

Use of biochar as a remediation technique for hydrocarbon contaminated soils in Peru

Uso de biocarbón como técnica de remediación de suelos contaminados con hidrocarburos en el Perú

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RESUMEN

En el Perú, la industria de hidrocarburos es de gran importancia económica y energética; sin embargo, trae consigo diversos problemas ambientales, como los derrames de petróleo, los cuales tienen graves consecuencias en los suelos y la biodiversidad de la zona afectada. Existen múltiples métodos que se usan para descontaminar el suelo, pero algunos pueden ser incompatibles con el medioambiente o son muy costosos. Esta es una revisión bibliográfica que da a conocer las propiedades del biocarbón y su uso en suelos contaminados, con especial énfasis en suelos contaminados por hidrocarburos. El biocarbón es el producto de la pirólisis de la materia orgánica, que da como resultado una enmienda porosa que en su superficie lleva diversos radicales libres, los cuales inmovilizan a diversos contaminantes, posibilitando la recuperación de suelos contaminados con hidrocarburos y otros agentes. Además, entre sus propiedades se encuentran la retención de humedad y el aumento del porcentaje de C, H, O y N, lo que mejora la calidad del suelo. Finalmente, el uso del biocarbón se puede asociar a otras técnicas como la fitorremediación o la inmovilización de contaminantes.

Palabras clave: biocarbón, hidrocarburos, inmovilización, contaminación, pirólisis, Perú

ABSTRACT

Peru's hydrocarbon industry is critical in economic and energy terms; however, it is associated with a number of problems, such as oil spills and the resulting grave consequences for soil quality and biodiversity. Several methods exist for the decontamination of soils, some of which are incompatible with the environment or extremely expensive. This bibliographic review addresses the properties of biochar and its use in contaminated soils, with an emphasis on those soils contaminated by hydrocarbons. Biochar is a product made from organic matter that has been subjected to a pyrolysis process, the thermo-chemical conversion of dry organic material that produces biochar, the persistent free radicals of which are effective in pollution control. Biochar captures moisture and increases the percentage of C, H, O and N, thereby contributing to soil quality. Use of biochar can also be combined with other techniques, such as phytoremediation or pollutant immobilization.

Keywords: biochar, hydrocarbons, immobilization, pollution, pyrolysis, Peru



Introduction

The global economy has undergone enormous changes during the 21st century, due principally to industrialization and production activities (Tamayo Pacheco *et al.*, 2015). Consequently, the demand for liquid hydrocarbons has increased, and Peru has been forced to diversify its energy industry, exporting and producing mainly liquefied petroleum gas (LPG) (Gallegos, 2014; Tamayo Pacheco *et al.*, 2015). According to national energy plan projections, this sector is of great importance for the country's future and will contribute 52 % of the nation's energy needs by the year 2025 (Tamayo Pacheco *et al.*, 2015).

Crude oil is obtained from areas where the resource is found in large quantities and which are authorized by the government for extraction through a process involving underground drilling in the form of oil wells (Osinergmin, 2010; Perupetro S. A., 2012). Many of these areas are located in the western Amazon, where the region's greatest biological diversity is also located, across a territory of approximately 668,000 square kilometers, of which more than two-thirds is situated in Peru (Finer *et al.*, 2008). Between 2009 and 2018, more than 1,400 oil wells were drilled in Peru (Perupetro S. A., 2018). Unfortunately, during the same period spills occurred amounting to approximately 25,000 barrels of crude oil in the Peruvian Amazon alone, resulting in multiple adverse effects on surrounding communities and ecosystems, and costing in excess of USD 300 million in environmental damage alone (Mongabay, 2018; Romo, 2017; Sandoval del Aguila, 2008).

