POLITECNICO DI MILANO
FACOLTÀ DI INGEGNERIA CIVILE E AMBIENTALE
Corso di Laurea Magistrale in Ingegneria per l'Ambiente e il Territorio

BIOCHAR FROM GRAPEVINE CANES: STUDY UPON PHOSPHATE SORPTION AND WATER RETENTION

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Anno Accademico 2015 - 2016

Ho il piacere di dedicare
questo traguardo
alla mia famiglia,
eterno punto di riferimento,
in segno di gratitudine e affetto.

Acknowledgements

This thesis is based on a part of the research carried out at the University of Adelaide, under the supervision of Dr. Philip Kwong, who is gratefully appreciated for the opportunity of join in this project.

The author of this thesis gratefully acknowledges the wonderful person of Mr. Jon Marshall, main developer of the research, for the supervision, the patience and the help given under many aspects.

The author also thanks all those who helped for the realization of this work.

Abstract

Biochar is a carbon solid product by the pyrolysis process of organic matter. It is structurally similar to charcoal, but differ for the purpose: biochar, produced from organic matter, is used as soil improver, waste management strategy and tool for the mitigation of climate change [Read, 2009].

In this work, two promising aspects of biochar produced from grapevine were studied: phosphate sorption and Water Holding Capacity (WHC).

Grapevine cane is an abundant and underutilized biomass that could be pyrolysised for environmental and economic benefits. Based on an industry typical ratio of fruit yield to pruning weight of 1:5-10 [Smart et al., 1991] and the 2015 winegrape yield in Australia of 1.67 million tonnes [Winemakers Federation of Australia, 2015], between 8 and 16 million tonnes of grapevine cane that are pruned in Australian vineyards per annum at present largely go un-utilised. As only 2% of the world's surface area under vine is located in Australia [International Organization of Vine and Wine, 2015], grapevine cane could be 50 times greater. The production of biochar from the cane could form an environmentally sustainable secondary revenue stream for vineyards [Roberts et al., 2009].

Biochars containing calcite produced from grapevine cane were found to be effective low-cost absorbents of phosphate, with a maximum adsorption capacity of 32.9 mg g^{-1}, an order of magnitude higher than unmodified biochars from raw feedstocks. Increasing the pyrolysis temperature increased the adsorption effectiveness at lower phosphate concentrations.

With a calcite adsorption mechanism, the pH may provide a method for the release of phosphate from the spent biochar via application to acidic soil. Surface area had no effect on adsorption capacity due to the narrow size of the pores.

This biochar has potential applications in both wastewater treatment and tile drainage systems as a low-cost high-capacity phosphate absorbent.

The second study focuses on bulk density and WHC of biochar produced from grapevine stalks and pruning. Bulk density was found to reach 0.20 g cm^{-1}, much lower than other biochars and common soils, indicating a high porosity. Application of this biochar into soil could strongly improve the texture resulting in a better soil-plant-atmosphere system.

Studying of contact angle proved that biochar produced at 400ºC has a low wettability due to the possible content of oil that remains at this temperature [Kinney et al., 2012].

WHC results range within 0.47 and 0.79%, reaching the maximum at 700ºC. These values are higher that some other agricultural soils, so these biochars could be mixed into soil in order to reduce water demand and irrigation needed.

Estratto

Il biochar è il prodotto carbonaceo derivante da un processo di pirolisi o di gassificazione della materia organica, per cui è chimicamente simile al più ben noto carbone. Il biochar, così come il processo di produzione, non è una tecnologia nuova, ma antica ed abbondantemente utilizzata nel passato. La necessità di coniare un nuovo termine per un materiale così antico deriva dal suo uso e dalla volontà di sottolineare l'origine rigorosamente vegetale (mentre il carbone può avere origine fossile).

Il biochar è un prodotto di particolare interesse perchè è in grado di affrontare alcune tra le problematiche più critiche della società contemporanea: mitigazione dei cambiamenti climatici, gestione dei rifiuti, economia circolare, bonifica dei terreni, trattamento delle acque, etc. L'interesse verso questo prodotto si è sviluppato negli ultimi decenni e la ricerca lo testimonia: nel 2014 ci sono state più di 900 pubblicazioni riguardanti il biochar, il doppio rispetto il 2013 e 9 volte in più rispetto al 2008.

L'applicazione del biochar in campo agricolo apporta dei benefici in termini di resa agricola e riduzione del fabbisogno idrico e di fertilizzanti. Questi vantaggi sono dovuti alla struttura altamente porosa che trattiene nutrienti, acqua e microorganismi e al miglioramento delle proprietà fisico-chimiche del terreno.

Lo studio eseguito per questa tesi intende fornire nuove conoscenze per valutare la fattibilità di queste ed altre applicazioni. Il lavoro svolto è parte di una ricerca più ampia condotta presso la University of Adelaide che vuole affrontare

alcune tra le principali sfide del South Australia: aumentare la produzione di cibo e di energia con un impatto minimo sull'ambiente e ridurre l'uso di acqua nell'industria vinicola.

Le potature e i raspi dell'industra vinicola sono le materie prime utilizzate per la produzione del biochar oggetto di studio. In questo lavoro sono stati studiati due aspetti promettenti del biochar prodotta da vite: assorbimento di fosfato e la capacità di ritenzione idrica (WHC).

Il potere assorbente del biochar lo rende interessante per l'estrazione di preziosi nutrienti, come i fosfati, dalle soluzioni acquose. Il biochar può quindi essere utilizzato per un circolo virtuoso per il recupero di fosforo: assorbe i fosfati dalle acque reflue e le rilascia nei terreni agricoli come fertilizzante. I benefici che se ne ricaverebbero sono riciclo del fosforo per ridurre la dipendenza dal fosforo minerale (risorsa non rinnovabile), minore fabbisogno di fertilizzante e minore eutrofizzazione delle acque di scarico. Per poter dar credito a questa applicazione, è necessario studiare i meccanismi di adsorbimento e desorbimento del fosforo.

Nel primo lavoro, è stato studiato il potere assorbente del biochar prodotto. La massima capacità di assorbimento del biochar è di 32.9 mg/g, un ordine di grandezza maggiore rispetto al biochar prodotto da altro materiale non trattato. Questo risultato non inaspettato è dovuto all'elevata concentrazione di calcite nelle potature di vite (e quindi nel biochar risultante), sul quale viene assorbito il fosforo secondo il meccanismo ipotizzato da Karageorgiou et al (2007). Questo meccanismo è governato dal pH della soluzione acquosa, quindi può essere sfruttato anche per il rilascio di fosforo in ambienti acidi e neutri (come alcuni suoli agricoli), ma questo aspetto richiede ulteriori studi.

Il rateo di rimozione del fosforo è superiore al 99.5% per concentrazioni iniziali fino a $120\,\mathrm{mgPO_4/L}$. Il biochar prodotto da potature vinicole è quindi un possibile strumento efficace ed economico (non richiede pretrattamenti) per il recupero di fosforo dalle acque. Questa considerazione richiede ulteriori studi e analisi di fattibilità per poter essere confermata.

Il biochar post adsorbimento è ricco di fosforo e potrebbe essere utilizzato come fertilizzante agricolo. E' necessario approfondire il meccanismo di rilascio di fosforo nel suolo e i possibili effetti collaterali.

Nel secondo lavoro, è stata indagata la ritenzione idrica del biochar prodotto dalle potature e dai raspi di vite a diverse temperature.

Si stima che in tutto il mondo solo il 56% dell'acqua d'irrigazione sia effettivamente utilizzata dalle colture, il resto è perso per evaporazione o percolazione. Inoltre nel prossimo futuro aumenterà il fabbisogno idrico in agricoltura a causa dell'aumento demografico, delle variazioni nella dieta e dei cambiamenti climatici. L'alta porosità del biochar permette di trattenere l'acqua nel suolo più a lungo, riducendone le perdite.

Il WHC (Water Holding Capacity) del biochar prodotto tra 500°C e 700°C varia tra 0.47% e 0.79% in funzione della temperatura. In base agli studi dell'angolo di contatto, il biochar prodotto a 400°C si rivela idrofobico. La densità apparente minima è di 0.20 g/cm che indica una elevata porosità.

Questo tipo di biochar, avendo elevata ritenzione idrica e bassa densità apparente, può essere utilizzato per migliorare le qualità fisiche dei terreni, in quanto ne migliora la tessitura del suolo e il sistema suolo-pianta-atmosfera.

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Chapter 1

What is Biochar

"Despite their artistic pretensions,
sophistication, and many accomplishments,
humans owe their existence to a six-inch layer
of topsoil and the fact that it rains."

Anonymous

1.1 Origin of the Name

Biochar is a solid carbonauceus, fine-grained and porous material obtained from the pyrolysis of wood or other organic material. Aesthetically and in the elemental composition, biochar is similar to charcoal, which is perhaps the most ancient industrial technology developed by humankind, used more than thirty thousand years ago [Harris, 1999].

Figure 1.1: Example of Biochar

The necessity of define a new name to distinguish biochar to charcoal is due to the different functions: while charcoal is used as fuel, biochar is produced to store carbon (C) to mitigate climate change, to improve the soil and crop productivity, soil remediation, wastewater treatment, air filtration, as well as other uses. The term 'Bio' emphasizes the biological origin, distinguishing it from charred plastics or other non-biological material. A precise definition has been expressed by the International Biochar Initiative (IBI):

> *Biochar is a solid material obtained from the carbonization thermochemical conversion of biomass in an oxygen-limited environments.*

1.2   Terra Preta de Indio

Biochar was widely used for agricultural purposes in the past by ancient civilizations. Maybe the most well known case is the one of Terra Preta, the Portuguese name used to identify the biochar used by Amazon tribes centuries ago. The first European that explored the Amazon River was Francisco de Orellana during the Pizarro's expedition in Perù in 1541. In his testimony (that strengthened the myth of El Dorado) he sustained that there lived an advanced civilization populating cities with millions of people [De Oviedo et al., 1853].

Figure 1.2: Map of Orellana's route down the Amazon. Source: Athena Review, Vol. 1, No.3

For many years, his claims were dismissed as the following expedition (in 1637)

led by Captain Pedro de Teixeira found no trace of what Orellana had reported [de Acuña et al., 1641]. It is also reasonable that an advanced civilization cannot develop in the middle of the Amazon rainforest, because the typical Amazon soil is not adequately fertile for crops.

Figure 1.3: Left: nutrient-poor Oxisol. Right: Oxisol transformed into fertile Terra Preta. (Photo credit: Julie Major and Bruno Glaser)

The mistery was solved by the American explorer and geologist James Orton in 1870 [Orton, 1870]. Exploring the Amazon Basin, he noted different layers of soil. The common soil, composed of 46% of Oxisol and 29% of Ultisol Ferrasoils [Woods et al., 2003], is grey, acidic and tended to leach. Orton found a deep black, basic and very fertile soil, that covered huge areas and could reach also 2 m in depth (Figure 1.3). He discovered *Terra Preta de Indio* (or Indian Black Earth, or ADE), possibly the oldest and most popular and old example of biochar known, which origin can be traced back to 450 B.C. [Neves et al., 2004].

The properties of Terra Preta allowed abundant crops and flourishing development of the Amazonian tribes. This was the proof that an advanced civilization was possible in the Amazon rainforest. The report of Orellana of a flourishing civilization was correct, but Captain Pedro de Teixeira saw no trace of these civ-

ilizations because his voyage was quite one century later and the population was already decimated by European diseases [Mann, 2005].

1.3   Production Process

Biochar can be produced from any kind of organic matter through several thermal degradation processes: hydrothermal conversion, torrefaction, slow pyrolysis, fast pyrolysis, gasification and various permutation [Lehmann and Joseph, 2012]. If biochar is the main product target, the choice falls on pyrolysis due to its conversion rate of around 35% [Kammen and Lew, 2005].

Pyrolysis is a chemical decomposition process (thermolysis) driven at relative low temperature (around 400-700ºC) in absolute absence of oxygen. If the temperature is higher than 700-800ºC and a non-null amount of amount of oxygen is present, the result is a process of *gasification*. The presence of oxygen affects the amount of char produced: the more oxygen a production unit can exclude, the more biochar it can produce [Lehmann and Joseph, 2012].

Co-products of pyrolysis are gaseous (*syngas*) and liquid (*bio-oil*), both which possess good energetic and economic potential. Syngas is typically used to generate electricity after suitable treatments, and bio-oil can be converted into green gasoline and green diesel [Elliott, 2007]. Product yield is strongly affected by feedstock and operation conditions such as pressure, heat rate and temperature (Figure 1.4).
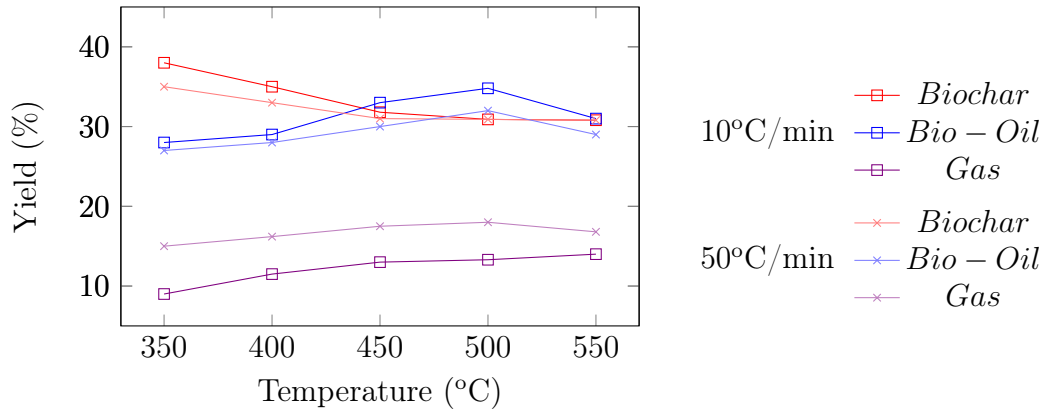
Figure 1.4: Yield of production at various temperature from pyrolysis of olive bagasse with a heating rate of 10ºC/min and 50ºC/min. *Redrawn from [Şensöz et al., 2006]*

During pyrolysis, the first reaction to occur is the dehydration of biomass with the loss of large amounts of Hydrogen and Oxygen. Above 120ºC the degradation of lignocellulose starts through depolymerization which is completed between 250-350ºC with a significant mass loss. The outcome is the production of an amorphous Carbon matrix which is converted into polyaromatic graphene sheets at 350ºC.

During the process, a certain amount of Carbon is lost by volatilization, howevere there is a relative concentration increase of Carbon with the process temperature. If in the feedstock the Carbon content is 40-50%, it can reach 70-80% by weight in the biochar after pyrolysis between 250ºC and 600ºC, and it can reach over 90% through carbonization [Antal and Grønli, 2003]. The mineral content of the feedstock usually remains the same in the biochar due to the difficulty for the elements to volatilize [Laird et al., 2011].

The feedstock composition and process conditions are crucial aspects for the characteristics of the final biochar. The diversity of feedstocks which can be processed by pyrolysis and the large number of design variables make it difficult to identify the optimum pyrolysis technology for a given situation. On the other hand, the large amount of combinations make it possible to obtain the most suitable products (Table 6.1).

Table 1.1: Variants that regulate plant decision

Target	Particle size	Reactor type	Heating rate	Operation mode
Bio-oil		Fixed bed	Slow	Batch
Syngas	Chips	Moving bed	Fast	Continuous
Biochar	Fine particles	Fluidized bed		Intermittent
Heat				

1.3.1   Fast and Slow Pyrolysis

Slow pyrolysis, or conventional carbonization, is the oldest industrial technology developed by humankind [Harris, 1999]. It is based on a low heating rate (2-10 ºC/min) and high residence time (30 min) that lead to high char yields. The slow heating induces the thermal decomposition of lignocellulosic biomass producing approximately equal masses of syngas, bio-oil and biochar.

