University of São Paulo
"Luiz de Queiroz" College of Agriculture

Biogeochemistry of arsenic and lead in sediment and water amended with biochar

Matheus Bortolanza Soares

Thesis presented to obtain the degree of Doctor in Science.
Area: Soil and Plant Nutrition

Piracicaba
2022

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To my family who always believed and supported me.

The people that believe in science.

All Brazilians who paid for my studies.

I dedicate

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"We are what we repeatedly do. Excellence, then, is not an act, but a habit."

Aristóteles

"The secret of happiness is not found in seeking the most, but in developing the ability to enjoy the least."

Sócrates

"All our science, compared to reality, is primitive and childish – and yet it is the most precious thing we have."

Albert Einstein

CONTENTS

RESUMO

Biogeoquímica de arsênio e chumbo em sedimento e água condicionado com biocarvão

Elementos potencialmente tóxicos (EPTs), como arsênio (As) e chumbo (Pb), constantemente ocasionamo desenvolvimento de doenças em seres vivos devido à ingestão contínua de água e alimentos com teores elevados desses elementos. Práticas antropogênicas diárias, como atividades domésticos, de saúde, industriais, agrícolas e de mineração podem contribuir para aumento da concentração de As e Pb em solos e sedimentos expostos à superfície terrestre, e isso aumenta a probabilidade de contato com os seres vivos. Embora a ocorrência de As e Pb no meio ambiente não seja necessariamente recente, ela se tornou mais relevante nas últimas décadas devido ao seu efeitos nocivo e à preocupação global em recuperar recursos naturais. Como forma de retomar a funcionalidade de ecossistemas contaminados por As e Pb, a comunidade científicia tem buscado utilizar técnicas de remediação que visam a reduzir os teores biodisponíveis desses elementos no solo e na água. Dentre elas, tem se destacado o uso de biocarvão devido à sua capacidade de imobilização de contaminantes, fornecimento de nutrientes e estoque de carbono. A remediação *in situ* com biocarvão é alternativa ecológica e que pode ser economicamente viável quando comparada a outras técnicas convencionais de remediação que geram resíduos e/ou são de alto custo. O biocarvão é um produto da pirólise de compostos orgânicos, e sua efetividade na imobilização de contaminantes está condicionada às condições de fabricação, dentre elas a temperatura de pirólise. Além disso, as condições ambientais como flutuação redox, elevada precipitação e exposição ao tempo são fatores que podem alterar o potencial do biocarvão em (i)mobilizar EPTs como As e Pb no ambiente. Neste trabalho foram avaliados *(i)* o efeito da temperatura de pirólise do biocarvão na dinâmica de As e Pb em sedimento exposto a ambientes com presença total e parcial de oxigênio; *(ii)* a biogeoquímica de As e Pb em sedimento e água submetidos a aplicação de biocarvão *in natura* e modificado com cloreto férrico; e *(iii)* efeitos do carbono orgânico dissolvido (COD) na competição por sítios específicos de sorção com As. Para avaliar a dinâmica de As e Pb, foram realizados diversos experimentos com sedimento e água contaminada com As e Pb devido à atividade antropogênica associada à mineração e benefíciamento de minério. As amostras contaminadas com As e Pb foram condicionadas com biocarvão de palha de cana-de-açúcar (*Saccharum officinarum*) pirolisado a 350 (BC350), 550 (BC550) e 750 ºC (BC750), enquanto a potencial competição por sítios de sorção foi avaliada em amostras de água contaminadas artificialmente com arsenato [As(V)]. A competição por sorção foi realizada na presença de oxihidróxidos de ferro (Fe) biogênico (BIOS), que é um biomineral de Fe(III) amplamente conhecido por ser sumidouro natural de As. A temperatura de pirólise exerceu papel fundamental nas características fisico-químicas do biocarvão, e isso afetou a capacidade de (i)mobilização de As e Pb em sedimento e água. A aplicação de biocarvão reduziu a atividade da β-glicosidase e aumentou a atividade da fosfatase, o que evidencia a dificuldade da microbiota em degradar o carbono do biocarvão, assim como sua facilidade em fornecer hidrolase capaz de mineralizar fosfato presente em formas orgânicas. O tempo de envelhecimento do biocarvão ocasionou aumento nos teores biodisponíveis e trocáveis de As, na mesma medida em que reduziu os teores biodisponíveis e trocáveis de Pb. O aumento dos teores biodisponíveis e trocáveis de As esteve relacionado às mudanças nos reservatórios de carbono ocasionados pela oxidação de superfície do biocarvão e pela biodegradação promovida pelos microorganismos. Em ambientes com elevada precipitação, a aplicação de biocarvão aumentou a liberação e a mobilidade de As sem afetar a distribuição das espécies de As. A modificação química do biocarvão, como forma de aperfeiçoar um filtro de água, aumentou a velocidade e capacidade de sorção de As e Pb e tornou o biocarvão

modificado com cloreto férrico uma alternativa promissora para filtro de água contaminada com esses elementos. A presença do DOC do biocarvão foi capaz de reduzir em até 30% a sorção de As(V) em BIOS. No entanto, a presença de DOC não alterou os mecanismos de sorção de As(V) em BIOS, o que mostra que o principal meio responsável pela redução da sorção de As(V) é o bloqueio de sítio. Já no sedimento em ambientes com presença parcial de oxigênio, o biocarvão foi capaz de reduzir a mobilidade de As. Além da mudança na mobilidade de As e Pb, verificou-se que o fornecimento de biocarvão ao sedimento aumentou consideravelmente o teor de DOC em solução, o que possívelmente tamponou a redução biótica assimilativa de Fe(III) e As(V) e reduziu a metilação de As.

Palavras-chave: Especiação, Remediação, Oxihidróxidos de ferro biogênico, Arsenato, Arsenito, Temperatura de pirólise

ABSTRACT

Biogeochemistry of arsenic and lead in sediment and water amended with biochar

Potentially toxic elements (PTEs), such as arsenic (As) and lead (Pb), constantly cause the development of diseases in living beings due to the continuous ingestion of water and food with high levels of these elements. Daily anthropogenic practices, such as domestic, health, industrial, agricultural, and mining activities can contribute to the increase in the concentration of As and Pb in soils and sediments exposed to the Earth's surface, and this increases the probability of contact with living beings. Although the occurrence of As and Pb in the environment is not necessarily recent, it has become more relevant in recent decades due to their harmful effects and to the global concern to recover natural resources. To restore the functionality of ecosystems contaminated by As and Pb, the scientific community has sought to use remediation techniques to reduce the bioavailable levels of these elements in soil and water. Among them, the use of biochar has stood out due to its ability to immobilize contaminants, supply nutrients, and store carbon. *In situ* remediation with biochar is an ecological alternative that can be economically viable when compared to other conventional remediation techniques that generate waste and/or are expensive. Biochar is a product of the pyrolysis of organic compounds, and its effectiveness in immobilizing contaminants depends on the manufacturing conditions, including the pyrolysis temperature. In addition, environmental conditions such as redox fluctuation, other factors as high precipitation, and exposure to weather can alter the potential of biochar to (i)mobilize EPTs in the environment. The following itens were evaluated in this study: *(i)* the effect of biochar pyrolysis temperature on As and Pb dynamics in sediment exposed to environments with total and partial presence of oxygen; *(ii)* the biogeochemistry of As and Pb in sediment and water submitted to the application of *in natura* biochar and modified with ferric chloride; and *(iii)* effects of dissolved organic carbon (DOC) on the competition for specific sorption sites with As. To evaluate the dynamics of As and Pb, several experiments were carried out with sediment and water contaminated with As and Pb due to mining and ore processing. Samples contaminated with As and Pb were conditioned with biochar from sugarcane straw (*Saccharum officinarum*) pyrolyzed at 350 (BC350), 550 (BC550), and 750 ºC (BC750), and the potential competition for sorption sites was evaluated in water samples artificially contaminated with arsenate [As(V)]. Sorption competition was performed in the presence of biogenic iron (Fe) (oxyhydr)oxide (BIOS), which is a Fe(III) biomineral widely known to be a natural sink for As. The pyrolysis temperature played a key role in the physicochemical characteristics of the biochar, and this affected the ability to (i)mobilize As and Pb in sediment and water. The application of biochar reduced the β-glucosidase activity and increased the phosphatase activity, which demonstrates the microbiota's difficulty in degrading the carbon in the biochar and, at the same time, its ease in providing hydrolase capable of mineralizing phosphate present in organic forms. The aging time of the biochar caused an increase in the bioavailable and exchangeable contents of As to the same extent that it reduced the bioavailable and exchangeable contents of Pb. The increase in bioavailable and exchangeable As contents were related to changes in carbon pools caused by surface oxidation of biochar and by biodegradation promoted by microorganisms. In environments with high precipitation, biochar application increased As release and mobility without affecting As species distribution. The chemical modification of biochar, as a way to improve a water filter, increased the speed and sorption capacity of As and Pb and made biochar modified with ferric chloride a promising alternative for filtering water contaminated with these elements. The presence of DOC from biochar was able to reduce As(V) sorption in BIOS by up to 30%. However, the presence of DOC did not