When oil is spilled on the ground surface, it produces a hydrophobic layer that inhibits or reduces plant growth and modifies microbial populations, in addition to generating physical and chemical changes in the soil, such as variations in organic matter, changes in structure, and increased density (Martínez and López, 2001; Velásquez, 2017). In Peru, 34 % of the economically active population is engaged in agriculture, and farming is one of the most important economic activities in rural and jungle areas, which are the most affected by spills (Ortiz Guevara *et al.*, 2009; Zegarra and Orihuela, 2005).

The goal of this review was to compile bibliographical information regarding the effectiveness of biochar in the immobilization of hydrocarbons in contaminated soils, and to propose biochar as an effective decontamination method which constitutes a clean alternative for addressing the problem of oil spills in Peru and facilitating the recovery of the flora and fauna of those areas affected. This issue is of particular importance, given that most oil extraction activities are located in the vicinity of protected natural areas. Therefore, this review presents methods for the recovery of such life zones, as well as proposals for the management of organic waste in Peru, through an economically viable product with the potential to return life to soils affected by crude oil spills.

Importance of soils

Soil is a dynamic system in which multiple ongoing physical, chemical and biological processes occur (Martínez Rodríguez, 2017). It is considered a non-renewable natural resource, in which recovery is slow and complex once it has been degraded (FAO, 2015a; INIA Tacuarembó, 2015). This resource is a crucial component of development, since it provides multiple ecosystem services (Burbano-Orjuela, 2016), the most recognized of which are the supply of food and the supporting of human activities. In addition, soils are also a key component in the biogeochemical cycles of several chemical elements, such as sulfur, nitrogen and phosphorus. At the same time, soils capture or retain atmospheric gases, contributing to climate regulation and constituting the largest store of carbon in its gaseous form, which is a greenhouse gas, found in nature (Burbano-Orjuela, 2016; GLOBE, 2005; M. López, 2016).

Soils are also a reservoir of biodiversity, ranging from microorganisms to higher organisms, making them essential in ensuring ecosystem services (FAO, 2015b, 2017). Furthermore, proper soil management contributes to economic growth, sustainable agriculture and food security, thereby helping to combat poverty and climate change, while improving biodiversity conservation and access to water (FAO, 2015b).

Soil contamination

Unfortunately, soil pollution is a growing problem, resulting in the partial or total loss of soil productivity; one of the principal causes is the increase in the concentration of toxic substances that exceed the buffering capacity of soils (FAO, 2018; Ortiz *et al.*, 2007). Although pollutants can be naturally occurring, most of are of anthropogenic origin, resulting from industrial activity and the production and use of agrochemicals (Rodríguez Eugenio *et al.*, 2019).

Soil contamination can occur in two ways: specific and diffuse (Silva and Correa, 2009). The former occurs in situations where the source of contamination is easily identified in a determined area and is usually related to landfills, spills, mining activities and industry (Rodríguez Eugenio *et al.*, 2019; Silva and Correa, 2009). Diffuse pollution is when pollutants are widely spread, making it challenging to identify the source, although in affected areas agriculture, flooding and atmospheric pollutants are usually the primary sources (FAO, 2016; Rodríguez Eugenio *et al.*, 2019).

In the industrial energy sectors, the most polluting activities are mining, manufacturing, metal processing, chemical industries and installations, and waste management (Rodríguez Eugenio *et al.*, 2019). Contaminated soils result in physical, chemical and biological limitations on the development of nature and human health. (Soraya Puga, 2006). Currently, pollution of anthropogenic origin is considered one of the most

critical threats to soil function worldwide (Rodriguez Eugenio *et al.*, 2019).