Fast pyrolysis, on the other hand, is the first choice if the final target is bio-oil. The production can reach a 75% yield, which, after refinement, at least 40% could be converted into green gasoline and green diesel [Jones et al., 2009].

Biochar is also produced through gasification, but in really low amount because the primary product is syngas (up to 85% of yield), a mixture primarily composed by CO, H_2 and CO_2 [Laird et al., 2011]. The process generates considerable heat that can be used to support the process. Gasification is mainly designed to optimize syngas production, so it is rarely take into account as a source of biochar.
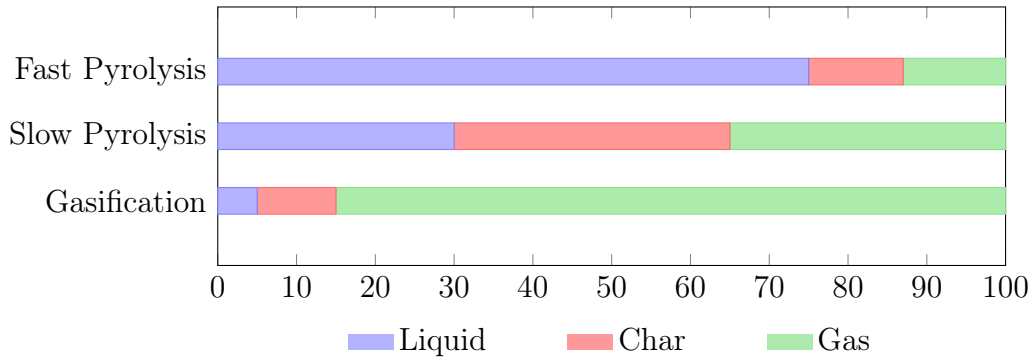
Figure 1.5: Typical production yield (dry basis) for different modes of pyrolysis. The liquid component decreases with temperature with an increase of gas due to the volatilization. Source: [Lehmann and Joseph, 2012]
Fast Pyrolysis: temperature = 500°C, vapor residence time = 1 sec
Slow Pyrolysis: temperature = 500°C, vapor residence time = 5-30 sec
Gasification: temperature > 750°C, vapor residence time = 10-20 sec

1.4 Feedstock

Biochar can theoretically be made from any feedstock with carbon content. Lignocellulosic biomass is an obvious choice because it is the most abundant biological material produced. However it is preferible to use biomass residues (agricultural waste, manures, municipal organic waste, etc.) to solve also the challenge of the waste management.

Not all organic matter is good feedstock: some organic matter can contain undesirable contaminants, and low-quality physical and chemical properties in some feedstocks could lead to low-quality biochars.
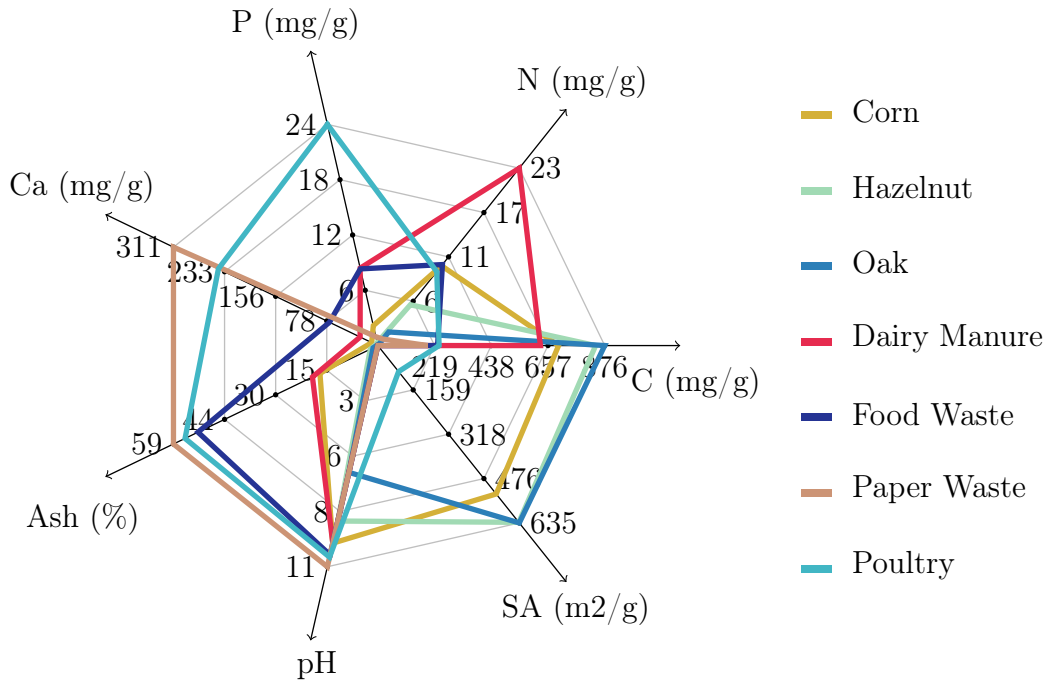
Figure 1.6: Physical properties and elemental components of biochars made from different feedstocks. It is noticeable how different feedstock define greatly the characteristic of the final biochar. SA = Surface Area measured with CO_2. Data source: [Rajkovich et al., 2012]

The choice of the feedstock depends on the desired biochar, due to physical and chemical properties are reflected into the product after the process (Figure 1.6). While a certain percentage of Carbon, Oxygen and Hydrogen is lost in the thermal process, much of the mineral content in the feedstock is retained in the biochar where it is more concentrated. For example, biochar produced from animal litter has higher Phoshprus (P) and Potassium (K) content than the biochar from wood, which as an higher level of Carbon (C). The feedstock can be also treated in order to increase the quality of the final biochar.

1.5   Characterization

Due to high variety of the physical properties and chemical composition of the biochar, it is difficult to identify an elementary characteristic shared by all biochars.

The main component is obviously Carbon, followed by Hydrogen, Oxugen and Nitrogen, but their content range is very wide. In hardwood biochar, the C-content can reach over 90% [Cheng et al., 2008], while it can be lower than 50% in biochars made from rice straw, pea straw or ryegrass [Fernandes and Brooks, 2003, Tsai et al., 2007]. The range is even wider for total Phosphorus (2.7 g kg^{-1} to 480 g kg^{-1}) or total Nitrogen (1.8 g kg^{-1} to 56.4 g kg^{-1}), all with a coefficient variation higher that 100% [Chan et al., 2007, Topoliantz et al., 2005, Lehmann and Joseph, 2012].

Carbon is usually organized in aromatic rings (rings of six C atoms linked together without O or H) arranged in a graphitic structure (stacked and aligned sheets, Figure 1.7).
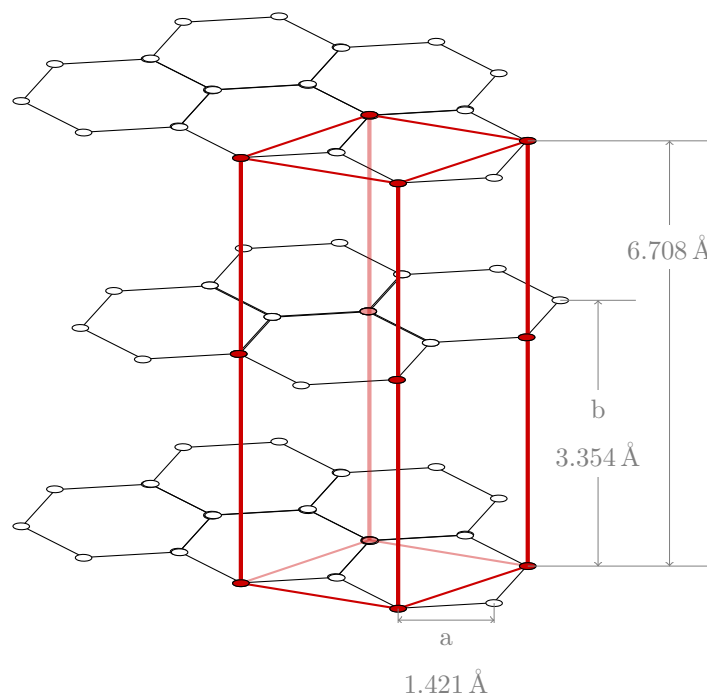
Figure 1.7: Graphite structure

The presence of other elements is strongly dependent on the feedstock, generally the main elemental constituents of biomass minerals are Si, Ca, K, Na and Mg, with smaller amounts of S, P, Fe, Mn and Al [Raveendran et al., 1995] and

some of those remain in the final biochar. For example in the biochar produced from coir pith the K concentration is 10 times than that of the bagasse biochar, while the rice husk biochar has 1000 times the Si concentration of the coconut shell biochar [Raveendran et al., 1995].

Process conditions are another factor that influences the composition, for example elements such as K, Na and Cl, that are present in form on high mobility ions, can start to vaporize at relatively low temperatures [Yu et al., 2005]. Also the amount of ash is controlled by feedstock and process conditions. In woody feedstocks it is lower than 1% by weight, while in grass, straw and grain husks contain up to 25% by weight [Raveendran et al., 1995].

The quality of biochars can be quantified from elemental ratios such as H/C and O/C, that are good indicators to measure the degree of aromatic and maturation of biochar [Baldock and Smernik, 2002]. pH is another highly variable parameter, ranging within 4 and 12 [Lehmann and Joseph, 2012]. This is actually positive, because it allows for a suitable biochar for each application.
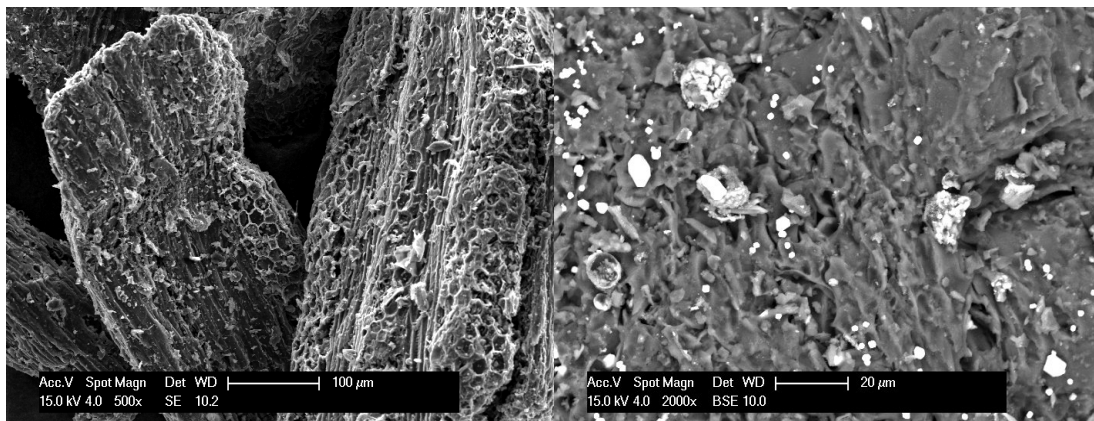
Figure 1.8: SEM image of a grapevine cane derived biochar produced in batch by slow pyrolysis at 400ºC. The high porosity is evident.

A feature shared by all biochars is the porous structure with a high internal surface area. Typically sand has a specific surface area of 0.01-0.1 m^2 g^{-1}, clay of 5-750 m^2 g^{-1} and biochar of 750-1360 m^2 g^{-1}, with an average pore volume of

0.2-0.5 m^3 g^{-1} [Laine et al., 1991]. The presence and size distribution of pores provides a suitable habitat for many microorganisms by protecting them from predation and desiccation [Saito and Marumoto, 2002, Warnock et al., 2007]

1.6 Stability

Thanks to its graphitic structure, biochar is the most stable form of organic matter [Krull et al., 2006], and because of this, it is a great tool for the mitigation of climate change (Section 2.1). While a fraction of C is labile and easily microbially degraded within short periods of time, a larger amount is stable and can remain in the soil for centuries of even millennia.

The range of possible ages is huge, at least for one order of magnitude due to differences in the decomposition processes. Lehmann calculated that the most likely and conservative scenarios under the dry land conditions of Northern Australia had a residence time between 1300 and 2600 years [Lehmann et al., 2008]. Measurements of biochar from coastal temperate rainforest of western Vancouver suggest an averange half-life of more than 6000 years [Preston and Schmidt, 2006].
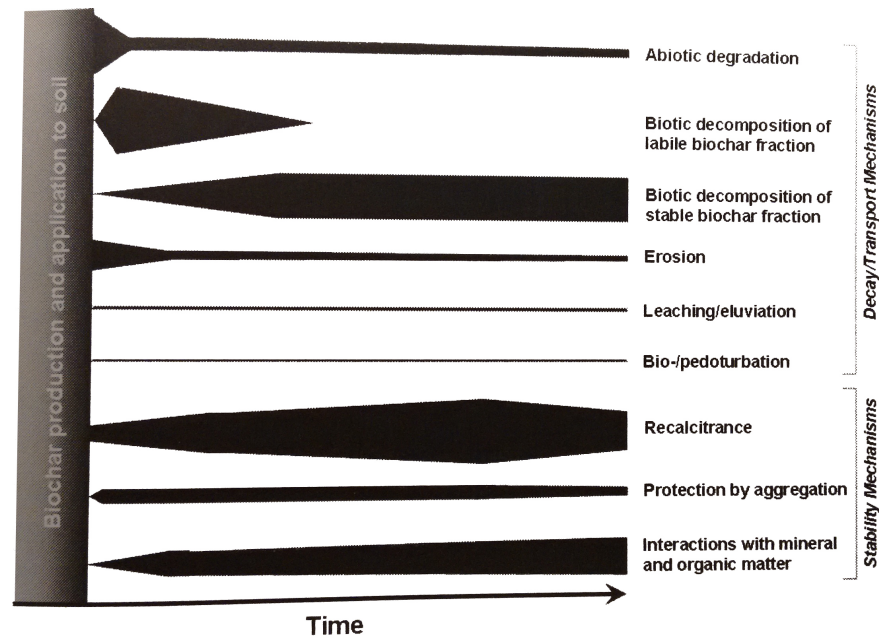
Figure 1.9: Schematic representation of the factors that can influence stability, decay and transportation of biochar, and their proposed importance over time (indicated by the thickness of the bars). Source: [Lehmann and Joseph, 2012]

Factors that affect biochar stability are sundries and their influence varies in time (Figure 1.9). The main processes are the biotic activity and the mineralization, however their contribution is difficult to measure. Biochar decay is a process that is still not thoroughly understood, but there are different studies focused upon it and theere is the real possibility to increase the stability of biochar [Lehmann and Joseph, 2012].

Chapter 2

Applications

"Anche in un fazzoletto da naso può esserci un firmamento,
basta sapercelo vedere."
"Even in a handkerchief can be a firmament,
you have just to know how to see it."
Scherzi di gioventù, Aldo Palazzeschi, 1956

The interest in biochar in the last decades has been driven by its physical and chemical properties, thanks to it is a good tool for solve some of the most important challenges of our time. From soil remediation to the building sector, farming and water treatment, biochar has more than 55 uses [Schmidt, 2012] and the number can only increase in the future.