alter As(V) sorption mechanisms in BIOS, which shows that site blocking the main mechanism responsible for reducing As(V) sorption. The biochar was able to reduce the mobility of As in the sediment under environments with partial presence of oxygen. In addition to the change in the mobility of As and Pb, it was verified that the supply of biochar to the sediment considerably increased the DOC content in the solution, which possibly buffered the assimilative biotic reduction of Fe(III) and As(V) and reduced the As methylation.

Keywords: Speciation, Remediation, Biogenic iron (oxyhydr)oxides, Arsenate, Arsenite, Pyrolysis temperature

1. GENERAL INTRODUCTION

The acceleration of industrialization and urbanization and the demand for natural resources increased the attention of the society to environmental and food security (Lin et al., 2022). Among these processes, soil and sediment contamination with potentially toxic elements (PTE), such as arsenic (As) and lead (Pb), has become a major problem that negatively affects human health, and environmental and food security.

The World Health Organization (WHO) recommends the regulatory limit of As concentration in drinking water at 10 μg L^{-1} (WHO, 2022) while the US Environmental Protection Agency (USEPA) has set the maximum Pb content in drinking water at zero due to to the effects of this element on human health even at low exposure levels (USEPA, 2020). Contamination of water by As and Pb is considered a major health problem because prolonged exposure favors health disorders such as cancer, anemia, skin lesions, and neurological problems (Feitosa et al., 2021; Gracia and Snodgrass, 2007; Karim, 2000; Obasi and Akudinobi, 2020).

Due to the problems associated with exposure to PTEs, several remediation studies have emerged to develop ways to reduce exposure to PTE and to recover ecosystem services previously provided by impacted sites (Beesley et al., 2011; Lee, 2020; Singh et al., 2015; Tangahu et al., 2011). Several remediation techniques can be used to try to recover a contaminated area, such as phytoremediation, excavation and stabilization. However, phytoremediation and excavation techniques are limited, either by the plant's potential to tolerate and/or remove multiple contaminants or by the cost of the technique (Thomé et al., 2019). In addition to the high cost, excavation is extremely aggressive, which makes the spontaneous recovery of natural vegetation difficult (Kumpiene et al., 2019). Therefore, less expensive and less invasive techniques are recommended for decontamination and/or stabilization of PTEs in soils and sediments.

In situ stabilization is an efficient and low-cost remediation technique (Qiu et al., 2021). With this technique, the mobility of PTEs can be reduced by adding a sorbent that stabilizes them in chemical forms unavailable to living beings, which reduces their bioavailability and toxicity (Chen et al., 2019). Several organic compounds have been explored to remedy areas contaminated with PTEs (Rinklebe et al., 2016) and, among these organic materials, biochar stands out (Li et al., 2017). Biochar is able to immobilize a wide range of contaminants due to its characteristics, negative charge, specific surface area, cation exchange capacity and functional groups such as phenol - OH, C = C and C = O that favor the formation of complexes with PTEs (Wang and Liu, 2017).

Organic sources influence the mobility of PTEs in soils and sediments, and the effectiveness of biochars is affected by the pyrolysis temperature, which is the predominant parameter in determining the applicability of biochar for (i)mobilization of PTEs (Xing et al., 2019). The low temperature of pyrolysis (~ 300 ºC) favors the preservation of functional groups that contain oxygen, which may contribute to PTEs sorption (Chen et al., 2015). On the other hand, at high pyrolysis temperatures (~ 700 ºC), there is a contribution to the formation of aromatic structures and porosity structures, which

play an important role in the physical adsorption of PTE (Mimmo et al., 2014). As the pyrolysis temperature alters the chemical composition, surface morphology, thermal stability, as well as the fate of PTE in the biochar structure (Xiao and Chen, 2017), studies that assess the effect of pyrolysis temperature on the biochar structure are essential to point of view of PTE biogeochemistry.

The disasters in Brazil involving mining tailings, such as the Samarco dam in 2015 and the Brumadinho dam in 2019, raised concerns about the composition and geochemical process intensified by the release of the ore present in the mines. The exposure of PTEs to the environment poses risks to environmental health, and understanding PTE dynamics is a way of predicting their fate and transport in the environment (Siddiqi, 2018).

In this study, the dynamics of As and Pb in sediment, water, and pure material [biogenic iron (oxyhydr)oxide - BIOS] were investigated by spectroscopic techniques at different scales. The study with pure material allows for isolating the effects of some variables such as ionic strength, pH, bond aging, and surface charge. This approach allows an atomic scale description of the mechanisms that govern the sorption of As or Pb, allowing the development of sorption or surface complexation models when the liquid and/or solid phase of the biochar is present.

The objectives with this study were to evaluate: *(i)* the effect of biochar pyrolysis temperatures on the enzymatic activity of microorganisms in the sediment; *(ii)* the effect of biochar pyrolysis temperature on As and Pb availabilities over time; *(iii)* changes in carbon pools during biochar aging; *(iv)* whether pyrolysis temperatures affect As and Pb leaching, and identify the main As species leached; *(v)* whether the modification with $FeCl_3$ improves the performance of the biochar as a water filter; *(vi)* how dissolved organic carbon from biochar affects arsenate binding mechanisms onto BIOS; and *(vii)* the effect of pyrolysis temperature and biochar application on the release and transformation of As in sediment subjected to redox fluctuation.

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2. DOES THE BIOCHAR OF SUGARCANE STRAW PYROLYSIS TEMPERATURE CHANGE THE AVAILABILITY OF ARSENIC AND LEAD AND THE ACTIVITY OF THE MICROORGANISMS IN A CONTAMINATED SEDIMENT?