Hydrocarbon contaminated soils: current situation

In Peru, hydrocarbon soil contamination has been associated with exploration, extraction and exploitation processes since oil industry activities began in the north of the country 150 years ago, and later in the northern jungle region, some 50 years ago (Rangel, 2020). In northern Peru, between 2013 and 2017, a total of 3750 environmental incidents involving the hydrocarbon sector were identified, of which 57 % involved contaminated soils. Of these, 86 % occurred in farmed areas, 10 % in conservation and ecological protection areas, and 4 % in urban or industrial areas (Mandujano Reyes, 2019). In the northern jungle of Peru, soil contamination through hydrocarbons has reached critical levels, with the most affected areas being those adjacent to «Lot 8» and «Lot 192», which have contaminated the basins of the Pastaza, Corrientes and Tigre rivers, as well as the Trompeteros district, producing environmental damage from 2014 to 2015, and affecting from 2011 to 2019 an area of approximately 45.6 hectares (Angeles Mendiola, 2018; Hinojosa, 2020a).

One problem that makes the situation more complicated is that the Peruvian Ministry of Energy and Mines (MINEM) has been unable to identify those responsible for the spills. (Hinojosa, 2020b). The evading of responsibility by well-known companies also occurs, as in the case of the oil company Pluspetrol, which despite owning the biggest oil field in the country and causing significant damage to the Peruvian jungle, has refused to pay for damage caused six years ago (Meneses, 2020). According to the Peruvian Environmental Assessment and Enforcement Agency (OEFA), between 2013 and January 2020 a total of 3448 sites were impacted throughout the country, and in the province of Loreto alone the estimated cost for the remediation of 632 impacted sites was USD 183 million (Hinojosa, 2020b).

Currently, the situation is still not under control; between March and August 2020 there were 14 oil spills in Peru (Hinojosa, 2020a). Such incidents seriously affect communities, their social and economic activities, and the surrounding natural environment (Hinojosa, 2020a).

Methods for soil remediation

Remediation means reducing the concentration of pollutants, making soils suitable for use again without producing environmental damage (Demcak and Balintova, 2016; Finer *et al.*, 2008).

Soil recovery techniques can be categorized as *in-situ* and *ex-situ*, with the former employing a set of methods that treat the soil in the area where the contamination occurred, while the latter technique involves methods that require excavation and removal of soil for treatment

outside the affected area (Khan *et al.*, 2018). The methods used include physicochemical, thermal and biological processes (Hurtado, 2011). In order to select the method to be used, the area requiring intervention is first assessed through the examining and collecting of relevant data regarding pollutants (Demcak and Balintova, 2016). Economic considerations are also decisive, and the methods chosen must be both efficient and economically viable, which is why, in recent decades, bioremediation techniques have generated considerable interest and gained importance (Megharaj and Naidu; 2017).

Bioremediation is a biological decontamination method employing living organisms and microorganisms, or their biological derivatives (Abatenh *et al.*; 2017). Techniques must be selected which are best suited to the situation encountered in the contaminated area. One method is biostimulation, which consists of adding organic substrates to provide nutrients to (micro)organisms, thereby increasing their metabolic activity and stimulating the degradation of the pollutant (Megharaj and Naidu, 2017). An example of biostimulation is remediation using biochar, which has been shown to be an effective source of nutrients for microorganisms, making it an effective method for the remediation of soils containing a variety of pollutants, including hydrocarbons (Zhang *et al.*, 2020).

Biochar

Biochar is a material made from organic waste or biomass, usually destined for agricultural use (Escalante *et al.*, 2016). For its production, the organic matter must pass through a thermochemical process such as pyrolysis, gasification or hydrothermal carbonization (Cha *et al.*, 2016). Of these, the process most commonly employed is pyrolysis, which consists of subjecting organic matter to high temperatures (greater than 300°C) in the absence of oxygen (Duku *et al.*, 2011).

The pyrolysis process may be slow or fast. The main differences between these two procedures are the parameters temperature and time: the slower process is conducted at temperatures of around 300 °C to 400 °C and may last for several minutes or hours, while the faster process occurs at a temperature of around 500 °C and is continued for only a few seconds (Solís, 2016). During this process, the cellulose, hemicellulose, and lignin of the organic matter are decomposed, resulting in a set of crystalline graphene sheets and amorphous aromatic structures associated with carbon-oxygen or carbon-hydrogen bonds (CO and CH), and known as biochar (Escalante *et al.*, 2016).