The most interesting use of biochar is by far the mitigation of climate change, because the graphitic structure stores carbon into soil for centuries. In farming, biochar increases crop production and the fertilty of soil and reduces soil degradation due to its high porosity. Biochar is also a good tool for the water and emission gasses treatment. If biochar is activated, its characteristics improve, increasing the efficiency in the use.
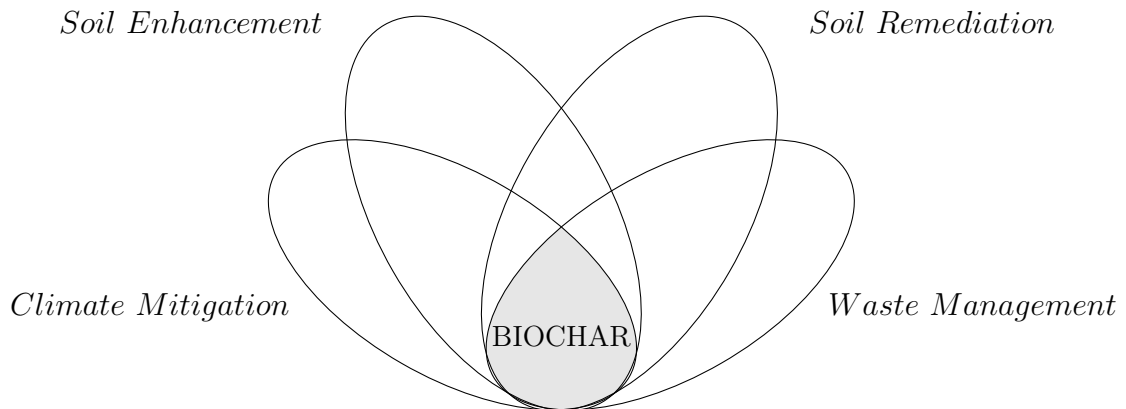
Figure 2.1: Main goals of biochar

2.1 Mitigation of Climate Change

Biochar is mostly composed of stable Carbon (C), organized in graphitic structure. It represent a good strategy to sequestrate C into soil for centuries or even millenia. Storage of C through biochar is an efficient and long-term method to remove Greenhouse Gases (GHGs) from the atmosphere, and then mitigating the climate change [Woolf et al., 2010].

Photosynthesis of plants captures 120 Gt C from atmosphere annually, most of which is emitted into the atmosphere through plant and soil respiration, while the rest is stored as biomass [Lal, 2008]. Under BAU[1] scenarios, this C stored in biomass is released back into the atmosphere as CO_2 or other GHGs through decomposition or burning.

When biomass dies or is slashed, it is easily decomposed by microorganisms releasing carbon back in atmosphere mainly as CO_2 in few years, depending on the composition [Jenkinson and Ayanaba, 1977]. Composting can increase the stability of biomass, but there are evidences that the turnover of C is similar to the un-composted organic matter (within 10 and 20 years [Lynch et al., 2005]).

The most efficient solution is converting biomass in biochar through pyrolysis

---

[1]Business As Usual

in order to obtain the most stable organic structure: graphite. Lehmann (2007) estimates that annually 160Mt C (600Mt CO_2) can be stabilizedby converting the current 'slash-and-burn' practices to 'slash-and-char'.
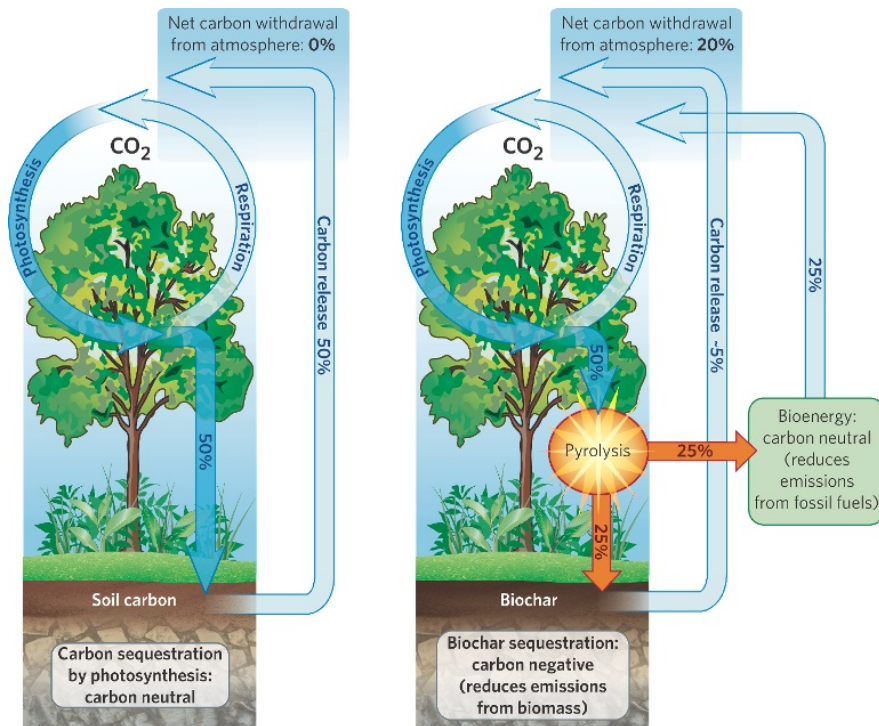
Figure 2.2: Comparision of the carbon cycle between BAU (left) and biochar (right) scenarios. Source: biochar-international.org

Current management practices are said to be *carbon neutral* because they release in atmosphere the same C taken through photosynthesis, without any addition into the C cycle. Biochar, on the other hand, stores C in the soil for a long time, removing matter from C cycle. For this reason biochar is one of the few *carbon negative* technologies.

Incorporating biochar into soil increases the uptake of methane (CH_4) and reduces the release of nitrous oxide (NO_2), two powerful GHGs with a GWP[2] of 34 and 298 respectively [IPCC, 2013], but the mechamism is still not well understood.

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[2]Global Warming Potential. 1 GWP is equal to the effect of 1 ton of CO_2 in 100 years.

The difficult in defining a biochar carbon offset methodology is the reason why carbon stored into biochar still cannot be trade in the Carbon Market.

2.2   Soil Improver

The application of biochar in soil leads to various benefits by changing soil properties. Crop production is widely proved to increase incorporating biochar into soil [Lehmann and Joseph, 2012] and in some cases biomass production increase can reach up to 300%[3] (Table 2.1). The main effects of biochar incorporation in soil are:

- increased water holding capacity;

- increased nutrient retention and cation exchange capacity (CEC);

- increased crop nutrient bioavailability;

- increased microbial activity;

- increased aeration, structure, porosity, and tilth;

- pH amelioration;

- reduced nutrient leaching.

The high reproduction rate of microorganisms [Steiner et al., 2004] explains why biochar accelerates composting and deodorize manure when applied to organic waste [Yoshizawa et al., 2007, Ogawa, 1994]. Biochar reduces the leakage of nutrients and pesticides, saving fertilizers and chemicals with a greater environmental benefit.

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[3]Location: Tropical forest, Brazil. Soil: Oxisol. Crop: Rice. Biochar type: Wood biochar from local kilns. Quantity of biochar: 7.9 tC ha^{-1} [Nehls, 2002]

Table 2.1: Production yields above baseline due to the application of biochar to different crops and soils and in different percentage.

Type of crop	Reference	Location	Type of soil	Treatment (t ha⁻¹)	Yield
Rice	Lugato et al. 2013	Northern Italy	aguic hapludalf	40	**+36%[a]**
Maize	Uzoma et al. 2011	Tottori, Japan	sandy soil	15	**+150%[b]**
Maize	Oguntunde et al. 2004	Ejura, Ghana	-	N/A	**+91%[a]**
Soyabean	Tagoe et al. 2008	Gifu, Japan	-	3,8	**+43%[a]**
Bean	Rondon et al. 2007	Cali, Colombia	clay–loam oxisol	9%	**+46%[a]**
Wheat	Vaccari et al. 2011	Pistoia, Italy	silty loam	30	**+33%[a]**
Radish	Chan et al. 2008	NSW, Australia	chromosol	10	**+42%[a]**
Cabbage	Carter et al. 2013	Siam Reap, Cambodia	sandy acidic	100	**+750%[a]**

[a] compared to unamended soil
[b] compared to using fertilizer alone

The absorbency of biochar can also be used to recover nutrients such a Phosphate, Ammonium and pesticides from wastewater, reducing eutrophication and pollution [Lehmann and Joseph, 2012, Takagi and Yoshida, 2003].

2.3 Soil Remediation

Due to its large surface area and high cation exchange capacity, biochar is able to absorb organic and inorganic contaminants to its surface, reducing pollutant mobility, when amending contaminated soils [Beesley et al., 2011].

Like activated carbons, biochars seems to be able to reduce organic contaminant bioavailability in soils [Zhang et al., 2010, Gomez-Eyles et al., 2011, Yu et al., 2006, Wang et al., 2010]. Some studies are developed to evaluate how

biochar influence polluted water and soil. Beesley et al (2010) reported a PAHs reduction fo 40%, while Rhodes et al (2010) reached a reduction of Phenanthrene of 99% [Rhodes et al., 2010].

In terms of heavy metal remediation, biochar has been considered to be potentially effective [Tang et al., 2013, Fellet et al., 2011, Beesley and Marmiroli, 2011, Hartley et al., 2009, Beesley et al., 2010]. The effect of the incorporation of biochar produced from rice straw on the mobility and bioavailability of Cu(II), Pb(II) and Cd(II) in an Ultisol was investigated by Jiang et al. [Jiang et al., 2012]. The acid extractable Cu(II) and Pb(II) decreased by 19.7–100% and 18.8–77.0%, respectively with the increase of the biochar amendment dose [Jiang et al., 2012].

The application of biochar for soil remediation is still poorly developed and mechanisms involved are unclear. The interaction biochar-contaminant depends on many factors (related to contaminant, soil and biochar), so more studies are required to quantify the effects and to figure out which mechanisms are involved.

2.4   Organic Waste Management

Waste management is one of the contemporary challenges, the zero-waste production (or circular production) is the key for a sustainable civilization and a heavy goal to reach.

In agriculture and in some industrial production, organic waste represents a environmental and economic cost due to its management and the disposal. In a circular production, these by-products can be used as the raw material for the production of biochar, with an obvious economic benefit. In this case, the price of feedstock is negative, without the circular production the biomass would incur a waste disposal fee. The environmental benefits are remarkable: there is less waste in landfills, less energy demand and new material from waste.

Chapter 3

Phosphate Crisis

> *"We may be able to substitute nuclear power for coal,*
> *and plastics for wood, and yeast for meat, and friendliness for isolation;*
> *but for Phosphorus there is neither substitute nor replacement"*
>
> *Life's Bottleneck*, Isaac Asimov, 1959

3.1 Phosphorus Bottleneck

Phosphorus (P) is an essential nutrient for all life forms, an irreplaceable element for flora and fauna cellular growth. Plants take it up in the form of Phosphates through the soil and animals through food consumption. Phosphorus compounds are usually mobility limited, so the global Phosphorus cycle is dominated mainly by river P transport [Oelkers et al., 2008]. This results in the decrease of P amount in cropland because there isn't a natural flux that offsets the loss. The only way to keep crops flourishing is the artificially introduction of Phosphates with fertilizers that permit the continuation of global food production [Driessens and Verbeeck, 1990, Cordell et al., 2009]. Clearly, human livelihood is dependent on the P availability.

The world demand of Phosphate fertilizer is steadily increasing. In 2014, it

was of 42.7 Mt[1] P_2O_5, with a growth rate of 2.4% from 2013. There is expected to be an overall increase of 3.9 Mt P_2O_5 by 2018 [FAO, 2015b]. This increase is driven by food production, and, by extension, by world population growth and the changing of the world's eating habits [Metson et al., 2012]. Other elements like Nitrogen and Potassium are important for the growth of plants, but Nitrogen can be take up from air and Potassium reserves are adequate for several centuries. On the other hand, Phosphorus has to be mined and the available global supplies are running out which could lead to a serious food production crisis worldwide [Vaccari, 2009].
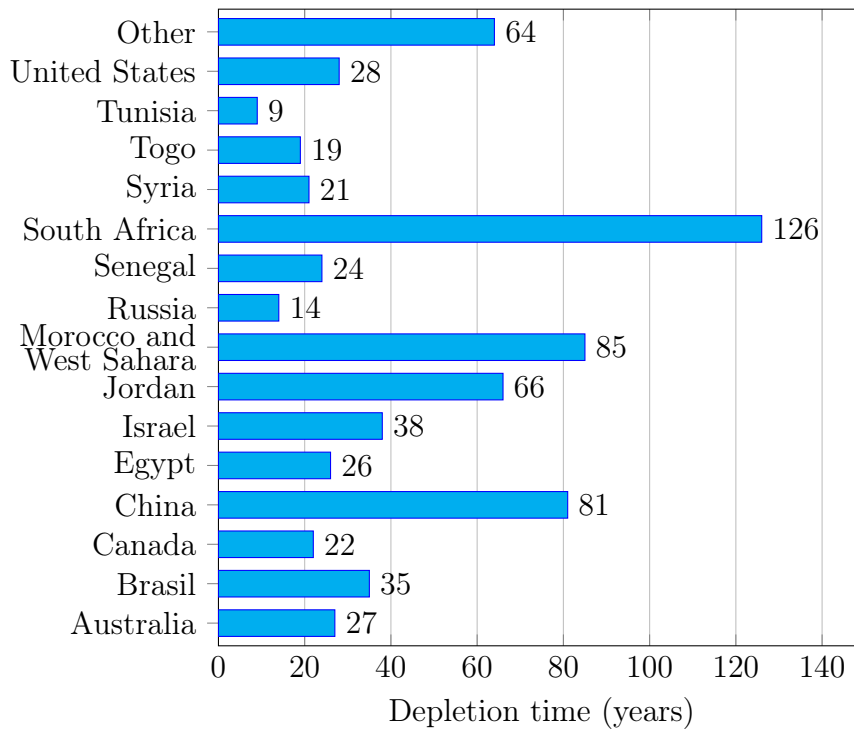
Figure 3.1: Phosphate rock: years of extraction remaining based on current reserves from 2006 using a 2% yearly increase. Source: USGS

Today, Phosphorus is mostly obtained from mined Phosphate rock which is a non-renewable resource. Reserves[2] are limited (Figure 3.1) and the fertilizer

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[1]1 Mt = 1.000.000 tons

[2]That part of an identified resource which could be economically extracted or produced at the time of determination. The term reserves need not signify that extraction facilities are in

industry recognises that the quality of reserves is declining and the cost of extraction, processing and shipping is increasing [Smil, 2000, EcoSanRes, 2003]. Global commercial Phosphate reserves are running out. China is drastically reducing exports to secure domestic supply, US has less than 30 years left of supplies and Western Europe and India are totally dependent on imports [Rosemarin, 2004].

The world mine capacity is difficult to evaluate. According to U.S. Geological Survey it is 67 Gt PR[3] in 2014, while FAO registred 12 Gt PR in 2001 [FAO, 2004]. This difference is due to several factors. First, technological progress and market price makes this value variable. In addiction, there isn't a common definition of "reserves" and "resources" [Edixhoven et al., 2014]. Moreover, most of the data is third-hand because Phosphate mines are predominantly private, so they are difficult to verify and in some cases they are affected by the will to make public the real capacity [Gilbert, 2009].
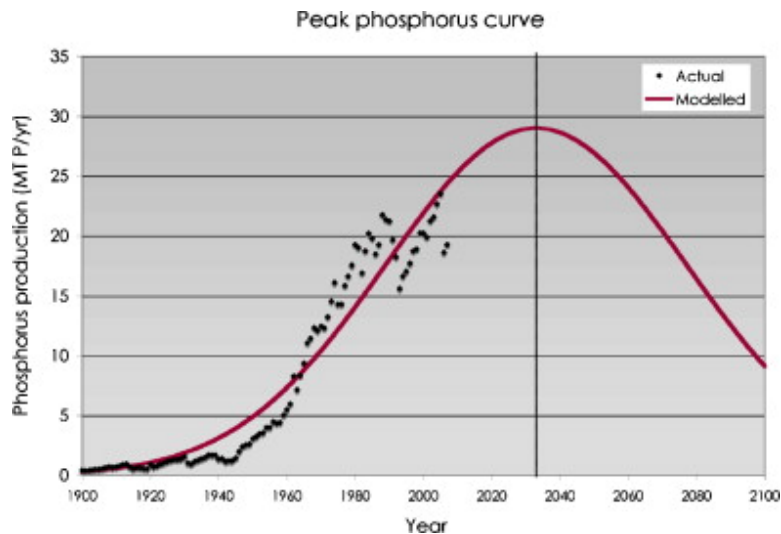
Figure 3.2: Cordell et al (2009) suggests that the peak of Phosphorus production wil be reached before 2040. [Cordell et al., 2009]

The volatility of the size of reserves affects the estimation of depletion and peak Phosphorus[4] prediction: some researchers estimate the depletion within

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place and operative. Reserves include only recoverable materials [Jasinski, 2002].