Abstract

Biochar is a promising alternative for the remediation of areas contaminated by mining waste. However, depending on the pyrolysis temperature, the biochar may not be equally effective for immobilizing cationic and anionic contaminants. Our objectives in this study were to evaluate: *i)* the effect of biochar on the availability of As and Pb in sediments of a contaminated area, and *ii)* the effect of the biochar pyrolysis temperatures on the enzymatic activity of the microorganisms. The contaminated sediment was sampled in an area that served as a lead ore refining plant for ten years in Brazil. The biochar was produced from sugarcane straw (*Saccharum officinarum*) and pyrolyzed at 350 (BC350), 550 (BC550), and 750ºC (BC750). We performed an incubation experiment to investigate the effects of pyrolysis temperature on the dynamics of As and Pb in the sediment. The availability of As and Pb was measured by the diffusive gradients in the thin-film, and the quality of organic carbon in the sediment, and in solution was investigated by laser-induced fluorescence spectroscopy and UV-vis spectroscopy. In addition, the effect of the application of the biochar on the microbial community was evaluated through the activities of the enzymes β-glucosidase, acid, and alkaline phosphatase. The application of biochar changed the chemical composition of the carbon structures and altered the availability of As and Pb. Increases in the availability of As after the application of biochar is directly linked to the chemical composition of the dissolved organic carbon present in BC350, with the activity of phosphatase and phosphorus release (BC550 and BC750) and, finally, with pH (B550 and BC750). The availability of Pb was reduced after the application of the B550 and B750, which suggests that pyrolyzed biochars at high temperatures may help to reduce the environmental risk associated with Pb contamination. The application of biochar reduced the activity of the enzymes β-glucosity and acid phosphatase, while the alkaline phosphatase activity increased and was dependent on the pyrolysis temperature. The increase in the availability of As after the application of biochar is related to the chemical composition of dissolved organic carbon and the increase in phosphatase activity. The availability of Pb has been reduced due to the increase in pH, which suggests that pyrolyzed biochars at high temperatures may help to reduce the environmental risk associated with Pb contamination.

Keywords: Contaminated sediment, Enzymatic activity, *Saccharum officinarum*, FTIR, LIFS, Remediation

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2.1. Introduction

Pollution by metals and metalloids in abandoned mines and activities related to ore processing are potential threats to both human health and the environment (Fazle Bari et al. 2020). Among the elements with the potential to cause toxicity, arsenic (As) and lead (Pb) stand out because of their persistence and non-biodegradability in the environment (Ouyang et al. 2018; Igalavithana et al. 2019). Contamination of the soil by As and Pb causes severe diseases in humans such as peripheral neuropathy, skin, and lung cancer (Cao et al. 2020; Wang et al. 2020; Setia et al. 2020).

Over the last few years, Brazil has been the victim of disasters involving mining tailings. One example is the rupture in 2015 of a dam with 50 million m^3 of tailings from iron ore extraction (Queiroz et al. 2018) in Mariana, in the state of Minas Gerais (MG) (20° 22' S, 43° 25' O), which was considered the biggest environmental disaster of its kind in the world (Almeida et al. 2018). In 2019, another dam broke in Brumadinho (MG) as a result of poor storage of iron ore tailings ($11x10^6$ m^3 of mining waste) (Silva Rotta et al. 2020).

Remediation of contaminated areas can be implemented by using techniques such as phytoremediation, excavation, and stabilization. *In situ* stabilization is an efficient and low-cost remediation technique (An et al. 2019), whereby the mobility of potentially toxic elements (PTEs) can be reduced by adding a sorbent that stabilizes the chemical forms of the contaminants via sorption and/or precipitation which reduces bioavailability and toxicity (Chen et al. 2019).

The addition of biochar is a promising alternative for the management of contaminated soils since it immobilizes PTEs (Beiyuan et al. 2017; Yang et al. 2019) through mechanisms such as *(i)* superficial complexation with functional groups, *(ii)* electrostatic interactions with the surface loaded with positive/negative charges, *(iii)* physical adsorption on the internal pore surface, and *(iv)* (co)precipitation on the conditioner surface (El-Naggar et al. 2019).

The ability to remove both organic and inorganic pollutants by biochar is related to its surface area, negative charge, cation exchange capacity, and the presence of functional groups, such as phenol-OH, C=O, and C=C that form organometallic complexes (Wang and Liu 2017). In addition to the direct effects of biochar on the dynamics of PTEs in the soil, there are indirect effects such as assistance in modulating the soil microbial community (Pratush et al. 2018), which directly affects the metabolic processes involved in the cycling of PTEs (Xiao et al. 2016).

The mechanisms of immobilization of contaminants by biochar are generally complex and vary according to the properties of the biochar imposed by the pyrolysis temperature. Depending on the pyrolysis temperature, increases in the amount of dissolved organic carbon (DOC) and inorganic compounds from biochar can increase the mobilization of As by competing for retention sites on the surface of the soil colloids (Li et al. 2018; Wu et al. 2019).

Beyond the competition for specific binding sites, soluble complexes of As-DOC or Pb-DOC (Fleming et al. 2013) can form. Low pyrolysis temperatures (< 450ºC) favor the preservation of functional groups that contain oxygen, which can contribute to the sorption of EPTs (Chen et al. 2015). On the other hand, under high temperatures of biochar pyrolysis (> 450ºC), aromatic structures and porous structures are formed and play an important role in carbon sequestration (Xiao and Chen 2017) and the physical sorption of PTE (Lyu et al. 2016).

There is no consensus on the influence of the addition of biochar on the mobility of As and Pb in the soil because several soil and biochar properties and the nature and concentration of pollutants can influence the immobilization of As and Pb (Silvetti et al. 2017). This implies there is a need to further

our knowledge of the interactions between As, Pb, and contaminated soils and/or sediments amended with pyrolyzed organic compounds at different temperatures.

Our objectives in this study were to *(i)* verify the influence of the addition of biochar on the dynamics and remediation of As and Pb in a contaminated area and *(ii)* evaluate the effect of pyrolysis temperatures of the biochar on the enzymatic activity of the microorganisms present in the sediment. To our knowledge, this is the first study to examine the influence of biochar pyrolysis temperature on the availability of arsenic and lead in sediment contaminated by mining in Brazil.

2.2. Conclusions

The application of biochar modified the sediment DOC and affected the availability of As and Pb.

The increase in As availability after application of biochar was related to (i) the chemical composition of DOC present in BC350, (ii) the increase in phosphatase activity and phosphorus release (BC550 and BC750), and (iii) the increase in the sediment pH (B550 and BC750).

The availability of Pb in solution was reduced after the application of biochar produced at 550 and 750ºC, which suggests that pyrolyzed biochars at high temperatures may help to reduce the environmental risk associated with Pb contamination.

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3. TEMPORAL CHANGES IN ARSENIC AND LEAD POOLS IN A CONTAMINATED SEDIMENT AMENDED WITH BIOCHAR PYROLYZED AT DIFFERENT TEMPERATURES

Abstract

Globally, tons of soils and sediments are experiencing degradation due to the presence of high concentrations of potentially toxic elements (PTEs), such as arsenic (As) and lead (Pb), in areas in the vicinity of metal mining activities. The addition of biochar to contaminated sediments is a promising *in situ* remediation approach, and the effects of pyrolysis temperature and biochar aging are important factors for the immobilization and fate of PTEs. In this study, we evaluated the temporal changes in pools of As and Pb in sediment amended with biochars produced from sugarcane (*Saccharum officinarum*) pyrolyzed at 350 (BC350), 550 (BC550), and 750ºC (BC750). Biochars were aged by natural process (without additional acid or heat), and changes in As and Pb pools were evaluated every 45 days until completing 180 days of incubation. Changes in the As and Pb pools were extracted with water (bioavailable), magnesium chloride (exchangeable), nitric acid (active geochemical fraction), and exchangeable Mehlich-3 (associated with organic matter). As and Pb available contents have increased over time. BC750 was more effective in reducing the bioavailable and exchangeable As contents, while BC550 and BC350 were more effective in reducing the contents of bioavailable and exchangeable Pb.

Keywords: Immobilization; Pyrolysis temperature; Sugarcane straw; Contamination; Sorption

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3.1. Introduction

The levels of arsenic (As) and lead (Pb) in the environment are a consequence of geological and anthropogenic factors (Tabelin et al., 2018). The main process of As and Pb release under geogenic contamination conditions is the dissolution of primary minerals while the anthropogenic sources are industrial processes such as coal combustion, mining, and smelting activities (Singh et al., 2015).