Properties of biochar

In terms of its physical and chemical properties, biochar is composed of black organic carbon, which contains mainly carbon, followed by hydrogen, oxygen, ash and, as trace elements, principally nitrogen and sulfur



(Abdul *et al.*, 2017; Cha *et al.*, 2016). Biochar is usually alkaline (Olmo, 2016).

Due to its high porosity, it is a material with a large surface area, with macropores derived from organic matter and micropores that are a product of the thermochemical process employed in its production (Abdul *et al.*, 2017; Escalante *et al.*, 2016). Other important characteristics include its density, electrical conductivity, the functional groups on its surface, and its moisture retention capacity (C. Zhang *et al.*, 2018).

However, the properties of biochar are mostly dependent upon the type of organic matter used and the temperature employed during the production process (Table 1).

Table 1. Variation in the characteristics of biochar processed at different temperatures.

Properties	Temperature			
	300 °C	400 °C	500 °C	700 °C
Yield (%)	72.30 %	63.70 %	57.90 %	52.50 %
pH	5.3	8.2	8.9	12.0
Volatile material (%)	33.80 %	25.70 %	20.70 %	15.80 %
Humidity (%)	4.30 %	4.20 %	3.50 %	3.40 %
C (%)	44.75 %	55.44 %	62.42 %	20.40 %
H (%)	3.98 %	2.34 %	1.69 %	0.51 %
N (%)	1.81 %	1.81 %	1.64 %	1.20 %
O (%)	19.37 %	15.06 %	3.68 %	0 %
Surface m ² g ⁻¹	2.90	4.80	175.40	175.40

References: Hossain *et al.*, 2011; Gaskin *et al.*, 2008; Kim *et al.*, 2012; Xiao *et al.*, 2018.

Effects of biochar on soils

The size and diameter of biochar pores constitute a suitable habitat for microorganisms (Lehmann and Joseph, 2009). In addition, Gomez *et al.* (2014) have demonstrated that the concentration of amendment used is directly proportional to bacteria concentration, mostly Gram-negative; however, the increase in microbiota is dependent upon the material used to make the biochar (Steinbeiss *et al.*, 2009).

Biochar increases water adsorption capacity in soils, thereby increasing the retention of liquids and relative humidity, and improving water infiltration (Balta, 2019; Hardie *et al.*, 2014; López *et al.*, 2013; Novak *et al.*, 2009). Another effect is increased soil porosity, which improves real density and apparent density, through the number of particles that occupy a given volume of soil, optimizing soil structure and increasing the mean particle diameter, which increases the weight per soil particle and therefore helps to prevent erosion (Ferreira and Sellés, 2013; Jien and Wang, 2013; López *et al.*, 2013; Ouyang *et al.*, 2013; UNLP, 2019).

Biochar increases the cation exchange capacity (CEC) of soil, which means that it improves its potential to retain and transfer cations from nutrients (Ayala Villa, 2016). Similarly, the surface of biochar contains functional, oxygenated and nitrogenous groups, free radicals, and organic groups that possess ionic charges, such as carbonyl, carboxyl, hydroxyl and quinone (Balta, 2019; Uchimiya *et al.*, 2010; Xiao *et al.*, 2018; Zimmerman, 2010). These characteristics influence the adsorption capacity of biochar, which allows various organic and inorganic elements to adhere to its surface (Durán, 2017).

The aforementioned attributes contribute to the enhancement of soil quality and fertility, thereby improving the nutrient cycle and increasing atmospheric carbon capture capacity (Jing *et al.*, 2019). This also has an effect on crops, which receive additional nutrients from biochar, resulting in increased soil yield (Mbah *et al.*, 2017).