[3]1 Gt PR = 1 Giga tons of Phosphate Rock

[4]Peak Phosphorus is a concept to describe the point in time at which the maximum global

80-90 years [Vaccari, 2009, Smil, 2000] while other more optimistic researchers suggest up to 100-130 years [Steen, 1998, Smit et al., 2009]. In any case the majority of experts agree that while high-grade reserves range from 50-100 years (Figure 3.2), the critical point could indeed occur decades before these depletion estimates [Cordell et al., 2009].

Upstream of the agricultural chain there is a serious problem with the lack of Phosphorus, downstream of the chain there is the opposite problem. A great amount of the P supplied to soil will be lost into the environment due to rain or other water flows, causing eutrophication in natural waters and environmental degradation. A good way to solve both the issues is to recover the P excess before it is released into the environment.

Phosphorus production rate is reached. Source: Wikipedia `http://en.wikipedia.org/wiki/Peak_phosphorus`

Aim of the Project

In South Australia, agriculture (viticulture in particular) is threatened by climate change [IPCC, 2013, p. 7]. Biochar is a powerful tool to solve problems related to soil and agriculture.

The aim of this project is to give a contribution to the solution of these problems, facing also with two of the seven strategic priorities of South Australia[5]: premium food and wine from our clean environment, unlocking the full potential of South Australia's resources, energy and renewable assets.

This part of the project is divided in two studies:

- The first study is to determine if an unmodified waste feedstock naturally high in calcium as grapevine canes could be used to produce biochar for phosphate adsorption. Following this, the study will identify possible mechanisms and determine if the production temperature of biochar has an effect on phosphate adsorption capacity.

- The second study is to investigate the bulk density and Water Holding Capacity (WHC) of biochar produced at different temperatures using grapevine stalks and prunings. High values of WHC and low of bulk density are desired, so that biochar can be applied to sandy soils to improve physical properties and reduce water demand and effects of droughts.

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[5]http://economic.priorities.sa.gov.au/

Chapter 4

Phosphate Sorption

4.1 Introduction

In literature is widely demonstrated the good adsorbance capacity of biochar for contaminants ranging from heavy metals to organic compounds. Some studies are now focused on the possibility to use biochar for the absorption of Phosphorus (P) from aqueous solutions in order to reduce eutrophication in wastewater and the dependency from P mining, recycling this nonrenewable nutrient.

Biochar can usually adsorb the ammonium cation due to carboxyl groups on the surface of the carbon that carry a negative charge. As the maximum temperature of pyrolysis is increased in the production of biochar, the net charge is reduced because carboxyl groups are removed and positive charges are introduced to the surface of the biochar [Cheng et al., 2008].

Given that P is usually in the form of phosphate that is an anion, most biochars' ability to adsorb P is quite low. This is clearly supported when 13 biochars were produced and tested for phosphate, nitrate and ammonium sorption capacity by Yao et al (2012). Nine showed the ability to adsorb ammonium but none showed significant sorption capacity of nitrate or phosphate, with 8 of the 13 biochars releasing P into solution instead [Yao et al., 2012].

As the properties of the biochar are highly dependant on the feedstock [Sun et al., 2014] a number of studies have looked at modifying the feedstock to increase phosphate adsorption. Iron-treated orange peel powders are used to produce magnetic biochar with a phosphate adsorption capacity of 1.2 mg g^{-1} [Chen et al., 2011]. Biochar produced from anaerobically digesting sugar beet tailings produced a phosphate adsorption capacity of 133 mg g^{-1} compared to a negligible capacity in biochar from the raw feedstock [Yao et al., 2011, Yao et al., 2012].

The biochar produced from the modified feedstock had a lower, but still negative zeta potential, likely reducing the electrostatic repulsion between the char surface and the phosphate cation [Yao et al., 2011]. In addition, the biochar had a higher surface area and significantly higher calcium and magnesium present when compared to raw sugar beet tailings[Yao et al., 2011]. Yao et al (2013) also correlated the level of magnesium to the removal rate of phosphate from solution and suggested that the mechanism involved precipitation of Mg-P salts followed by hydrogen bonding of phosphate to the salts [Yao et al., 2013b].

Jung et al (2015) studied phosphate removal from aqueous solution using 5 types of biochar (oak wood, soybean stover, bamboo wood, maize residue and peanut shell). Peanut shell had the best result with a phosphate capacity of 6.79 mg g^{-1} [Jung et al., 2015]. The biochar had high calcium and showed calcite ($CaCO_3$) present in X-ray diffraction (XRD) spectra. Importantly, as the pH was increased the adsorption capacity increased [Jung et al., 2015] suggesting that the mechanism of phosphate adsorption may be a reaction with calcite on the biochar surface.

According to Karegeorgiu et al (2007) P adsoption could be driven by a mechanism that works at high pH and high calcite content. With this study it is expected to satisfy both the conditions, in order to have a high P adsorbent non engineered biochar. Furthermore, by reversing the equilibrium of the reaction the phosphate may be exchangeable when applied to acidic soils [Karageorgiou et al., 2007].

4.2   Material and Method

4.2.1   Biochar Preparation

The feedstock used was grapevine canes sourced from the Limestone Coast, an Australian Geographical Indication (GI) associated with calcium-rich soils in limestone terrain.

Biochar was prepared by oven drying the feedstock at 105°C for 16 hours prior to pyrolysis. The dried feedstock is heated at 10°C/min in an Argon environment with a flow rate of 1 L/min using a three-zone tubular furnace (Lindberg Blue M, STF 55346C-1).

Feedstock was pyrolyzed at the target temperature of 400, 500, 600 and 700°C, and labelled BC400, BC500, BC600 and BC700 respectively. Once the goal temperature was reached, it was held for 1 hour before cooling overnight in an Argon atmosphere. The resulting biochar was then crushed to 90-500 microns and stored in sealed containers prior to use.

Figure 4.1: Grapevine pruning used in the study.

4.2.2   Characterization

To determine the composition of the feedstock and resulting biochars the Carbon (C), Hydrogen (H) and Nitrogen (N) contents of the samples were analysed in a CHN Elemental Analyzer (Perkin Elmer, 2400 Series II). Oxygen (O) was calculated by difference. Trace elements, including Zinc (Zn), Calcium (Ca),

Magnesium (Mg), Sodium (Na), Potassium (K), Phosphorus (P) and Sulfur (S) were analysed by the Inductively Coupled Plasma Array Optical Emission Spectroscopy (Spectro, CIROS CDD Radial ICP-OES) with nitric/perchloric acid digestion according to the method of Wheal et al (2011).

A Scanning Electron Microscope (Philips, XL-30) was used to determine the morphology and surface compositions of the biochars. Compositional analysis of the surface was conducted concurrently by Energy Dispersive X-ray spectroscopy (EDX).

Surface area was determined with CO_2 adsorption at 273K on the BELSORP-max (Bel Japan, BELSORP-max) using Density Functional Theory (DFT) method. The pore size distribution was also determined using DFT on the CO_2 adsorption/desorption isotherms for biochar.

Zeta potential was determined by a Zetasizer (Malvern Instruments, Nano ZS) with deionized water as the carrier fluid. An average of 20 runs were undertaken for each sample. The sample material used in calculations was carbon (lamp black, graphite) with refractive index of 2.420 and absorption of 0.9000.

The pH was measured by mixing 1 gram of biochar with 25 mL of deionized water. The solution mixture was shaken in an end-over-end shaker for 24h and the solution pH was used as the pH of biochar.

XRD patterns were recorded on the each biochar pre and post adsorption to identify crystalline compounds present before and after the sorption of phosphate using a Multi-purpose Diffractometer (PANalytical, X'Pert Pro) with Fe filtered Co $K\alpha$ 45kV, 55mA and λ of 0.17021 nm radiation, automatic divergence slit, $2°$ anti-scatter slit and fast X'Celerator Si strip detector. The diffraction patterns were recorded in steps of $0.017°$ 2θ with 0.5 seconds per step over the range of 3.975 to $80.01°$. Phase identification was performed on the XRD data using CSIRO in-house software (XPLOT) and HighScore Plus (PANalytical) search/match software.

4.2.3 Phosphate Sorption Procedure

Phosphate solutions were prepared with potassium phosphate monobasic (KH_2PO_4) dissolved in DI water with 0.01 M calcium chloride ($CaCl_2$) as an electrolyte and 1 g/L sodium azide (NaN_3) to inhibit microbial growth.

Based on procedure of Nair et al (1984), 1 gram of biochar was mixed in 50 mL centrifuge tubes with 25 mL of phosphate solutions at concentrations of 120, 245, 370, 490, 735, 860, 980, 1230 and 1470 mg PO_4/L. Phosphate is supplied through the addition of potassium dihydrogen phosphate (KH_2PO_4). The tubes were shaken for 24 h (see Section 4.2.4) at 50 rpm on an end-oven-end shaker at room temperature. Samples were centrifuged at 4000 rpm for 5 minutes before being filtrated with a 0.45 micron nylon filter (membrane solutions).

The ascorbic acid method[1] was used to determinate the phosphate concentrations of the solutions with a UV-Visible Sectrophotometer (Schmadzu UV-vis 1601) at a wavelength of 660 nm. The amount of phosphate sorption was calculated based on the difference between the initial and final solution concentrations. All tests were performed in triplicate, and the average experimental data are reported (Figure 4.10).

4.2.4 Contact Time

In literature, sorption data is often measured after 24 h of mixage because it is known to have reached equilibrium. The following kinetic study was developed to strengthen this thesis.

The kinetic was analyzed for BC600 in a solution of 1470 mg PO_4/L following the same procedure described in section 4.2.3. Measurements were taken after 6, 18, 24, 96 and 168 hours in order to analyze the sorption in the shortest period but also after a long-term period, to avert the possible release. All tests were

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[1]Applied following the method 365.3 approved by National Pollutant Discharge Elimination System (NPDES). `http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2007_07_10_methods_method_365_3.pdf`

performed in triplicate, and the average experimental data are reported (Figure 4.2).
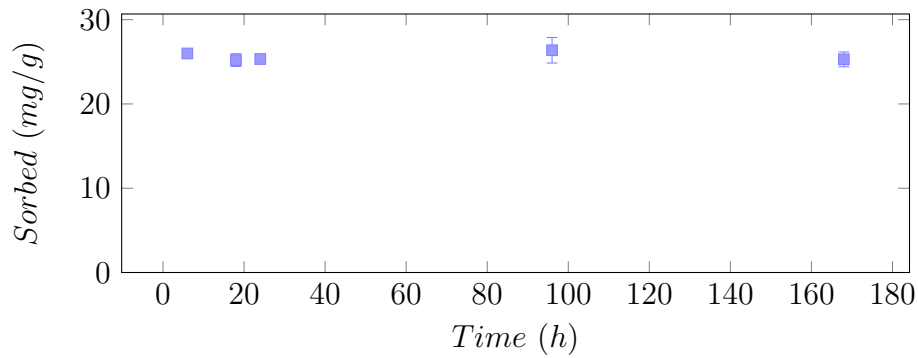
Figure 4.2: Kinetic was measured after 6, 18, 24, 96, 168 h showing that the plateau is quickly reached and held for long time.

The figure 4.2 shows that after 6 h the plateau is already reached. This analysis confirms that 24 h is enough to reach the equilibrium, and that there is no release after this point.

4.3   Biochar Properties

4.3.1   Elemental Analysis

Elemental composition analysis (Figure 4.3) shows that all biochars are carbon-rich which is typical of pyrolyzed biomass [Lehmann and Joseph, 2012], with C content that increases with temperature, ranging between 72 wt% and 80 wt%. The O and H contents of all the samples ranged 17-21 wt% and 2-5 wt%, respectively. These values decrease with temperature increase due to volatilization, resulting in an decreasing H/C ratio, that indicate a better carbon stability. N content is roughly costant around 1.5 wt%, doubling the concentration in the feedstock. Values for each biochar are collected in Table 7.1.

Table 4.1: Biochar yields (dry basis) decrease in relation to temperature.

Sample	BC400	BC500	BC600	BC700
Yield (%)	38.6	32.5	30.2	30.0
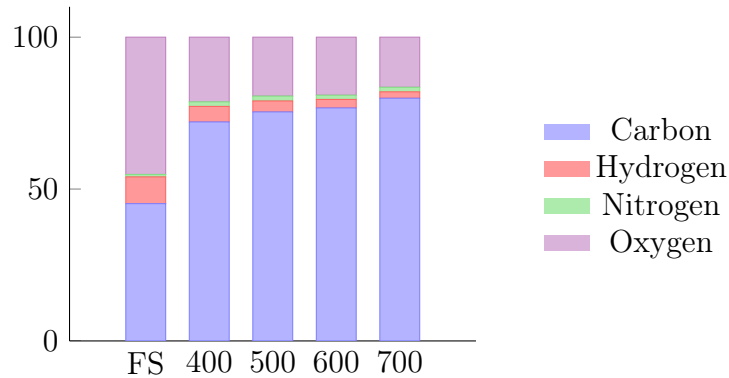
Figure 4.3: Elemental analysis (wt%) of feedstocks and biochars. FS: feedstock. Values are collected in Appendix (Table 7.1).

4.3.2 ICP Results

ICP results show that mineral concentration in biochars is higher than in feedstock because minerals are not apt to volatilization.

The feedstock used was rich in Calcium (0.82 wt%), higher than feedstocks used in other studies [Sun et al., 2014] and this is reflected in the Calcium content of the biochar (up to 2.60 wt%). Table 4.2 summarizes the main elements present.

Table 4.2: IPC-AES analysis wt%

	Zn	Ca	Mg	Na	K	P	S
Feedstock	0.01	0.82	0.14	0.08	0.35	0.11	0.07
BC400	0.01	1.99	0.31	0.29	0.96	0.24	0.09
BC500	0.02	2.40	0.40	0.21	1.15	0.43	0.15
BC600	0.02	2.60	0.46	0.19	1.14	0.36	0.11
BC700	0.01	2.60	0.45	0.17	1.12	0.37	0.11

[a] Co, Mo, Cd, Pb, As and Se all below detection limits that
are respectively 1, 1, 0.3, 3 4 and 8 mg/kg

[b] Fe, Mn, Cu, Ni and Al all below 0.01%

4.3.3   Zeta Potential

Zeta Potentials are all negative and increase as the production temperature increases (Figure 4.4). Given phosphate ion's negative charge, a negative charge on the biochar is likely to hinder adsorption. Zeta Potential increases in relation to temperature ($p = 0.028$), due to the remotion of carboxyl groups, as shown by Chen et al (2008).
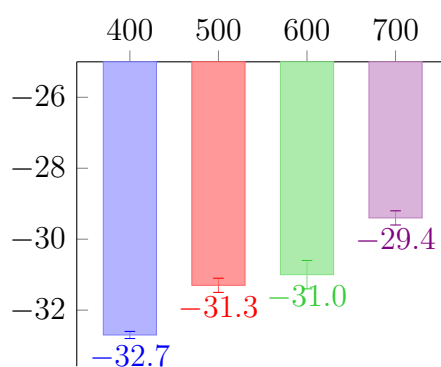
Figure 4.4: Zeta Potential (mV). It increases with temperature thanks to the remotion of carboxyl groups.

