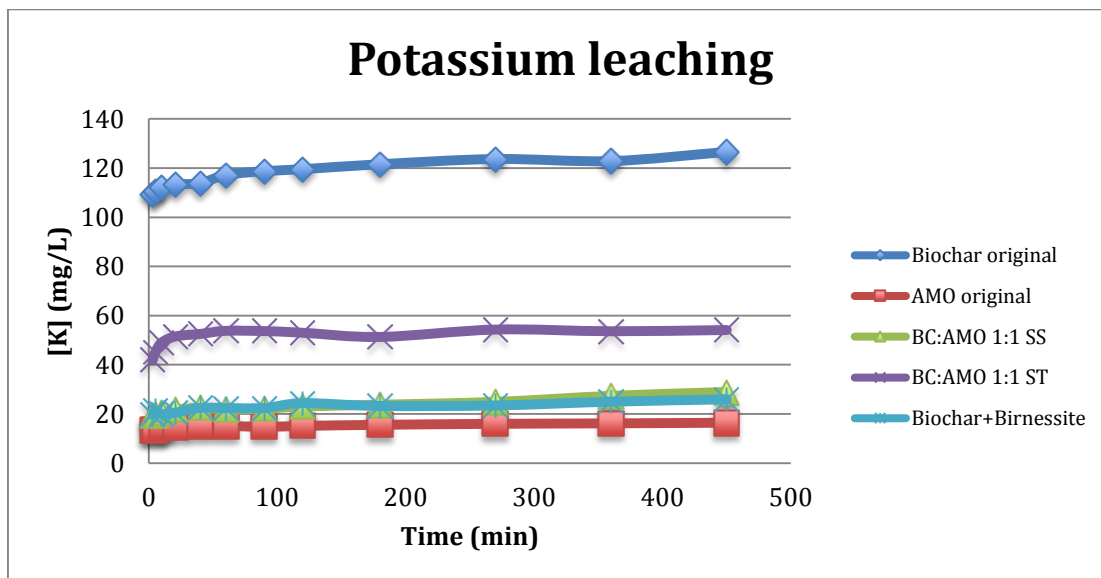


Figure A5. Potassium leaching in time during the batch experiment.

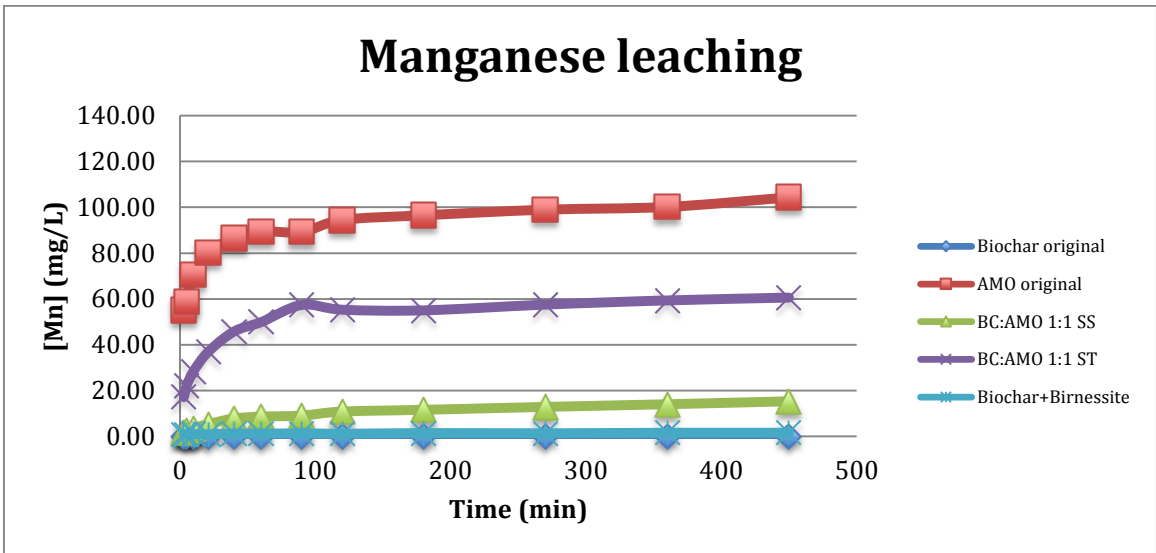


Figure A6. Manganese leaching in time during the batch experiment.

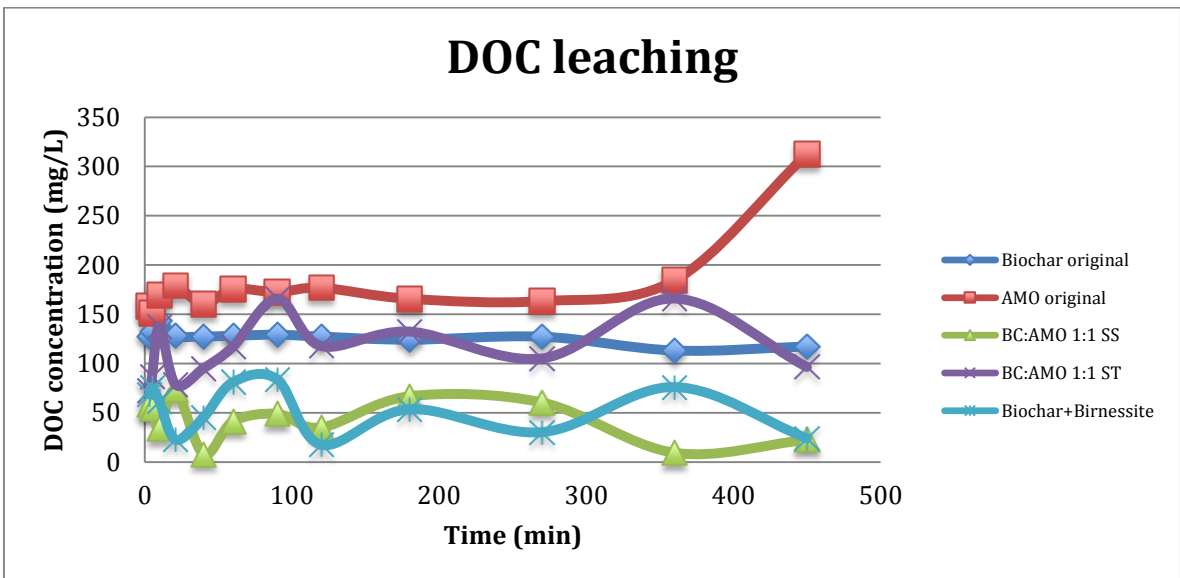


Figure A7. DOC leaching in time during the batch experiment.

The scale of the DOC leaching is higher because the concentration leached of DOC for all the composites is higher and can be observed in a better way.