In general, international environmental protection agencies classify the contents of potentially toxic elements (PTEs) based on their total concentration in the soil (CETESB, 2016; CONAMA, 2009; Panagos et al., 2012; USEPA, 2020). Total concentrations, however, do not necessarily represent the biological availability or the potential of the PTEs to cause toxicity in soil organisms, plants, or animals (Lu et al., 2021; Zulkafflee et al., 2020). The number and size of areas containing polluted soils have grown exponentially in the past few decades, and taking the total amount of PTEs into account to establish strategies to amend agricultural or mining-impacted soils are economically infeasible (Kumpiene et al., 2019, 2017).

Biochars have been used for stabilization *in situ* to reduce the (bio)availability of As and Pb in soils as well as to reduce the spread of contamination of the ecosystem (Koul et al., 2018; Li et al., 2016). Biochars immobilize PTEs through *(i)* superficial complexation with functional groups, *(ii)* electrostatic interactions with the surface charged with positive/negative charges, *(iii)* physical sorption

on the internal pore surface; and *(iv)* (co)precipitation on the amendment surface (El-Naggar et al., 2019).

The effectiveness of biochar in sorb contaminants is influenced by the temperature and pyrolysis conditions (Wang et al., 2013). The pyrolysis temperature affects the amount of functional organic groups, specific surface area, porosity, and reactivity of the biochar (Chen et al., 2015; Lyu et al., 2016; Wang and Wang, 2019), which makes its study essential to the verification of the effectiveness in remedying areas contaminated by multiple chemical elements.

As and Pb have a significant effect on health because prolonged exposure to As can cause hyperkeratosis, skin cancer, encephalopathy, and peripheral neuropathy (Nurchi et al., 2020), while exposure to Pb can cause peripheral neuropathy, forearm extensor weakness, anemia, and cancer (Gracia and Snodgrass, 2007). The degree and force of As and Pb retention by soil colloids vary over time (Borda and Sparks, 2007; Fendorf et al., 2004) and influence the transport of the contaminant (Diquattro et al., 2021) and its bioaccessibility for absorption by organisms.

Chemical extraction methods (such as chemical sequential extraction) have been widely used to assess the contaminant pools and to predict the fate of elements in the environment (Liang et al., 2014). The sequential extraction schemes are based on the use of reagents with growing capacities of extraction, chosen to solubilize sorbed elements and/or the mineralogical fractions responsible for the retention of the PTE (Shang and Zelazny, 2008).

The chemical sequential extraction has some problems related to the solubilized phase and/or the extracted fraction, in addition to the possibility of losing soil/sediment mass during the sequential extraction (Martin et al., 1987; Migoni et al., 2021). Non-destructive analyzes, such as those based on synchrotron radiation (Lombi and Susini, 2009) have been used as an alternative for sequential extraction. The access to synchrotron radiation, however, is limited, and the ways in which the results are obtained, and the data are processed are not trivial.

Although there are several articles published on the chemical methods used to assess the availability of As and Pb, there is still no definitive judgment in studies that assess the simultaneous extraction of available forms of these two elements in soils amended by biochar. Thus, our objective was to evaluate the temporal changes in the As and Pb pools in sediment amended with pyrolyzed biochar at different temperatures.

In this study, the biochars were naturally aged in the sediment, without any accelerated aging process. The biochar remained incubated in the sediment at 70% of field capacity for 180 days. Sugarcane (*Saccharum officinarum*) straw was chosen as the raw material for the production of biochar at temperatures of 350, 550, and 750ºC. The evaluation of soluble, exchangeable, active geochemical, and bioavailable As and Pb pools associated with the organic matter was determined by sequential chemical extraction using water, $MgCl_2$, HNO_3, and Mehlich-3.

3.2. Conclusions

The use of selective chemical extractors remained consistent during the 180 days of biochar aging.

The increase in the pyrolysis temperature resulted in an increase in phosphorus and a reduction in oxygen on the surface of the biochar, which could limit the immobilization of As and Pb.

The ability of biochars to immobilize As and Pb was affected by the temperature of pyrolysis and the aging process.

The BC550 and BC750 reduced most of the exchangeable Pb after 135 days of aging, while BC350 decreased only at the end of 180 days of aging.

The aging time of the biochar increased the bioavailable and exchangeable contents of As, to the same extent that it reduced the bioavailable and exchangeable contents of Pb.

There was a natural increase in the contents of As and Pb in all pools in the sediment.

Most of the content of As was associated with organic matter, while most of the Pb was associated with the geochemically active fraction.

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4. BIOCHAR AGING: IMPACT OF PYROLYSIS TEMPERATURE ON SEDIMENT CARBON POOLS AND THE AVAILABILITY OF ARSENIC AND LEAD

Abstract

Arsenic (As) and lead (Pb) are potentially toxic elements capable of developing several diseases in human beings such as cancer. Several adsorbent materials, including biochars, have been adopted as alternative measures designed to reduce the availability of As and Pb in water. The retention capacity of potentially toxic elements in biochars varies according to time, feedstock, and the pyrolysis temperature to produce the biochar. Our objectives in this study were to evaluate *i)* the aging effect of sugarcane straw pyrolyzed biochars at 350 (BC350), 550 (BC550), and 750ºC (BC750) and their ability to immobilize As and Pb; and *ii)* how the pyrolysis temperature and biochar aging alter the carbon content and quality of the solution and sediment. Biochars were applied at 5% (w/w), and their aging together with As and Pb immobilization effects were evaluated every 45 days over a total period of 180 days. The results were obtained using visible ultraviolet spectroscopy and diffuse reflectance infrared Fourier transform spectroscopy combined with physical fractionation of organic matter and multivariate statistics. The groups formed in the Principal Component Analysis indicated that the change in the availability of As and Pb was related to the aging of the biochar and the temporal changes in the content and quality of organic carbon in the sediment and solution. The pyrolysis temperature was a key factor in the (im)mobilization capacity of As and Pb during the aging of the biochar. The increase in polysaccharides and organic matter associated with the particulate fraction can enhance the release of As in solution (24%). Increasing the fraction of organic matter associated with minerals reduced the availability of Pb by 58%. These findings may provide new insights into understanding the dynamics of organic matter and its role in the immobilization of As and Pb during biochar aging.

Keywords: Remediation; *Saccharum officinarum*; Physical fractions of organic matter; DRIFT; Dissolved organic carbon

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4.1. Introduction

Industrial and mining activities are the main sources of soil and sediment contamination by metalloids and heavy metals (Awad et al., 2019). Among the potentially toxic elements (PTEs), arsenic (As) and lead (Pb) stood out on account of their toxicity to plants, animals, and humans. Approximately 140 million people worldwide may have been exposed to drinking water with an As content above the level considered by the World Health Organization (WHO) to be safe for drinking - 10 µg L^{-1} (Bagchi, 2007), while occupational exposure to Pb may have compromised the health of more than 3 million workers in the USA (Wani et al., 2015). For these reasons, they were listed by the United States Environmental Protection Agency (USEPA) as priority contaminants (Chaney et al., 2016).

As a result of the global problem posed by contamination, several researchers have demonstrated the need to investigate low-cost technological solutions aimed at remediating contaminated sites to promote the growth of plants (Liu et al., 2017). In the field of remediation technology, there is growing interest in the biochar's potential for immobilizing contaminants, either by fixing the PTEs in the

biomass or by stabilizing the contaminant in contaminated soil (He et al., 2019). Biochar can immobilize PTEs by mechanisms such as cation exchange, surface complexation, precipitation, porous diffusion, and electrostatic interaction, depending on the raw material and pyrolysis conditions (Bandara et al., 2021).