4.3.4   pH Values

Biochar is usually alkaline in nature [Lehmann and Joseph, 2012] and in this study pH ranges from 6.8 to 10.2 (Figure 4.5). The correlation between pH and temperature and zeta potential is well known [Lehmann and Joseph, 2012], and in this case p value is 0.021 and 0.012 respectively. Alkalinity is due to a high concentration of base cations (K^+, Ca^{2+}, Mg^{2+} and Na^+) and this could have good benefits if applied to soil.
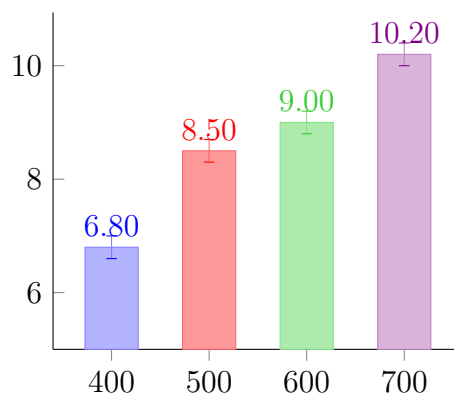
Figure 4.5: pH values of biochars. pH increases with temperature, probably due to Zeta potential variation.

The high pH of these biochars suggests their suitability for use to reduce soil acidity [Yao et al., 2011], by affecting macronutrient and micronutrient availability: biochar improves plant nutrient uptake and availability of N, P, Ca, and K while decreasing free Al in solution [Chan et al., 2008, Yamato et al., 2006].

4.3.5   Surface Area

Using CO_2 adsorption at 273 K, the surface area was measured and it increased with temperature (p = 0.011), doubling from 283 to 566 m^2 g^{-1} (Figure 4.6a). Pore volume doubles reaching 0.143 mL g^{-1} (Figure 4.6b).

Pore structure (pore volume, pore area and specific surface area) improves from BC400 to BC700 (p = 0.015) because volatile material (O and H) are

removed at high temperatures [Ahmad et al., 2012]. These structural analysis results could account for the higher uptake of phosphate due to a high surface area and well-developed mesoporous pores.

(a) CO_2 surface area (m^2 g^{-1})

(b) CO_2 pore volume (mL g^{-1})
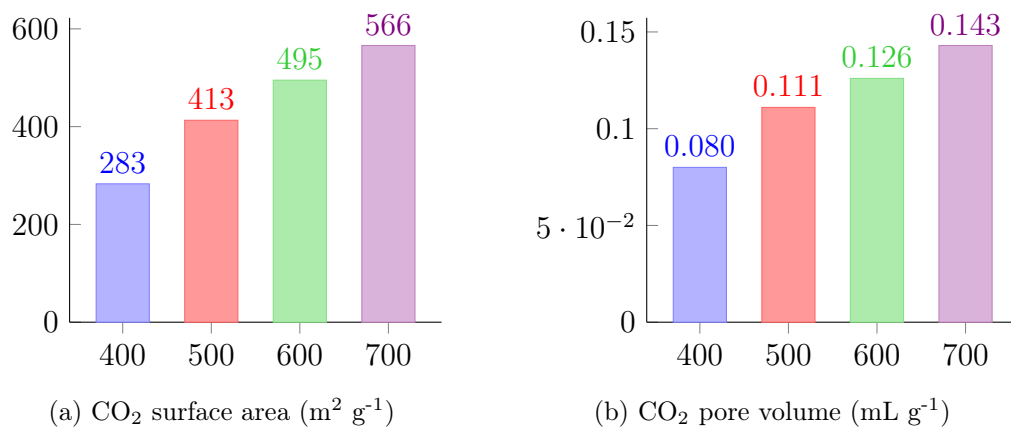
Figure 4.6: Surface measurements

Attempting to measure the surface area with N_2 at 77 K resulted in diffusion difficulties preventing equilibrium and an accurate isotherm. This indicated that the pore size of the biochar is too small for nitrogen (and potentially phosphate ions) to access the internal surface area as most of the pores for all the chars produced are smaller than 0.6 nm (Figure 4.7).
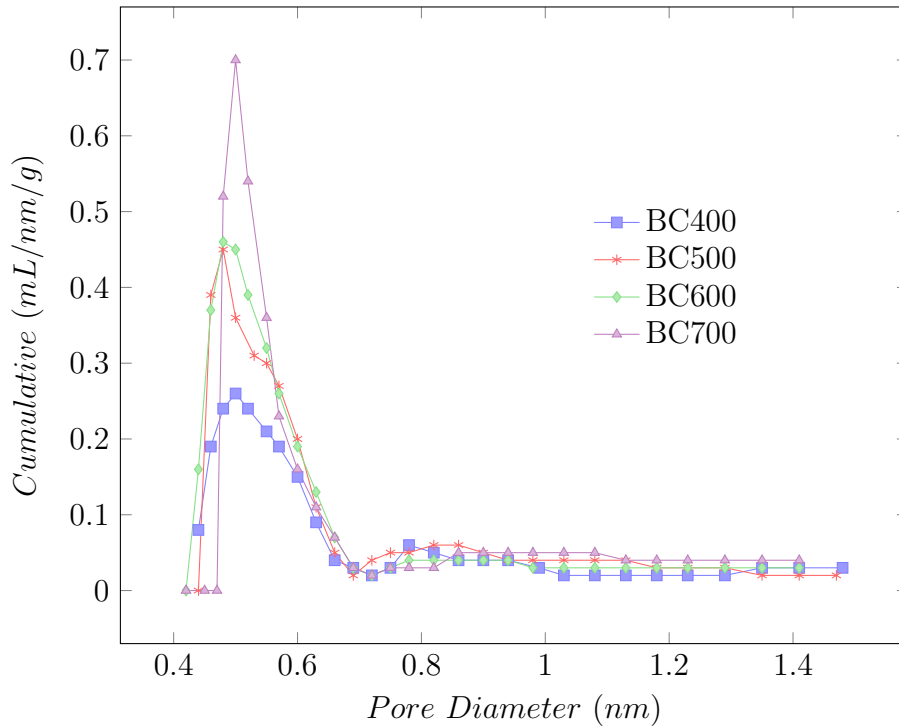
Figure 4.7: Pore Diameter distribution

4.4   Removal Rate

All the biochars produced reveal an high phosphate removal rate, ranging between 75.9% and 99.8% when applied to the solution at 123 mgPO$_4$/L. Removal rates decrease slowly and it is still higher than 10% at 1'230 mgPO$_4$/L (Figure 4.8). The removal rate of the BC700 remains highest up over the range of typical discharge limits, removing 99.87% of P from a 490 mg/L solution compared to the other biochars removal rates between 97.0-98.4%.
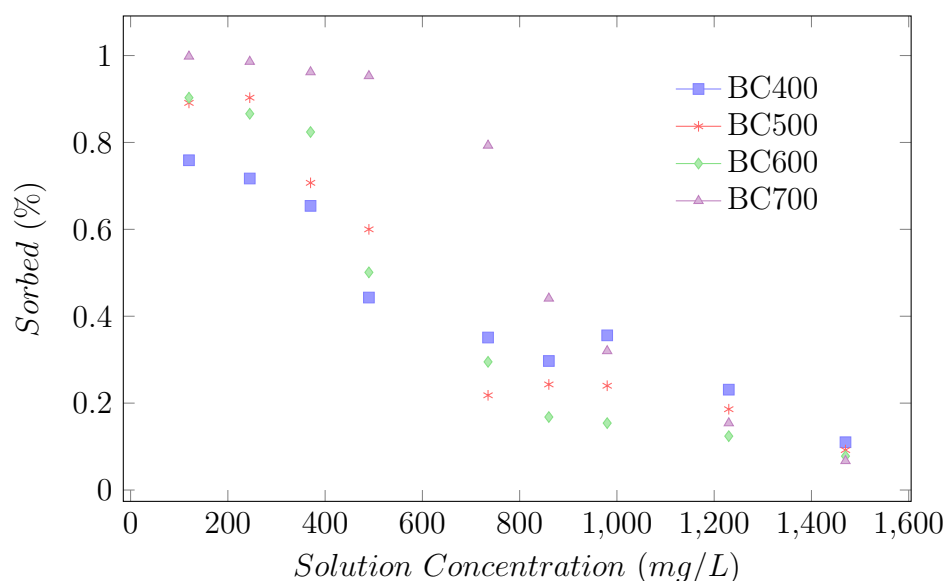
Figure 4.8: Removal rate at different concentrations increases with temperature. Data are collected in Appendix (Table 7.4).

Comparing these results with some similar studies found in literature is evident that grapevine cane biochar is one of the best non-engineered biochars for phosphate removal (Figure 4.9).
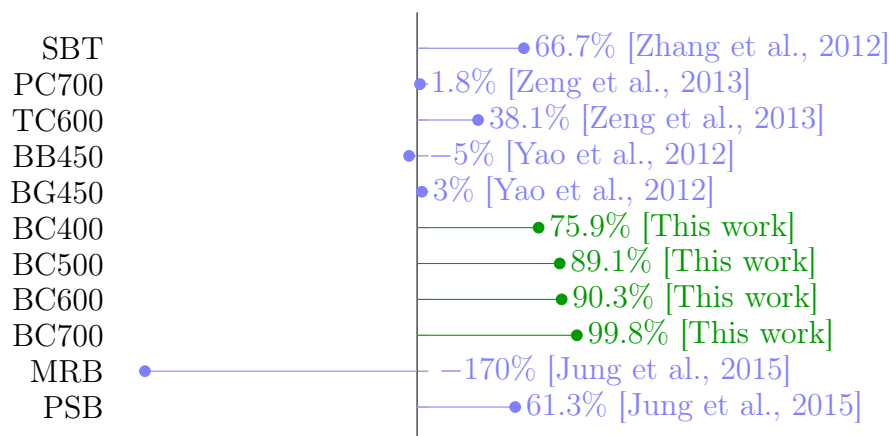
Figure 4.9: Removal rates obtained in this work compared to the best and the worst removal rate of other similar papers. Labels reported are the ones used by their authors to indicate the type of feedstock referenced. SBT: sugar beet tailings; PC700: *Phragmites* sp. 700°C; TC600: *T. dealbata* 600°C; BB450: bamboo 450°C; BG450: sugarcane bagasse 450°C; MRB: maize residue; PSB: peanut shell.

4.5   Adsorption Isotherms

All the biochars prepared have phosphate adsorption capacity greater than 27 mg g^{-1}, suggesting potential as a phosphate adsorbent (Figure 4.10). The most notable difference between each biochar produced at different temperatures was not the maximum adsorption capacity, which appears to be only weakly related to temperature, but rather the increasing steepness of the slope, which increases as temperature increases (Figure 4.11).
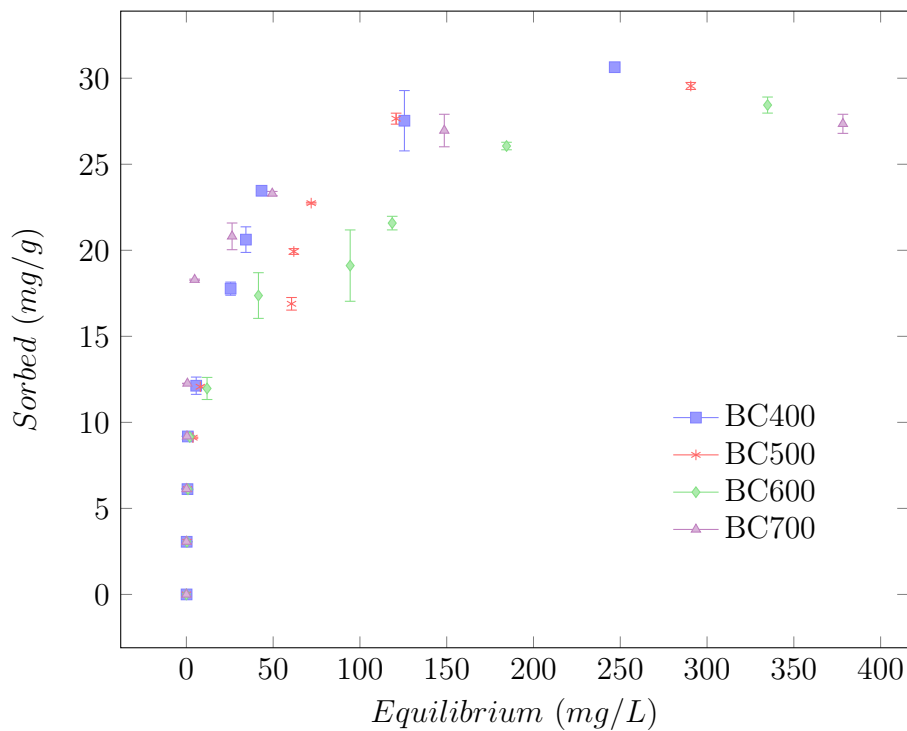
Figure 4.10: Phosphate adsorption data for biochar produced at diffferent temperatures.

The amount of P sorbed is calculated by the difference between the initial and final concentration of P dissolved in the solution. Three commonly used isotherm equations were used to simulate the experimental isotherms.

$$q_{\mathrm{e}} = \frac{KQC_{\mathrm{e}}}{1 + KC_{\mathrm{e}}} \qquad Langmuir \tag{4.1}$$

$$q_{\mathrm{e}} = K_{\mathrm{f}}C_{\mathrm{e}}^{n} \qquad Freundlich \tag{4.2}$$

$$q_{\mathrm{e}} = \frac{K_{\mathrm{lf}}Q_{\mathrm{lf}}C_{\mathrm{e}}^{m}}{1 + K_{\mathrm{lf}}C_{\mathrm{e}}^{m}} \qquad Langmuir - Freundlich \tag{4.3}$$

where:

q_{e} (mg g^{-1}): amount of P sorbed at equilibrium;

C_{e} (mg L^{-1}): equilibrium concentration of the solution;

K (L mg^{-1}): Langmuir bonding term related to interaction energies;

Q (mg g^{-1}): Langmuir maximum capacity;

K_{f} (mg$^{(1-n)}$ L^{n} g^{-1}): Freundlich affinity coefficient;

n (-): Freundlich linearity constant;

K_{lf} (L^{m} mg^{-m}): Langmuir-Freundlich affinity coefficient;

Q_{lf} (mg g^{-1}): Langmuir-Freundlich maximum capacity;

m (-): Langmuir-Freundlich linearity constant.