Effects of biochar on contaminated soils

The properties of biochar make it a suitable material for the treatment of contaminated soils; for example, it has been shown that biochar immobilizes heavy metals in their ionic forms, including Cd²⁺, Cu²⁺, Pb²⁺ and Zn²⁺, reducing their bioavailability and preventing phytotoxicity in plants (Bian *et al.*, 2014; Park *et al.*, 2011; Yang *et al.*, 2016). Furthermore, Jing *et al.* (2019) have shown that biochar reduces the Pb²⁺ and Cd²⁺ concentration in surface soils and is effective in the immobilization of these metals in subsoils. This property is a result of the negatively charged surface, which generates an electrostatic attraction (Patra *et al.*, 2017).

Soils are also polluted by pesticides, which can also be immobilized through the use of biochar (Liu *et al.*, 2018). Biochar is one of the most efficient sorbents of most pesticides, including Fluometuron, Diuron and Aminocyclopyrachlor, among others present in soils (Safaei Khorram *et al.*, 2016). Biochar also stimulates the biodegradation of pesticides. This is due to two main factors: the sorption effect of the pollutant, a product of the porosity and charged surface of the biochar; and high microbial stimulation, which increases the biological degradation of the pollutant (Liu *et al.*, 2018).

The porosity of biochar means that the leaching of some pesticides can also be reduced (Safaei Khorram *et al.*, 2016). Cederlund *et al.* (2017) have shown that biochar has a greater immobilization effect with the pesticides Diron and 2-methyl-4-chlorophenoxyacetic acid (MCPA), while the effect on glyphosate and chlorpyrifos was not significant; they also concluded that the immobilization of pesticides is more efficient when biochar is applied directly to the surface of the soil being treated.

Biochar in soils contaminated with hydrocarbons

The application of biochar in contaminated soils has increased because it functions as a bio-stimulator, stimulating microorganisms to degrade the pollutant *in-situ* (Singh *et al.*, 2020). The main properties of biochar that influence the degradation of hydrocarbons are porosity, water absorption capacity, and pH. Together, these factors convert the surface of each particle of biochar into a source of nutrients with optimal physicochemical characteristics for the harboring of microorganisms capable of degrading the pollutant (Anyika *et al.*, 2015).

Efficiency in the degradation of hydrocarbons is dependent upon the process used in the production of biochar, the size of the particles of the amendment, and the microbial communities found (Zama *et al.*, 2018). For example, if the biochar used is high in salts or volatile material concentrations, microorganisms will not be attracted to it, demonstrating the importance of the production process and temperature (Boonchan *et al.*, 2000). Aziz *et al.* (2020) have shown that biochar has great potential in the stimulation of diesel degradation, causing the pollutant to degrade by up to 70 %. For their part, Galitskaya *et al.* (2016) found that using biochar in the early stages of bioremediation stimulated microbial activity and biomass, concluding that aeration and soil moisture are essential factors in achieving optimal results.

Biochar also reduces the leaching of hydrocarbons in soils. Zand and Grathwohl (2016) confirmed that biochar is a rich sorbent and demonstrated that its particle size is inversely proportional to the hydrocarbon immobilization rate, with greater effectiveness when the powdered amendment is used. According to Sander and Pignatello, the sorption of hydrocarbons through the use of biochar is due to the presence of electron donor-acceptor interactions through π - π radicals on the surface of the amendment and the hydrocarbon; with biochar the donor and hydrocarbon the electron acceptor. According to Fang *et al.* (2014), free radicals adhere to pollutants, with an inverse correlation between the number of free radicals and the concentration of pollutants.

The amendment's effectiveness can be enhanced by adding bacteria such as *Corynebacterium variabile*, obtaining optimal results of up to 78.9 % effectiveness in the reduction of hydrocarbons in soils (H. Zhang *et al.*, 2016). Another method is to combine biochar with the *Eisenia foetida* worm in soil treatment. Both can reduce hydrocarbon bioavailability, but when applied together the reduction of heavy metals concentration found in the pollutant is improved (Gomez-Eyles *et al.*, 2011). Modification of the chemical bases of biochar improves its sorption from 60 % to 751 %, depending on the pollutant (Feng and Zhu, 2018). However, the effect of biochar is not always positive; Han *et al.* (2016) found that biochar inhibited the adsorption of hydrocarbons by ryegrass.