Once present in the soil or sediment, the biochar undergoes a natural aging process (Wang et al., 2017). The biochar's aging process alters the properties of the biochar which affects its ability to immobilize PTEs (Li et al., 2016). The aging intensity of the biochar depends on the biochar's properties such as aromaticity (Rechberger et al., 2017), carbon content, nitrogen content (Xu et al., 2018), specific surface area (SSA), and porosity (Suliman et al., 2016). A number of researchers have shown contradictory results for SSA and porosity during biochar aging. For example, Yuan et al. (2021) observed that blocking soil organic matter would reduce the SSA while the dissolution of organic matter (OM) and ash in the biochar resulted in increased SSA.

During its occupancy of the soil, the biochar can change its negative surface charge density and form new sites for electrostatic metal-biochar interaction (Kumar et al., 2018). In general, there was an increase in the density of negative surface charges due to oxidation of the biochar surface (Dong et al., 2017). A number of researchers, however, believe that the accumulation of organomineral complexes on the surfaces of the biochar promotes an increase in functional groups due to the high concentration of pores below 10 μm in which the PTEs can be sorbed (Hagemann et al., 2017). On the other hand, with aging, there is a possibility that the PTE can be released from the particle or surface of the biochar and interact with the other components in the soil (Yang et al., 2018). Few researchers have focused on PTEs and the organic matter (OM) pools of the soil/sediment during the biochar aging process. The mechanisms that dominate the long-term stability of PTEs in contaminated soils amended by different biochars remain uncertain.

In Brazil, sugarcane (*Saccharum officinarum*) is the second-largest agricultural commodity under cultivation (annual production of 642,717,800 tons), and the majority of sugar cane production (90%) is concentrated in the south-central region of Brazil (Martíni et al., 2020). The removal of sugarcane straw may be a promising strategy for increasing bioenergy production in Brazil (Cherubin et al., 2021) and produce biochar.

Understanding the changes in the availability of PTEs and in the carbon pools of the soil during the biochar aging process is essential to any justification of the application of biochar in contaminated areas and prediction of the fate of the PTEs in the environment. Thus, our objectives were to assess *i)* the availability of As and Pb after the addition of pyrolyzed biochar at three different temperatures; and *ii)* the carbon quality of the bulk sediment and the sediment solution during the aging process of the biochars as evaluated by diffuse reflectance infrared Fourier transform (DRIFT) and visible ultraviolet (UV-vis) spectroscopy.

The aging of biochars by incubation in the sediment at 70% of field capacity was a natural process, without any accelerated aging process. In this study, sugarcane straw was selected as the raw

material to produce biochar at temperatures of 350, 550, and 750ºC. The quality assessment of the organic carbon (OC) of the sediment and solution was evaluated using spectroscopic tools (DRIFT and UV-vis) combined with the traditional method of physical particle size fractionation of the OM of the sediment.

4.2. Conclusions

Over time, the pyrolytic temperature affected the carbon pools and the capacity for As and Pb (im)mobilization. Contents of particulate organic matter and dissolved organic carbon increased during the aging period of the biochar, which resulted in an increase in As availability in solution. The application of biochar and the increase in the aging time of biochar promoted increases in the content of organic matter associated with minerals and an increase in Pb immobilization (58%). These findings may provide information for understanding the transformation of sediment organic matter after biochar remediation and how changes in stable and reactive organic matter fractions affect the long-term (im)mobilization of As and Pb.

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5. ROLE OF PYROLYSIS TEMPERATURE ON ARSENIC AND LEAD LEACHING POTENTIAL IN A BIOCHAR-REMEDIED SEDIMENT

Abstract

Human activities, such as smelting, mining, and improper agricultural practices, like the excessive use of pesticides and fertilizers, may lead to the presence of high concentrations of arsenic (As) and lead (Pb) in soil and water from agricultural and urban areas. The widespread contamination by these elements is a global concern issue, and a mitigation to overcome such scenarios is a big challenge. In this sense, environmentally friendly technologies that reduce the mobility of these contaminants have been increasingly sought. Among them, the use of biochar stands out due to its potential for immobilization in situ and storing carbon. The leaching of contaminants by rain is a dynamic non-equilibrium process involving a continuous scavenging of chemical elements, which makes leaching studies fundamental to evaluate the real potential of biochar to immobilize contaminants. Towards this direction, our aims in this study were to evaluate the effect of biochar pyrolysis temperature on controlling the fate of As and Pb in sediments subjected to leaching. Before leaching, biochar was homogenized with sediment and aged by a natural process for 365 days. Biochar was produced from sugarcane (Saccharum officinarum) straw pyrolyzed at 350 (BC350), 550 (BC550), and 750 ºC (BC750). The assessment of changes in dissolved organic carbon quality was measured by UV-vis spectroscopy, and geochemical changes were assessed by mass spectrometry coupled to high performance liquid chromatography (HPLC-ICP-MS). The addition of biochar reduced Pb mobility and increased As mobility. The immobilization potential was related to the pyrolysis temperature, with BC750 being able to reduce Pb leaching by 54%, while BC350 increased As mobility by 2.5 times. We did not identify the leaching of monomethylarsonic (MMA) and dimethylarsinic (DMA) acids, but BC350 and BC750 increased by 2.5 times the leaching of As(III).

Keywords: Arsenite; Arsenate; Sugarcane straw biochar; Speciation; Amendment; Leaching

5.1. Introduction

Human exposure to As and Pb causes several health problems such as cancer, diabetes, anemia, kidney failure, and damage to the central nervous system (Chiu and Yang, 2007; Eslami et al., 2022; Mohammadi et al., 2022). The persistence of As and Pb in soil and their toxicity to organisms is a matter of concern worldwide (Hartley et al., 2004). In Latin America alone, it is estimated that 14 million people are exposed to drinking water containing 10 μg L^{-1} of total As, which is an action limit value by most countries in the world (Huang et al., 2014; Saint-Jacques et al., 2014). In turn, Pb has the potential to expose more than 18 million people to health risks in the United States because of the water distribution pipelines infrastructure conditions (Lobo et al., 2022).

Several countries have increasingly sought strategies to reduce human exposure to potentially toxic elements (PTE) through the immobilization/removal of these contaminants present in water and soil (Palansooriya et al., 2020; Wang et al., 2021). The general approach to remediation of contaminated soils is excavation followed by backfilling in clean soil. This strategy, however, is extremely expensive and disruptive (Aparicio et al., 2022; Krok et al., 2022). As an alternative, *in situ* stabilization has been adopted using the addition of inorganic compounds (Dong et al., 2017; Shen et al., 2019; Tu et al., 2022). Alternatively, among the compounds used *in situ* stabilization, biochar stands out, as it is a low-cost by-

product obtained from the pyrolysis of biomass in a medium with partial or total removal of oxygen (Oni et al., 2019; Qiu et al., 2021).

Besides being environmentally friendly due to its ability to store carbon (Chen et al., 2017), biochars can immobilize a wide range of inorganic contaminants by electrostatic attraction, ion exchange, complexation, and precipitation (Cui et al., 2021) due to specific properties such as high stability, charge density, microporous structure, and high specific surface area, biochars can immobilize contaminants

The efficiency of biochar in immobilizing inorganic contaminants depends on several factors, such as feedstock, pyrolysis, and edaphoclimatic conditions where the biochar will be applied (Hassan et al., 2020). The pyrolysis temperature and the feedstock affect the composition and structure of the biochar, so this can either enhance or reduce the immobilization capacity of inorganic contaminants (Yaashikaa et al., 2020). This makes studies with evaluations of new feedstocks and pyrolysis temperatures increasingly necessary.