Best-fit sorption curves for the four different temperatures are plotted in the figure 4.11.
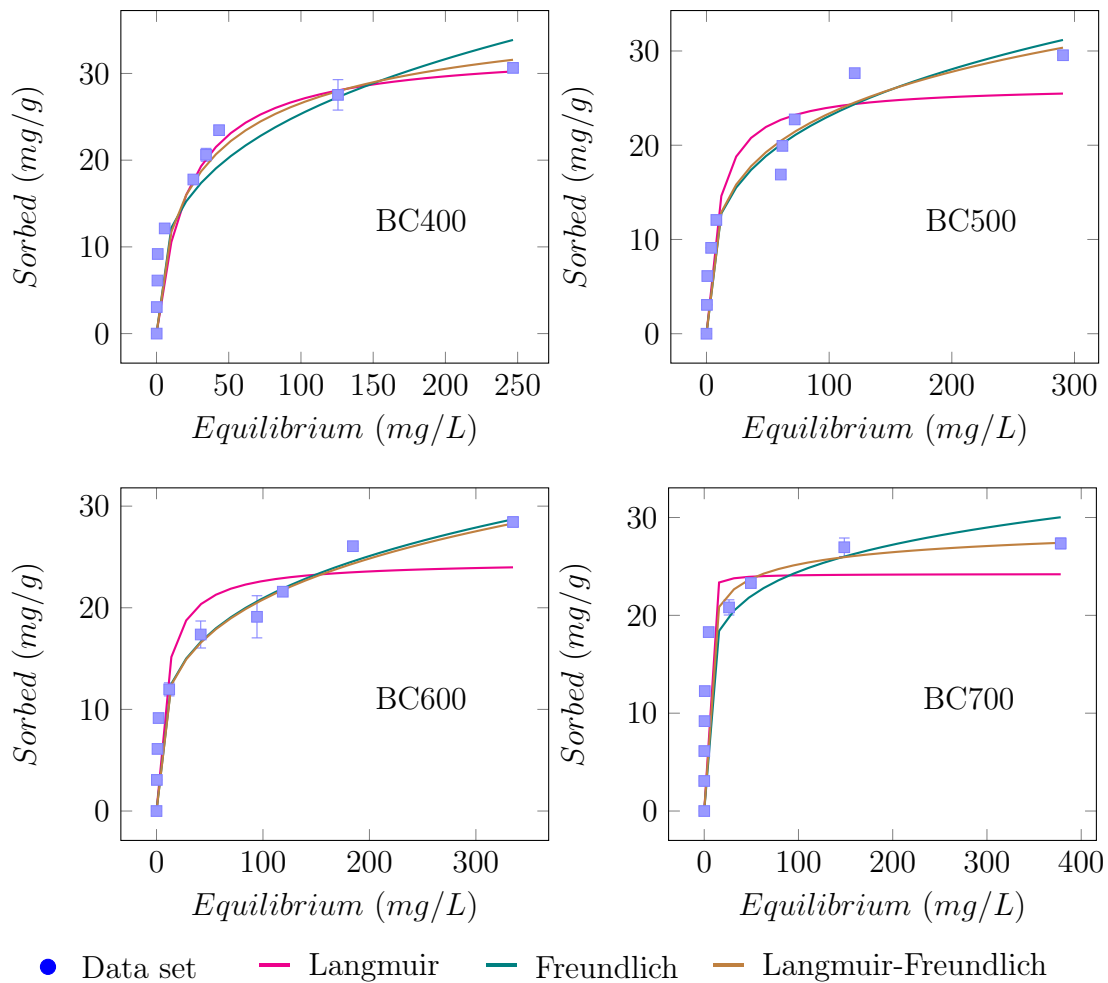
Figure 4.11: Phosphate adsorption isotherm data (dots) and models (lines) for biochar produced at diffferent temperatures.

Best-fit parameters for each model are listed in Table 4.3 and discussed later, with no model correlation less than an R^2 of 0.917. Unsurprisingly, the three parameter Langmuir-Freundlich model consistently fitted each isotherm best, with regression coefficient (R^2) values ranging from 0.972 to 0.997.

Table 4.3: Best-fit parameter values for models of phosphate adsorption

Sample	Parameter 1	Parameter 2	Parameter 3	R^2
		Langmuir		
400°C	K=0.046	Q=32.9	-	0.952
500°C	K=0.103	Q=26.3	-	0.969
600°C	K=0.115	Q=24.6	-	0.969
700°C	K=1.690	Q=24.2	-	0.917
		Freunlich		
400°C	K_f=5.78	n=0.321	-	0.932
500°C	K_f=6.33	n=0.281	-	0.987
600°C	K_f=6.30	n=0.261	-	0.997
700°C	K_f=12.04	n=0.154	-	0.950
		Langmuir-Freunlich		
400°C	K_{lf}=0.084	Q_{lf}=40.7	m=0.675	0.972
500°C	K_{lf}=0.072	Q_{lf}=86.9	m=0.354	0.988
600°C	K_{lf}=0.021	Q_{lf}=297	m=0.277	0.997
700°C	K_{lf}=0.673	Q_{lf}=31.5	m=0.388	0.976

While the difference in maximum adsorption capacity is negligible between each biochar, it can be visible at low concentration. Figure 4.12 show Langmuir-Freundlich curves in the range 0-5 mg/L, encompassing typical discharge limits. In this range BC700 has the highest adsorption capacity that is the double of the other biochars. It is evident by comparing the Freundlich parameter K_f that is the double (Table 4.3). Using the Freundlich-Langmuir model at 1 mg/L equilibrium concentration, the resulting adsorption capacity is 12.7 mg/g using BC700, 6.2 mg/g using BC600 and a mere 3.2 mg/g with BC400.
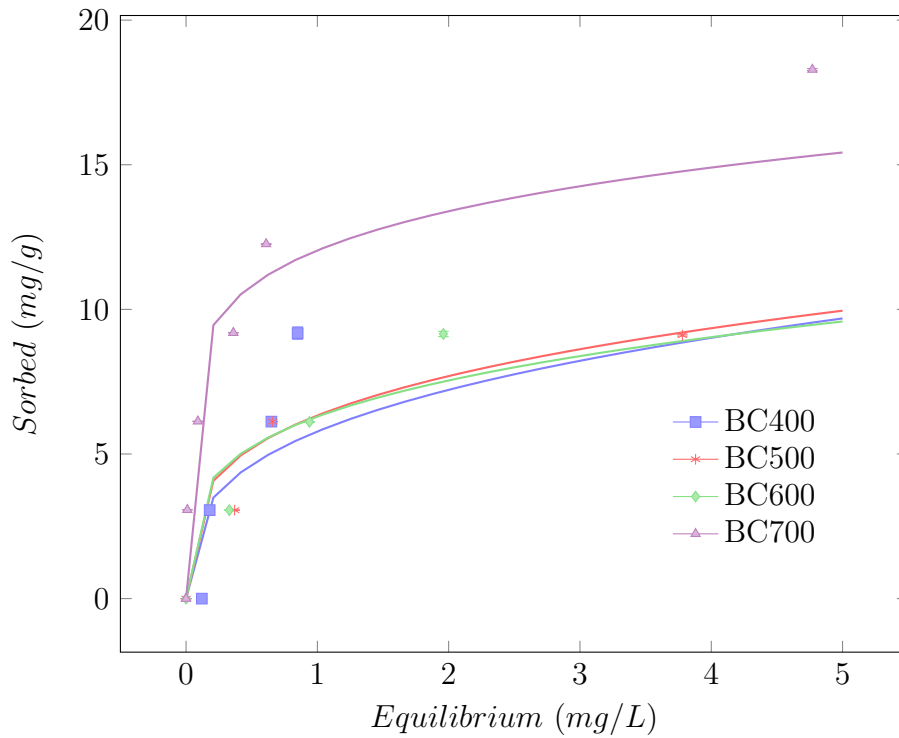
Figure 4.12: Langmuir-Freundlich curves over a equilibrium range of 0-5 mg/L.

4.5.1 Langmuir Model

The Langmuir equation assumes monolayer adsorption with a finite number of identical and equivalent adsorption sites with no steric hindrance or lateral interaction [Foo and Hameed, 2010], while the other models, empirical or semiempirical equations as well, are often used to describe heterogeneous sorption processes [Yao et al., 2013a].

(a) Parameter K (L mg^{-1}) (b) Parameter Q (mg g^{-1})
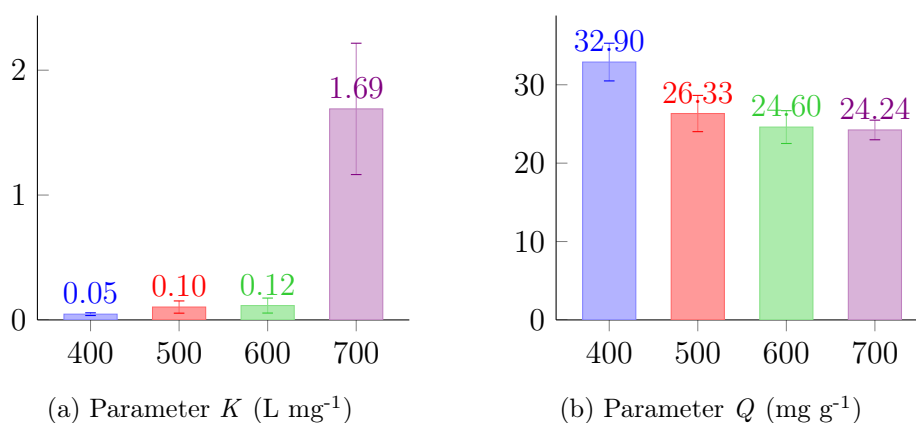
Figure 4.13: Parameters of the Langmuir model

The parameter K indicates the slope of the curve, which corresponds to the availability of the adsorption sites. It seems that it is not affected by temperature, except for BC700, in which is much higher that the others.

The parameter Q indicates the maximum adsorption capacity. The value decreases but it is not a significant change.

4.5.2   Freundlich Model

The Freundlich model can be applied to multilayer adsorption. The slope, indicated with the parameter n, can be used to describe adsorption intensity or surface heterogeneity, as the slope varies from 1 to 0 the surface is more heterogeneous [Foo and Hameed, 2010].

(a) Parameter K_f (mg$^{(1-n)}$ L^n g^{-1})		(b) Parameter n (-)
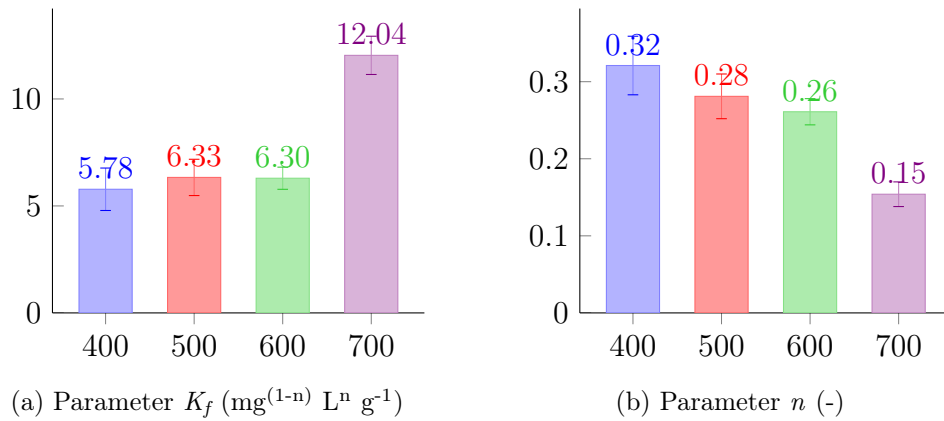
Figure 4.14: Parameters of the Freundlich model

The parameter K_f represents the affinity of the surface. It doubles in BC700, indicating a higher affinity to surface, probably due to the higher zeta potential that reduces sorption inhibition.

The parameter n is well lower than 1, so the distribution is heterogeneous and the phosphate removal is a chemical process, as it might be supposed. The parameter decreases with the temperature, halving from BC400 to BC700.

4.5.3 Langmuir-Freundlich Model

The three parameter Langmuir-Freundlich model is based on both the two-parameter models and often it results in a better fit [Yao et al., 2013a]. As in the Freundlich model, it is used to describe chemisorptions onto heterogeneous surface [Yao et al., 2011].

(a) Parameter K_{lf} (L^m mg^{-m})

(b) Parameter Q_{lf} (mg g^{-1})
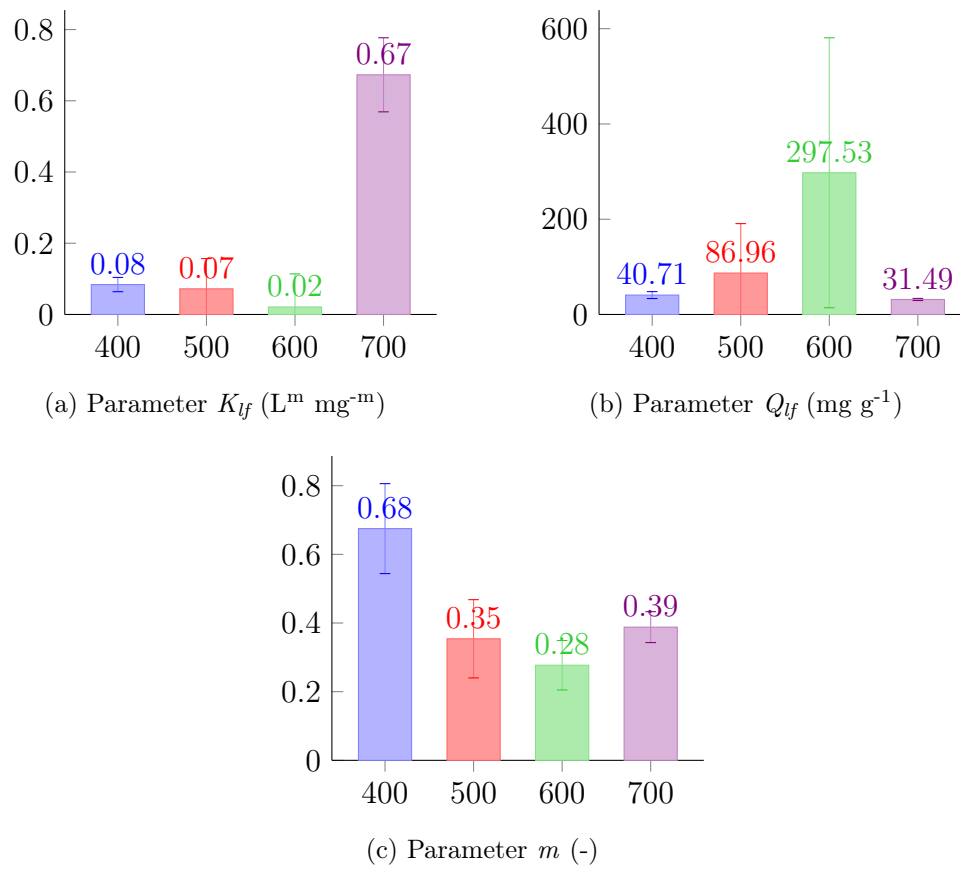
(c) Parameter m (-)

Figure 4.15: Parameters of the Langmuir-Freundlich model

4.5.4 Statistics

	Langmuir	Freundlich	Langmuir-Freundlich
■ BC400	0.952	0.932	0.972
■ BC500	0.969	0.987	0.988
■ BC600	0.969	0.997	0.997
■ BC700	0.917	0.950	0.976
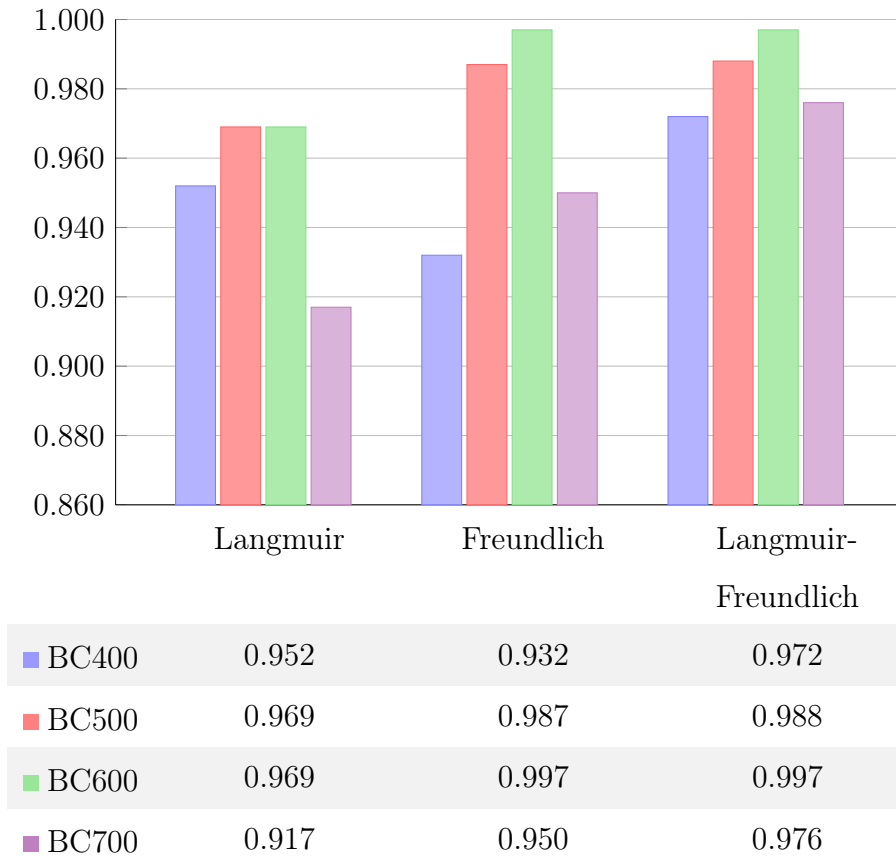
Figure 4.16: Regression coefficients (R^2) for different models. LF model fits more than others, and for all of them the fitting is lower for BC400 and BC700.