Organic waste for biochar production in Peru

Considering that more than 18,000 tons of waste is generated every day in Peru and only 15 % is recycled, there is much remaining material with the potential to be reused (WWF Peru, 2018). Biochar is an amendment composed of organic matter; in Peru, 54 % of the waste generated is of organic origin. However, only 1 % is used to produce compost, and the rest is discarded (Grandez Barrón, 2019; MINAM, 2019).

In 2019, there were more than 5 million tons of organic waste, and of these, the agricultural sector was the most important source (MINAM, 2019). As of 2018, the main crops in Peru were potatoes, rice, corn, onions and cotton, all of which generate potentially energetic residues (MINAGRI, 2018). Other food products such as sugar cane, yellow corn, cotton brushwood, asparagus brushwood, rice husk and straw, shavings, bagasse and other by-products can also be used to generate high-quality biochar (Assureira Espinoza and Assureira Espinoza, 2014; Marcelo Aldana *et al.*, 2016).

Current use of biochar in Peru

Biochar in Peru is used mainly for soil and crop improvement, displaying considerable effectiveness in accelerating the germination of certain plants, such as *Quararibea cordata*, and increasing yield and profitability in the production of cereals such as corn, thereby contributing to the development of sustainable agriculture in Peru (Andina, 2016; Herrera *et al.*, 2018; Ladd *et al.*, 2017; MINAM, 2015). The popularity of this material is increasing over time, leading to the implementation of biochar processing plants and the addition of the pyrolysis process in some solid waste treatment plants, in order to obtain biochar as a by-product (*El Comercio* newspaper, 2019).

Research conducted in Peru has reported the potential of biochar in the immobilization of heavy metals such as cadmium and copper (Balta, 2019; Nunes Dias *et al.*, 2019). For this reason, the effect of the amendment in the restoration of soils affected by mining tailings is being studied, and positive low-cost results have been obtained in the recovery of biodiversity affected by mining activity in Peru (Cabanillas *et al.*, 2019).

However, studies on the application of biochar in hydrocarbon contaminated soils have been limited in Peru. Most of the studies that have been conducted have been in the form of laboratory-level analysis, showing positive results. For example, Cornejo Escurra (2016) demonstrated that use of the totora plant in combination with biochar reduced by 92.93 % the hydrocarbon present in contaminated soils. Given the significant problem of hydrocarbon contaminated soils in Peru, laboratory and field research are urgently required in order to minimize the impact of the oil industry through the use of biochar,



which has been shown to be an economically viable alternative for the remediation of affected areas.

Conclusions

Soil is one of the most important resources we have, as it performs primary biological functions as a storehouse for nutrients and is a key component of biogeochemical cycles. Unfortunately, Peru has serious soil contamination issues, with the hydrocarbon sector one of the primary sources of contamination.

Multiple methods can be used for soil decontamination, but some methods, such as incineration, can be incompatible with the environment or prohibitively expensive. Biochar is composed of organic residues which are subjected to a pyrolysis process in order to create the amendment. This process gives the biochar properties that enable it to improve soil quality and immobilize pollutants.

The use of biochar to remedy hydrocarbon-contaminated soils has shown positive results in a number of studies due to two main factors: the free

radicals formed on the surface of the amendment; and the biostimulation of soil microorganisms, accelerating pollutant degradation.

The potential for biochar production in Peru is high, since more than 50 % of the waste generated is of organic origin. In addition, biochar can be used to improve soil and crop quality. However, further research will be required regarding the effectiveness of its use in hydrocarbon-contaminated soils, and its application in areas affected by the industry, and therefore in the conservation of Peru's exceptional biodiversity.

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