There are many agro-industrial residues to produce biochar. Among them, the sugarcane straw (*Saccharum officinarum*) left in the field after the sugarcane harvest (~ 20 Mg ha^{-1} $year^{-1}$ of dry mass) has shown the potential to be used as feedstock for producing biochar. Brazil holds about 40% of the world's production of sugarcane cultivated in, approximately, 10 million hectares cultivated with sugarcane (Cherubin et al., 2019). The amount of sugarcane straw production in Brazil is estimated at 200 million tons ha^{-1} $year^{-1}$.

The potential immobilization of PTEs by biochars is affected by soil and climate conditions. The volume and chemical composition of rain interfere with the biochar's ability to sorb PTEs in the long term (Jia et al., 2021). Rainwater has an acid composition (pH < 7), and this results in the interaction of H^+ from the rain with the biochar in the soil, which can affect the (de)protonation of functional groups on the surface of the biochar (Munir et al., 2020). Furthermore, as the rain is leached into the soil, the alkaline components of the biochar will be neutralized, and the dissolved organic carbon (DOC) will be removed. These interactions of rain with biochar cause part of the PTEs sorbed in the soil and in the biochar to be released into the soil solution and transported to the aquatic environment (Kim et al., 2022).

The biogeochemistry of PTEs in the environment depends on edaphoclimatic conditions but can be affected by the quality of the biochar used in the remediation. The pyrolysis temperature plays a crucial role in the biochar characteristics and, consequently, in its potential to either sorb PTEs or to change the electrochemical conditions of the soil solution. The increase in the temperature can reduce DOC availability and increase the ash content of the biochar, which can reduce the organometallic complex formation and increase the alkalinity of the solution (Amen et al., 2020; Beesley et al., 2011; Wang and Wang, 2019). These changes may favor the precipitation and complexation of Pb and, at the same time, increase the availability of As in solution, which makes it essential to study the quality of biochar from the point of view of pyrolysis temperature in multi-contaminated environments.

The leaching of PTEs in the soil profile after a rain is a dynamic non-equilibrium continuous desorption process. By this, studies for investigations of the real effects of biochars on the mobility of PTEs in soil are necessary. Our objective was to evaluate the effect of biochar pyrolysis temperature on the immobilization capacity of As species and total Pb in sediment subjected to leaching. Before carrying out the leaching, the biochar was incorporated into the sediment and aged through a natural process for 365 days.

In this study, sugarcane straw was selected as feedstock for pyrolysis and the temperatures chosen were 350, 550, and 750 ºC. Assessment of DOC quality changes were measured by UV-vis spectroscopy and geochemical changes were assessed by optical emission spectrometry coupled to the mass detector and high-performance liquid chromatography (HPLC-ICP-MS). It is expected that the results obtained in this study can provide valuable information for the establishment of a new option for As and Pb remediation and to identify the changes responsible for the fate and mobility of As and Pb in the environment.

5.2. Final Remarks

We observed that the addition of biochar at different temperatures affected the fate of As and Pb in the environment. An important aspect is that the aging for one year of the biochar in the sediment reduced the mobility of Pb, with higher pyrolysis temperatures being more efficient in reducing the mobility of this contaminant, such as the pyrolyzed biochar at 750 ºC that reduced the leaching of Pb in the sediment by 54%. The exogenous supply of dissolved organic carbon and phosphorus favored the increase of As leaching.

All these findings bring information towards a better understanding of biochar pyrolysis temperature on As and Pb mobility in the environment, thus providing insights for future studies devoted to improve the use of biochar for the remediation of multi-contaminated areas.

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6. IRON-MODIFIED BIOCHAR FROM SUGARCANE STRAW TO REMOVE ARSENIC AND LEAD FROM CONTAMINATED WATER

Abstract

The presence of arsenic (As) and lead (Pb) in water above tolerable levels is a global concern, as both elements are extremely toxic and can compromise the health of millions of people. In this study, we evaluated biochars pyrolyzed at 350 (BC350) and 750ºC (BC750) and then modified with ferric chloride ($FeCl_3$) to remove As and Pb from water samples contaminated by mining activity. The use of $FeCl_3$-modified biochar was an efficient strategy to remove As and Pb from water. Sorption on biochars followed the pseudo-second-order kinetics, represented by two sorption speeds, being higher at the beginning of the reaction and falling over time. The modification with $FeCl_3$ increased the specific surface area, removed the dissolved organic carbon, and increased the capacity of BC350 to sorb Pb. These physical and chemical alterations of the biochar played a significant role in the sorption capacity and speed of As and Pb.

Keywords: Ferric chloride; Dissolved organic carbon; Kinetics; Contamination; Sorption

Soares, M.B., Santos, F.H., Alleoni, L.R.F. Iron-Modified biochar from sugarcane straw to remove arsenic and lead from contaminated water. Water, Air & Soil Pollution, v.807, 2021.

6.1. Introduction

Arsenic (As) and lead (Pb) are potentially toxic elements (PTEs) for plants and animals and can be found in water, soil, sediment, and vegetation (Zhang and Wang, 2020). The mobilization of As and Pb in sediments due to weathering reactions and biological activity, such as redox, complexation, and methylation, can contaminate surface and groundwater (Bakshi et al., 2018). The presence of As and Pb in groundwater above critical levels has become a worldwide environmental problem (Obasi and Akudinobi, 2020; Shaji et al., 2020).

Exposure to excessive levels for a prolonged time can cause pose problems to human health, such as skin lesions, cancer, acute encephalopathy and disorders in the central nervous system (Chisolm and Harisson, 1998; Karim, 2000; Papanikolaou et al., 2005). The main routes of exposure are ingestion of contaminated food and water, dermal contact and inhalation of particles suspended in the atmosphere (Boim et al., 2020).

As contamination by As and Pb affects millions of people worldwide (Hu et al., 2015; Zhang and Wang, 2020), new techniques and new products to remove contaminants from drinking water and wastewater are increasingly in demand. The main technique used to remove contaminants from water is based on the sorption principle, due to the ease of operation and relatively low cost (Barreto et al., 2020; Hu et al., 2015). In the past, several sorbents have been explored for the removal of PTEs from water, among which are iron oxyhydroxides, considered to be efficient sorbents in removing As from aqueous solutions (Saharan et al., 2014). However, the isolated use of iron oxyhydroxides as a water filter requires recovery processes such as sedimentation or filtration, which add an additional cost to the process (Tuna et al., 2013).

Another sorbent widely used to remove PTEs from water is biochar (Ahmad et al., 2014), which can be produced from the waste of poultry, livestock, and agriculture (Adegbeye et al., 2020). Biochar has been widely used to remove contaminants from water as it has a large number of phenolic and carboxylic functional groups and a high specific surface area which provide the sorption of cationic contaminants (Inyang et al., 2016). However, biochar is not the best material for removing anionic contaminants from aqueous solutions such as As (Ahmed et al., 2016). To overcome this inconvenience, sorbents are used that combine biochar compounds with materials containing iron (Fe). One of the compounds used in the modification of the biochar is ferric chloride ($FeCl_3$), which forms Fe oxyhydroxides on the biochar's surface (Wang et al., 2015; Wu et al., 2018).

$FeCl_3$ is usually used in the recovery of phosphorus from domestic effluents (sewage). The excess of phosphorus in the effluent causes water eutrophication with consequent growth and proliferation of algae, resulting in the irreversible destruction of the ecosystem balance (Ren et al., 2020). The addition of $FeCl_3$ at strategic points during sewage treatment is desirable from the point of view of sewage treatment (preventing environmental problems) as the sustainable recovery of agricultural fertilizer (Li et al., 2020).

In addition to the modifications to biochar with compounds containing iron, the temperature of pyrolysis is a fundamental factor affecting the capacity of sorption of contaminants. It changes the characteristics of the biochar, such as cation exchange capacity, specific surface area, and quantity of functional organic groups which directly interferes with the ability to sorb contaminant (Ahmad et al., 2014). For this reason, it is necessary to investigate the impact of the way of preparing the biochar on the sorption capacity of PTEs. We aimed to evaluate the effect of pyrolytic temperature and ferric chloride modification on the biochar's ability to remove As and Pb from water contaminated by mining activity.