After comparing regression coefficients, it is clear that Langmuir-Freundlich model fits the best, suggesting that the interaction between phosphate and the biochar could be affected by both the Langmuir and the Freundlich processes, as hypothesized by Yao et al (2013). Fittings of the Freundlich and Langmuir–Freundlich matched the experimental data better than those of the Langmuir model, suggesting the adsorption of phosphate is probably more controlled by heterogeneous processes.

4.6   Possible Sorption Mechanism

Surface characterization (Figure 4.6a) showed that biochars had a relatively high surface area measured with CO_2 ranging from 283 to 566 m^2 g^{-1}, which is generally desirable for phosphate adsorption.

The increasing surface area appears to have no significant effect on adsorption capacity. This is likely due to the size of the pores, with the most of pores for all the chars smaller than 0.6 nm in diameter, blocking phosphate ions from accessing the internal surface area.

ICP results show that the mineral with the highest concentration is calcium, with 1.99-2.60 wt% in the biochars produced (Table 3). XRD shows the presence of calcite ($CaCO_3$) in the biochar before adsorption of phosphate and both calcite and brushite ($CaHPO_4$) after adsorption, indicating that calcium is likely involved in adsorption of phosphate (Figure 4.17).
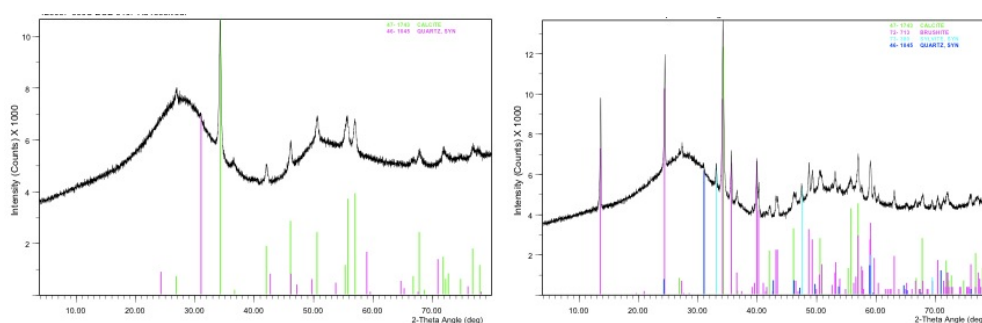
Figure 4.17: XRD spectrum before (top) and after (bottom) the phosphate adsorption

Calcite is a complex mineral, undergoing various hydrolysis and complex formation reactions of its constituent species. These reactions determine its electrokinetic and physicochemical properties as well as its behavior in solution [Karageorgiou et al., 2007].

Based on the following reactions (Equation 4.5), calcite could reach with the protonated phosphate species on the biochar surface, as suggested by the Karageorgiou's study (2007).

$$CaCO_3 \longrightarrow Ca^{2+} + CO_3{}^{2-} \qquad pK = 3.25 \qquad (4.4)$$

$$Ca^{2+} + HPO_4{}^{2-} \longrightarrow CaHPO_4 \qquad pK = -7.0 \qquad (4.5)$$
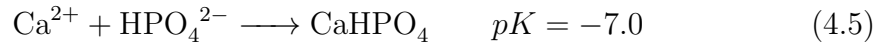
At a pH of 10 almost all phosphate are present as $HPO_4{}^{2-}$. As the pH becomes more acid, is present a second species of phosphate $H_2PO_4{}^-$. If the adsorption occurs according to equation 4.5, the pH increase would increase the concentration of $HPO_4{}^{2-}$ available to be adsorbed into calcite and increase adsorption intensity (Figure 4.18).
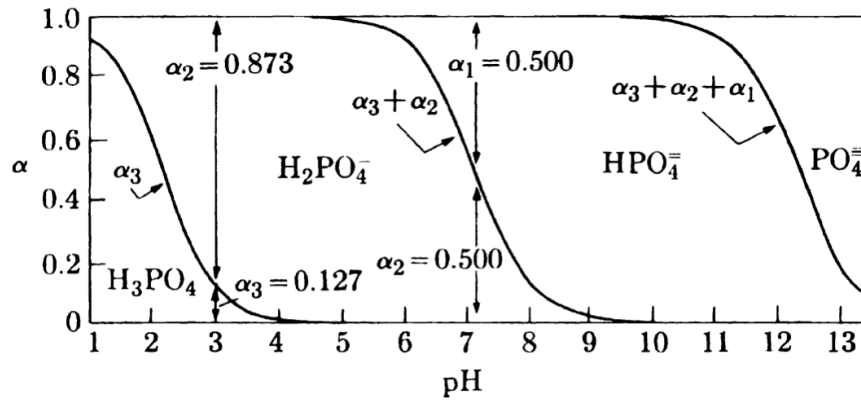
Figure 4.18: Distribution diagram for phosphate present as different protonated species as a function of pH [Karageorgiou et al., 2007].

SEM images of pre-sorption biochar also show calcite followed by both calcite and a calcium phosphate compound on the post-sorption biochar (Figure 4.19). These clearly show that phosphate species have been adsorbed on the calcite surface. This proves that the supposed mechanism could have a relevant role in phosphate sorption into grapevine cane biochar, but it remains unknown the relation with other possible mechanisms.
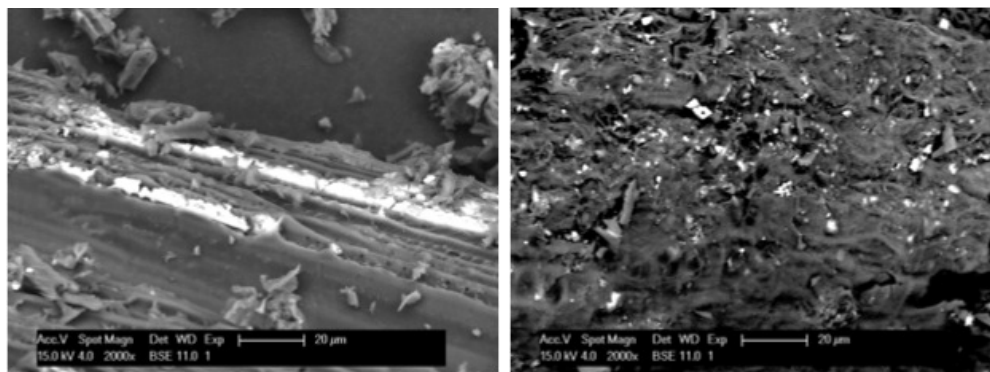
Figure 4.19: SEM before (top) and after (bottom) the phosphate adsorption. Calcite particles as revealed by EDAX are clearly plentiful in the char prior to adsorption of phosphate. Following adsorption of phosphate, however, EDAX indicates the presence of brushite in addition to calcite, additional confirmation that calcium on the biochar surface reacts with the phosphate ion to adsorb P.

Furthermore, pH may be used as a driver for the release of phosphate. When this biochar is applied to acidic or neutral soils, pH drops and phosphate are released, working as fertilizer and soil conditioner [Karageorgiou et al., 2007].

4.6.1 Comparison with Other Studies

With a phosphate sorption higher than 24 mg g^{-1}, biochars used in this work reveal to be very efficient comparing with other no-engineered biochars. In figure 4.20 Langmuir maximum capacity of the biochar produced in this work is compared with the same parameter calculated by other authors. In comparison with other no-engineered biochars, biochar produced from grapevine cane ranks among the most efficient.

Phosphate sorption can also be highly improved by engineering the feedstock (e.g. carbon activation, Mg- or Ca-enrichment) as Yao et al (2013) did with tomato leaves.
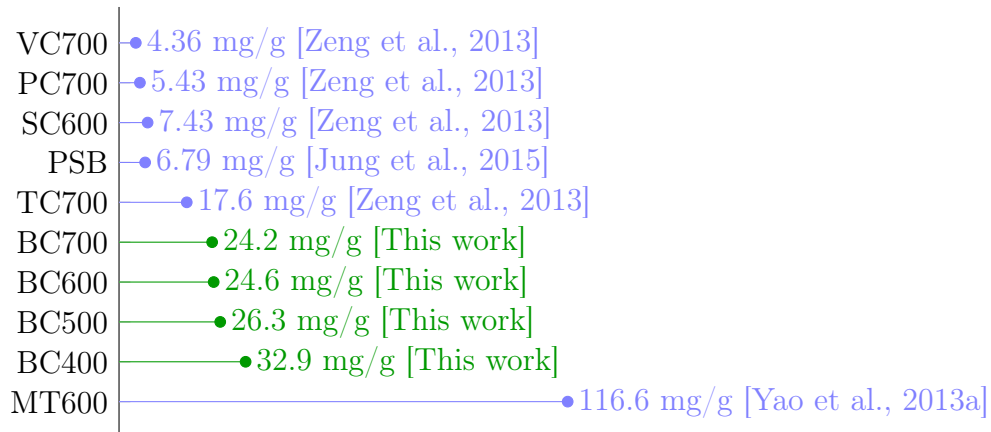
Figure 4.20: Langmuir maximum capacity Q (mg g^{-1}) of the biochar produced in this work compared with the same parameter calculated by other authors. The method they used is very similar, so the comparison is consistent. MT600 is the only engineered biochar reported. Labels reported are the ones used by their authors to indicate the type of feedstock referenced. MT600: Mg-enriched tomato leaves 600°C; TC700: *T. dealbata* 700°C; PSB: peanut shell; SC600: *S. rosthornii* Seemen 600°C; PC700: *Phragmites* sp. 700°C; VC700: *V. zizanioidees* 700°C.

4.7 Conclusion

The hypothesis that unmodified waste feedstock naturally high in calcium could have good results for phosphate adsorption, is verified.

Biochar from grapevine cane is an effective low-cost absorbent of phosphate with a maximum adsorption capacity of 32.9 mg g^{-1}, an order of magnitude higher than unmodified biochars. Increasing the pyrolysis temperature increased the adsorption effectiveness at lower concentrations, with an adsorption capacity of 12.7 mg g^{-1} using biochar pyrolysised at BC700 at an equilibrium concentration of 1 mg g^{-1} compared to just 3.2 mg g^{-1} with BC400.

Given the low-cost of unmodified biochar compared to other adsorbents such as activated carbon, biochar produced from grapevine cane has a potential as an adsorbent for phosphate. The mechanism previously described can be exploited for a virtuous production cycle. Biochar is used to treat wastewater by reducing phosphate and the resultant P-enriched biochar is incorporated into agricultural

tile drainage systems as fertilizer.

This cycle could be applied to avoid problems, such as eutrophication, its concomitant effects on living organisms and environment and the needed of a green fertilizer.

Other studies are required to verify the technical and economic feasibility, as well as the possible presence of pollutants that may jeopardize the applicability to soils.

Chapter 5

Water retention

5.1 Introduction

Water has always been the main factor limiting crop production in much of the world where rainfall is insufficient to meet crop demand [FAO, 2012].

Although only the 20% of the world's cropland is irrigated, agriculture uses approximately 70% of globally available fresh water [Brown, 2012, p. 22]. The need to increase crop production, due to the growing food demand, will require higher irrigation water withdrawal up to 14% [Bruinsma, 2003, p. 15]. The effort is hard to bear and increase the irrigation water use efficiency is crucial (only around 56% of the irrigated water is used by the crops, the rest is lost by evaporation and percolation) [FAO, 2015a]. These considerations, plus the threat of climate changes, are challenging agriculture and water availability, new strategies must be applied.

In literature is widely demonstrated the potential of biochar to hold high amount of water [Karhu et al., 2011, Basso et al., 2013, Dugan et al., 2010], that is in some cases higher than perlite, up to 1.3 - 1.6 times according to Zwart [Kor Zwart, 2014]. Pietikäinen et al (2000) reported that two biochars, one prepared from humus and one from wood, had a WHC of 2.9 mL g^{-1}, while

pomice's WHC is 1.0 mL g^{-1} [Pietikäinen et al., 2000].

Biochar is also proved to have low bulk density comparing to soil, indicating high porosity and aeration [Oguntunde et al., 2008, Laird et al., 2010]. This may have a positive effect on root and microbial respiration if applied to soil, with a better soil-plant-atmosphere system. Pastor-Villegas et al (2006) found that the bulk densities of biochars made from different types of woods processed in different types of kilns ranged from 0.30 g cm^{-3} to 0.43 g cm^{-3} [Pastor-Villegas et al., 2006].

Biochar produced from grapevine canes is expected to have low bulk density and high WHC. If this is verified, it could be applied into soil to retain water from rainfall into cropland, which should increase crop production in non-irrigated dryland regions [Jeffery et al., 2011], and reduce the amount of irrigation water needed to grow crops in irrigated regions. In this case, new studies are required to quantify these benefits.

5.2 Material and Method

5.2.1 Biochar Preparation

The feedstock used was grapevine stalks and pruning from Padthaway Region in South Australia, characterized by a Mediterranean climate.

Biochar was prepared by oven drying grapevine canes at 100ºC for 16 hours prior to pyrolysis. The dried feedstock is heated at 10ºC/min in an Argon environment during pyrolysis in a three-zone tubular furnace (Lindberg Blue) to the goal temperature, then held for 60 min. The resulting biochar was then crushed to 90-500 micron and stored in sealed containers prior to use. Feedstock is pyrolized at 400, 500, 600 and 700ºC. Each kind of biochar is label as reported in Table 5.1.

Table 5.1: Sample names

Type	Feestock	400ºC	500ºC	600ºC	700ºC
Pruning	F-Pa-Pr	4-Pa-Pr	5-Pa-Pr	6-Pa-Pr	7-Pa-Pr
Stalks	F-Pa-S	4-Pa-S	5-Pa-S	6-Pa-S	7-Pa-S

5.2.2 Characterization

To determine the composition of the feedstock and resulting biochars the Carbon (C), Hydrogen (H) and Nitrogen (N) contents of the samples were analysed in a CHN Elemental Analyzer (Perkin Elmer, 2400 Series II). Oxygen (O) was calculated by difference. Trace elements, including Zinc (Zn), Calcium (Ca), Magnesium (Mg), sodium (Na), Potassium (K), Phosphorus (P) and Sulfur (S) were analysed by the Inductively Coupled Plasma Array Optical Emission Spectroscopy (Spectro, CIROS CDD Radial ICP-OES) with nitric/perchloric acid digestion according to the method of Wheal et al (2011).

A Scanning Electron Microscope (Philips, XL-30) was used to determine the morphology and surface compositions of the biochars. Compositional analysis of the surface was conducted concurrently by Energy Dispersive X-ray spectroscopy (EDX).