6.2. Conclusions

The sorption capacity of As and Pb after modification with $FeCl_3$ was affected by the pyrolytic temperature, with a temperature of 750ºC favoring the highest sorption of As while the pyrolysis at 350ºC promoted the highest sorption of Pb.

The *in natura* biochar pyrolyzed at 750ºC promoted the greatest removal of As and Pb from the contaminated water.

The sorption speed was 2.5 times faster for As and 3 times faster for Pb after the addition of $FeCl_3$ in the biochar pyrolyzed at 750ºC.

The biochar morphology was not affected by the modification with $FeCl_3$, but the presence of $FeCl_3$ altered the biochar surface composition according to the pyrolytic temperature. After treatment with $FeCl_3$, the biochar pyrolyzed at 350ºC replaced P and Mg by Cl and Fe, while the biochar pyrolyzed at 750ºC replaced Al and P by Fe and Cl.

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7. THE ROLE OF DISSOLVED ORGANIC CARBON FROM BIOCHAR IN THE SORPTION OF AS(V) IN BIOGENIC IRON (OXYHYDR)OXIDES

Abstract

The contamination of water by arsenic (As) affects greater than 200 million people worldwide. Iron (oxyhydr)oxides, and in particular biogenic Iron (oxyhydr)oxides (BIOS), are known for their potential to sorb As and may play key roles in regulating As cycling in circumneutral environments. However, little is known about the potential of BIOS to sorb As(V) in the presence of dissolved organic carbon (DOC) from biochar, a common soil additive, or if the temperature of biochar production impacts the how pyrolytic DOC interacts with As(V) and BIOS. To investigate this, we conducted As(V) sorption experiments with BIOS at circumneutral pH conditions and in the presence of DOC from sugarcane (*Saccharum officinarum*) straw biochar at pyrolyzed 350 (BC350) and 750 ºC (BC750). The As(V) content was quantified by inductively coupled plasma mass spectrometry, and the BIOS structure and As(V) sorption mechanisms were investigated by X-ray absorption spectroscopy. In addition, the organic moieties comprising the DOC from biochars were investigated by attenuated total reflectance Fourier transform infrared spectroscopy. The BIOS is similar in structure to the 2-line ferrihydrite, and the addition of DOC did not change the biomineral structure or As(V) oxidation state. However, the presence of DOC reduced by 25% the sorption of As(V), with BC350 being responsible for the greatest reduction in As(V) sorption capacity. Structural modeling of the extended X-ray absorption fine structure spectra revealed As(V) predominantly formed binuclear bidentate surface complexes on BIOS. The presence of DOC and the pyrolysis temperature did not change the binding mechanism of As(V) in BIOS, suggesting that the reduction As(V) sorption to BIOS was due to site blocking by DOC.

Keywords: Biogenic oxides; Bidentate complexes; Biominerals; Dissolved organic carbon; X-ray absorption spectroscopy

7.1. Introduction

Arsenic (As) is a critical naturally occurring contaminant due to its potential toxicity, causing negative health outcomes such as birth defects, neurological problems, cancer, and diabetes (Bundschuh et al., 2022; Genchi et al., 2022). It is estimated that more than 200 million people in at least 105 countries are at potential risk of As poisoning due to continued ingestion of As contaminated water (Podgorski and Berg, 2020). In the US, the As ranks first on the Agency for Toxic Substances and Disease Registry's list of hazardous substances (Bundschuh et al., 2022).

Due to the health problems caused by exposure to As, there is a critical societal need to develop sustainable technologies and management strategies to immobilize or remove As from water. Both Fe(III) (oxyhydr)oxides (Aftabtalab et al., 2022; Chen et al., 2022; Huan et al., 2022; Sowers et al., 2021) and biochar (Lima et al., 2022; Soares et al., 2022; Yang et al., 2021) have been identified as potential low cost, high affinity sorbents for use in water treatment or remediation. Among the Fe(III) (oxyhydr)oxides studied, there is increasing recognition of bacteriogenic Fe(III) (oxyhydr)oxides (BIOS) commonly found in sediments, and natural waters can play an important role in the sorption of several potential inorganic contaminants (Field et al., 2019; Sowers et al., 2017; Whitaker et al., 2018; Whitaker and Duckworth, 2018). The BIOS have important structural differences, such as low crystallinity, high surface area, incorporation of organic matter, and reduced crystalline domain size

(Whitaker et al., 2021), attributes that can result in reactivity and sorption capacity superior to that of synthetic iron (oxyhydr)oxides sorbents.

Biochar is commonly used sorbent because is a sustainable and renewable product with the potential to sorb various organic and inorganic contaminants from soil and natural waters (Cheng et al., 2021). However, biochar also may release low molecular weight organic compounds that are dissolved and/or suspended in water (DOC) (Li et al., 2018; Soares et al., 2022), potentially affect the sorption of inorganic anions (such as arsenate) to Fe(III) (oxyhydr)oxides through competitive sorption. The release capacity and quality of DOC from biochar are mainly related to feedstock and pyrolysis conditions. As compared to high temperature pyrolysis, low pyrolysis temperatures produce biochar with a greater amount of DOC with a larger proportion of humic compounds (Gui et al., 2020).

Despite the potential of BIOS and biochar as As sorbents, no studies have examined the competition of As(V) and DOC from biochar for sorption in BIOS, resulting in a significant gap in our knowledge. A better understanding of the extent of DOC's effect on the sorption of As to BIOS is needed to better understand the potential of these materials in combination as As sorbents, as well as develop improved models of As transport and immobilization in environments where the presence of BIOS is significant. Therefore, the authors' objectives were to: *i)* determine the potential sorption of As(V) in BIOS when there is the presence of DOC from pyrolyzed biochars at different temperatures; and *ii)* identify if the presence of DOC alters the surface complexes formed by As(V) sorbed in BIOS.

7.2. Final Remarks

Our results confirm previous reports that indicate that BIOS is mineralogically similar to synthetic 2-line ferrihydrite. Furthermore, they suggest that the application of DOC to biochar does not change the Fe(III) structure of BIOS but do not exclude the interaction of DOC with the organic phase of BIOS. Furthermore, the K-edge As EXAFS analysis demonstrates that the presence of DOC and BIOS does not reduce As(V) to As(III), indicating that the presence of the oxyanion at circumneutral pH remains in its original oxidation state. The K-edge analysis of As(V) EXAFS reveals preferential As(V) sorption to BIOS via binuclear bidentate surface complexes. The presence of DOC does not alter the binding mechanism of As(V) on the BIOS but reduces the maximum As(V) sorption capacity, possibly by competitive adsorption of DOC and blocking the sorption sites. Additionally, the pyrolysis temperature affects only the extent of As(V) sorption, with no differences in the As(V) sorption mechanism or changes in the Fe(III) structure. However, ATR-FTIR analysis coupled with observations from a previous study (Sowers et al., 2019) suggest that the pyrolysis temperature provides distinct organic phases in the solution that prefer to be sorbed on the BIOS surface and thus affect the sorption of As(V).

The application of biochar for water and effluent treatment and for environmental remediation has increased in recent years due to the physicochemical properties of biochar and its advantages over traditional techniques such as ion exchange, membrane separation, chemical precipitation, which are

techniques that present high cost and inevitable generation of chemical residue. Our study shows minimal antagonistic interactions between biochar DOC and BIOS, suggesting biochar and BIOS could be used together in designed remediation or water treatment systems. Additionally, our study showed that the Fe(III) biominerals can, therefore, even under conditions of DOC presence, be important regulators of As(V) transport in slow-moving surface waters where the application of biochar may facilitate DOC contact with BIOS. We recommend that future studies seek to quantify the extent of the effects of DOC amount and contact time on the competition with As(V) by sorption in BIOS, in addition to evaluating the degree of As(V) retention through desorption study.

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8. PYROLYSIS TEMPERATURE AND BIOCHAR REDOX ACTIVITY ON ARSENIC AVAILABILITY AND SPECIATION IN A SEDIMENT

Abstract

Biochar has significant potential to serve as a globally applicable material for water and soil remediation. Its effectiveness depends on feedstock, pyrolysis temperature, and environmental conditions. Biochar is susceptible to natural aging and reoxidation processes caused by changes in soil or sediment moisture, which can alter its electrochemical properties and redox reactions with contaminants such as arsenic (As). In this study, we investigated the effect of pyrolysis temperature and biochar application on the release and transformation of As in sediments subjected to redox fluctuation. Biochar application and pyrolysis temperature played an important role in As species availability, while the content of dissolved organic carbon content and the biochar quality affected As methylation. The redox cycle was fundamental in the availability and mobility of As in the sediment since the redox variations increased the As content in the solution by seven times. The extra supply of carbon in the sediment reduced As availability after reoxidation of the surface of the biochar and proved to be an important mechanism in determining the mobility of organic As species.

Keywords: Arsenic methylation, Spatial variability, XPS, TOF-SIMS, DMA, MMA

8.1. Introduction

The contamination of soils, sediments, and water with potentially toxic elements (PTEs) has become a serious global environmental, agricultural, and public health problem (FAO and UNEP, 2021). Among PTEs, arsenic (As) has been highlighted due to its cytotoxic, genotoxic, and mutagenic effects on human health, such as increased risk of kidney, skin, lung, and bladder cancer (Liu et al., 2011). It was estimated that more than 200 million people in at least 105 countries were at potential risk of As poisoning in 2020 due to continued ingestion of As-contaminated water (Podgorski and Berg, 2020).

The risk of As contamination increases when a portion of the concentration of this element is present in mobile forms (El-Naggar et al., 2019) in soil and sediment. This mobilization is dynamically affected by biogeochemical conditions of the environment, such as reducing-oxidizing (redox) conditions in wetland ecosystems where the fluctuation of the semi-reaction potential (Eh) can play a key role in the availability and species of As (Rinklebe et al., 2017).

In general, As is present in the soil as arsenate and arsenite (Yang et al., 2022). The distribution of As species can be affected by redox potential and by the content and species of some elements, such as iron (Fe), nitrogen (N), manganese (Mn), sulfur (S) and carbon (C) (Lemonte et al., 2017; Shaheen et al., 2019). The presence of C in the environment can, directly and indirectly, favor the As availability in the environment. Directly, carbon in the solution can favor the reduction of arsenate to arsenite and compete with As for binding sites in Fe(III) (oxyhydr)oxides (Yanan et al., 2017). On the other hand, the addition of carbon in the environment can indirectly favor microbial metabolic processes responsible for the methylation of As (Zhai et al., 2021) and reduce activity of inorganic As in solution, favoring the displacement of inorganic As from the solid phase to the solution.

Despite the possibility of increasing As availability due to the addition of C in the environment, the application of biochar *in natura* or with chemical modification has been recurrent under aerobic and anaerobic environments as a strategy to immobilize As (Premarathna et al., 2019; Vithanage et al., 2017). Biochar is an ecologically friendly soil and sediment amendment that is used in remediation procedures due to surface complexation mechanisms with functional organic groups, electrostatic interactions, surface co-precipitation, and physical adsorption onto internal pore surfaces (Lyu et al., 2020).

In the environment, biochar can alter the redox reactions and the geochemistry of As, since biochar can increase electron transfer between oxidants and reductants in soils and sediments (Amen et al., 2020). However, little is known about the mobility and speciation of As, in particular organic species, caused by the addition of pyrolyzed biochar at different temperatures in sediment under fluctuating redox conditions.

Our hypothesis is that increasing the pyrolysis temperature could buffer the redox reactions and activity of microorganisms present in the sediment, and thus reduce As availability and methylation. In this study, we quantified the effect of pyrolysis temperature and biochar application on the release and transformation of As in a sediment subjected to redox fluctuation. For this, we combined X-ray photoelectron and time-of-flight secondary ion mass spectroscopic techniques to investigate the chemical state and spatial distribution of chemical elements in the sediment. In addition, we used UV-vis to assess the quality of dissolved organic carbon (DOC) and hydride generation-ICP-MS with cryotrapping to assess the As species in solution.

8.2. Final Remarks

We observed some interesting results: *i)* the effect of biochar application and the pyrolysis temperature in the availability of As species; *ii)* contents of DOC and the quality of the biochar directly affecting As methylation, and *iii)* the modification in the sediment solution induced by the biochar altered the redox conditions of the sediment and the spatial distribution and oxidation state of the elements.

Because of the supply of extra carbon in the sediment, DOC-biochar interaction may be an important, although underestimated, mechanism in guiding the mobility and, subsequently, the bioavailability of contaminants in sediments amended with biochar, especially on the organic species of As.

The redox cycle proved to be fundamental in the availability and mobility of As in the sediment. The redox variations favored the dissolution of As minerals, increasing the As content in solution by seven times when subjected to redox variation. Furthermore, the redox cycle affected the reoxidation of functional groups present on the surface of the biochar, altered the spatial distribution of carbon, and favored the formation of organometallic/mineral complexes.

In the future, the integration of advanced spectroscopic analyzes (scanning transmission X-ray microscopy) and microbiological methods (gene sequencing) will offer deeper information about the organomineral/metallic interaction and the biogeochemical behavior of As in sediments amended with biochar under different redox conditions. Furthermore, we suggest that future studies should been carried out to evaluate the potential fate and cycling of organic As species in environments naturally contaminated with As and amended with biochar.

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9. FINAL REMARKS

The nature of the As and Pb sorption and desorption processes in sediment submitted to biochar application is complex and depends on environmental factors, such as precipitation, aging time, and presence/absence of oxygen. More than one sorption mechanism may be involved in the (i)mobilization of As and Pb when biochar is present. Furthermore, the microorganisms present in the sediment have an important role in the release of inorganic phosphorus and in the biotic reduction of As(V) and Fe(III), possibly indirectly affecting the mobility of As.

Ashes present in the biochar promote an increase in the pH and the consequent precipitation of Pb into $PbCO_3$ and $Pb(OH)_2$, and it is necessary to assess over time whether the pH will remain stable and the Pb immobilization will be effective over time.

The use of biochar as a filter for water with multiple contaminants seems to be an interesting alternative after modification with $FeCl_3$, in which it is possible to increase the speed and immobilization capacity.

The release of DOC from biochar can reduce the As(V) sorption capacity without changing the binding mechanism. Such effectiveness, however, needs to be evaluated under different conditions, such as environments with variable DOC levels and under conditions of possible chemical bond aging.

The use of biochar proved to be effective in the reduction and methylation of As in environments with partial presence of oxygen. However, this occurs only after one oxidation cycle and shows that the oxidation of the biochar surface and/or recrystallization of Fe(III) minerals probably plays an important role as a sink for As or as a buffer for redox reactions.

Finally, the choice of the best pyrolysis temperature should not be based solely on the types of contaminants present in the environment. The effectiveness of contaminant immobilization needs to be addressed based on edaphoclimatic changes as well as the microbial community present in the environment. In this sense, the combination of spectroscopic techniques (XAS, XPS, STXM) with molecular techniques (16S gene sequencing and metagenomics) can lead to future research and bring new information about the behavior of As and Pb in complex environments, such as sediment and soil.