Zeta potential was determined by a Zetasizer (Malvern Instruments, Nano ZS) with deionized water as the carrier fluid. An average of 20 runs were undertaken for each sample. Sample material used in calculations was carbon (lamp black, graphite) with refractive index of 2.420 and absorption of 0.9000.

5.2.3 Bulk Density

Bulk density is the ratio of oven-dry mass (at 105ºC) to bulk volume [McKenzie et al., 2002, 38]. This property is dependant on the material and on how it is handled. Bulk density, as well as porosity, gives a good indication of the

suitability for root growth and soil permeability which are important for the soil-plant-atmosphere system [McKenzie et al., 2002, pp. 224-239]. Decreasing soil bulk density increases soil porosity and soil aeration, and may have a positive effect on root and microbial respiration.

In the case of biochar, the density depends upon the nature of the starting material and the pyrolysis process [Pandolfo et al., 1994].

Bulk density is calculated by weighting biochar content in a 24.63 mL plastic tube. Biochar was sifted at 90-500 μm and wasn't compressed or solicited. The exact volume of the plastic tube is measured weighing the water needed to fill it up (ρ_w=1.00 g/mL) using equation 5.2. Bulk density of biochars, ρ_b, was calculated by dividing the mass of biochar by the plastic tube volume, according following equations.

$$V = M_w/\rho_w \qquad \rho_w = 1.00 \ g/mL \tag{5.1}$$

$$\rho_b = M_b/V \tag{5.2}$$

In the 6-C-Pr test, a 6.94 mL plastic tube was used, and the same method was applied. All measured were triplicated and the average experimental data is reported and used for the analysis.

5.2.4   WHC measurements

Water retention is measured as the amount of water held at a certain pressure applied to the material. The pressure is expressed as head of water (m) and the water retention as volumetric content (v/v). Based on other studies [Grant et al., 2010], it can be expected that at 0 m and 150 m of pressure, saturation and the permanent wilting point are reached respectively. In this range, water retention was measured under 0, 1, 3, 10, 50 and 150 meters of water of pressure. Each

sample is put into the pressure plates, letting reach equilibrium over a long time period, and then weighted, dried for 24h, and weighted again. The water content is calculated as the difference between the two values. All tests were performed in triplicate, and the average experimental data is reported.

5.3 Results and Discussion

5.3.1 Chemical Properties

Elemental composition analysis (Figure 4.3) shows that all biochars are carbon-rich which is typical of pyrolyzed biomass [Lehmann and Joseph, 2012]. C content increases with temperature, ranging between 64 wt% and 78 wt%. The O and H contents of all the samples ranged between 19-30 wt% and 2-4 wt% respectively. These values decrease with temperature increase due to volatilization, resulting in an decreasing H/C ratio, that indicate a better carbon stability. N content is roughly costant at 1.1 wt%, doubling the concentration in the feedstock. Values for each biochar are shown in Table 7.1.
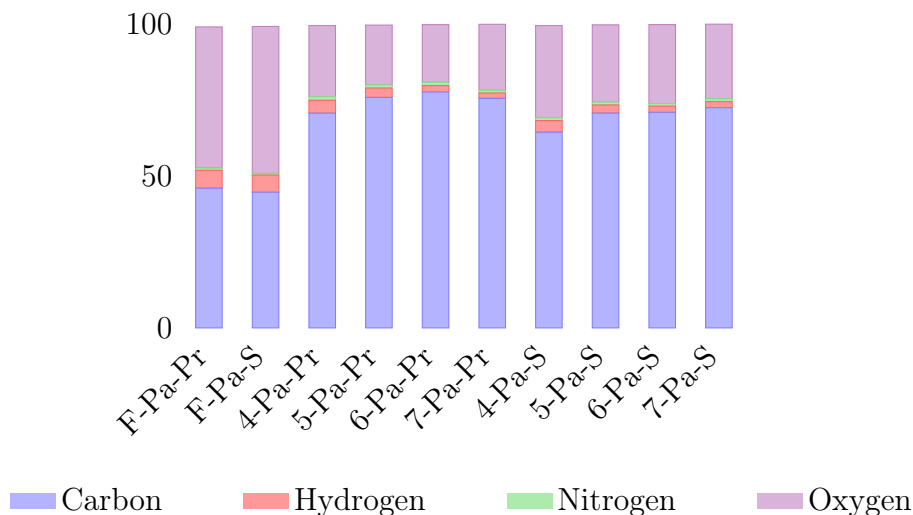
Figure 5.1: Elemental analysis (%w) of feedstocks and biochars. Values are collected in Appendix (Table 7.1).

5.3.2   Physical properties

Bulk density lies within the range of 0.18–0.36 g cm^{-3} collected in two clouds depending on the feedstock (Figure 5.2). Biochar from stalks and pruning have bulk density of 0.332±0.024 g cm^{-3} and 0.201±0.015 g cm^{-3} respectively. Temperature affects bulk density slightly, without a strong trende (p > 0.2).
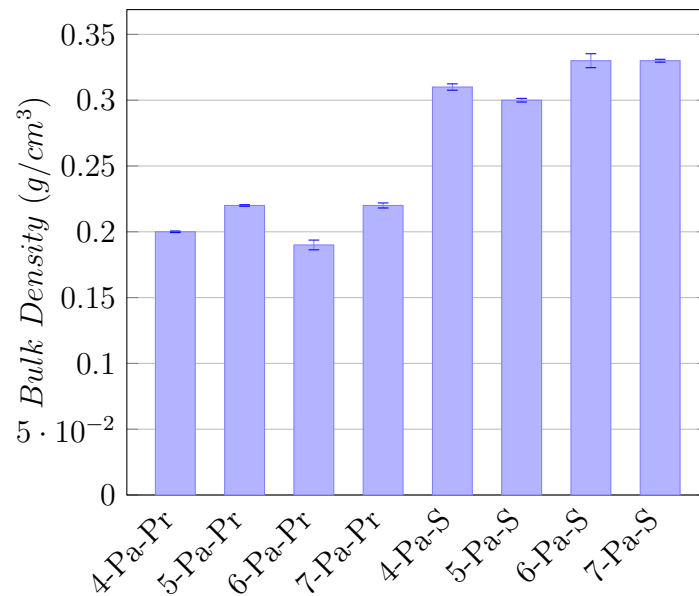
Figure 5.2: Bulk densities are significantly different between pruning and stalks, but they are not affeted by temperature (p > 0.3). Values are collected in Appendix (Table ??).

Comparing to literature [Rodríguez-Reinoso, 1997, Pastor-Villegas et al., 2006], these values are lower than most of other biochars, indicating high porosity and a good WHC. If this is the case, it could be used as soil texture improver, but more studies are required to quantify the benefits.

5.3.3   Contact Angle

The study of contact angle was conducted to determine the wettability of samples. Contact angle is the average angle measured between a liquid interface (water)

and a solid surface (biochar). Hydrophobic samples will not be considered for the WHC study because they aren't able to hold water.
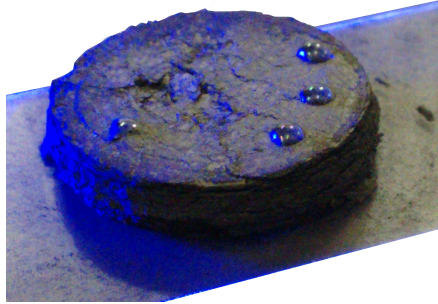
Figure 5.3: Water drops on the 4-Pa-Pr sample reveal its possible hydrophobicity.

Biochar was produced in a powdered form, so it must be compressed to obtain a solid surface for the test. Samples are compressed in tablets with a pressure of 15,000 kPa (1,530 ton m^{-2}). Tests are performed with an optical tensiometer with water drops of 3 μL and recorded every 83.2 ms for 10 sec in total.

Figure 5.4: Optical pictures of drops on 4-Pa-Pr and 4-Pa-S show high contact angles suggesting hydrophobicity of the samples.

On all the samples, drops are absorbed in less than 0.25 sec, too quickly to measure a significant contact angle (less than 4 frames), and enough to be considered good water adsorbents. On the other hand, there is no sorption in 4-Pa-Pr and 4-Pa-S samples revealing a possible hydrophobicity (Figure 5.3). The average contact angles of 4-Pa-Pr and 4-Pa-S are 94.09º and 56.59º respectively

(Figure 5.4). In the first case, the value was quite constant through time, while in the second it slightly decreased (Figure 5.5). 4-Pa-Pr and 4-Pa-S tend to hydrophobicity, so they will not be considered for the WHC study.
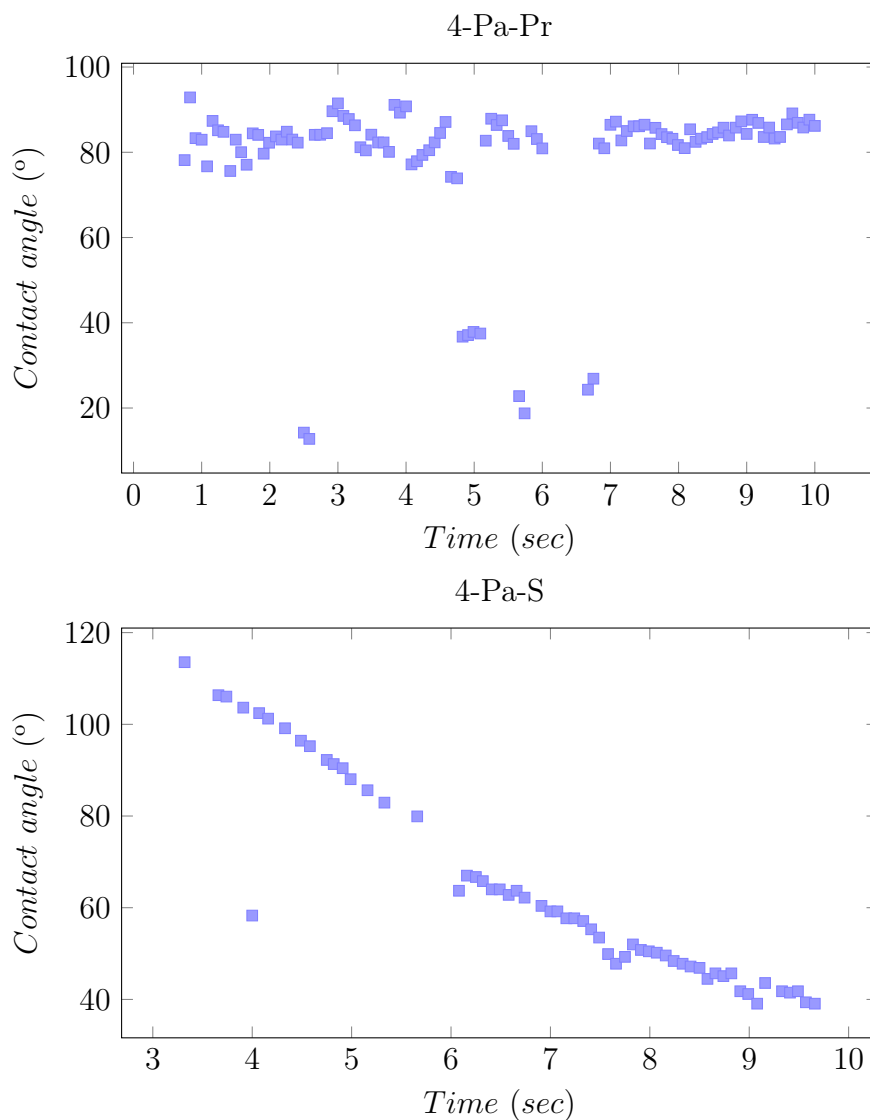
Figure 5.5: Trend of contact angle of 4-Pa-Pr and 4-Pa-S through time.

The low wettability is due to changes in the proportions of hydrophobic and hydrophilic functional groups [Kinney et al., 2012, Novak et al., 2012].

5.3.4 Water Retention Curve

The water retention curve is the relationship between the water content and the soil water potential. It is used to predict the soil water storage, water supply to the plants (field capacity) and soil aggregate stability. At potentials close to zero, a soil is close to saturation, and water is held in the soil primarily by capillary forces.

The Groenevelt-Grant model was used to explain experimental data [Grant et al., 2010] in which water retention function is expressed in terms of the water content as a function of the matric head, h, plotted on a linear scale (Equation 5.3).

$$\theta(h) = \theta_a + k_1 \left\{ exp\left[-\left(\frac{k_0}{h_a} \right)^n \right] - exp\left[-\left(\frac{k_0}{h} \right)^n \right] \right\} \tag{5.3}$$

where k_0, k_1, and n are freely adjustable fitting parameters. These values are obtained from the water retention data by curve-fitting, which must pass through an 'anchor' point (h_a, θ_a). The anchor point chosen is the saturation point $(0, \theta_s)$, which gives the equation 5.4.

$$\theta(h) = \theta_s - k_1 \left\{ exp\left[-\left(\frac{k_0}{h} \right)^n \right] \right\} \tag{5.4}$$

Resulting curves are plotted in figure 5.6. It is noticeable that biochars produced from stalks can hold the double of water of the biochar produced from pruning. Water retention also increase with temperature.
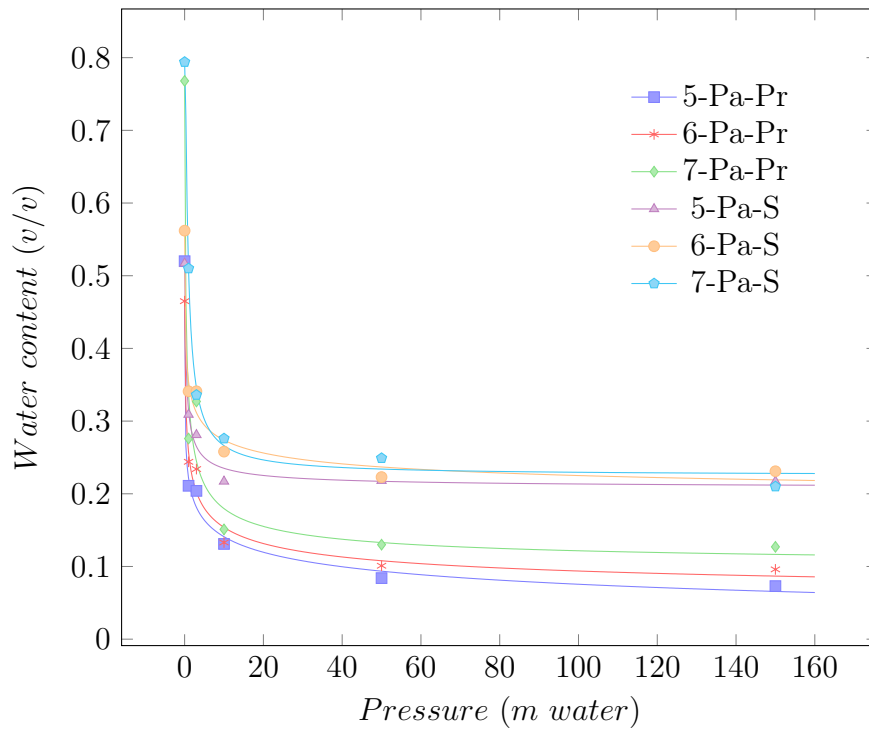
Figure 5.6: Water retention curve according to the best-fit Groenevelt-Grant model curve. Water content is higher in stalks than in pruning, in both cases it increases with temperature. Values are collected in Appendix (Table 7.5).

At pressure of 0 kbar, WHC ranges between 0.47 and 0.79%, reaching the maximum in the case of 7-Pa-Pr and 7-Pa-S. There is no evident trend depending on temperature but it can be supposed that WHC increases with temperature (p = 0.018 for 7-Pa-Pr; p = 0.056 for 7-Pa-S) due to the higher porosity and the lower content of hydrophobic substances.
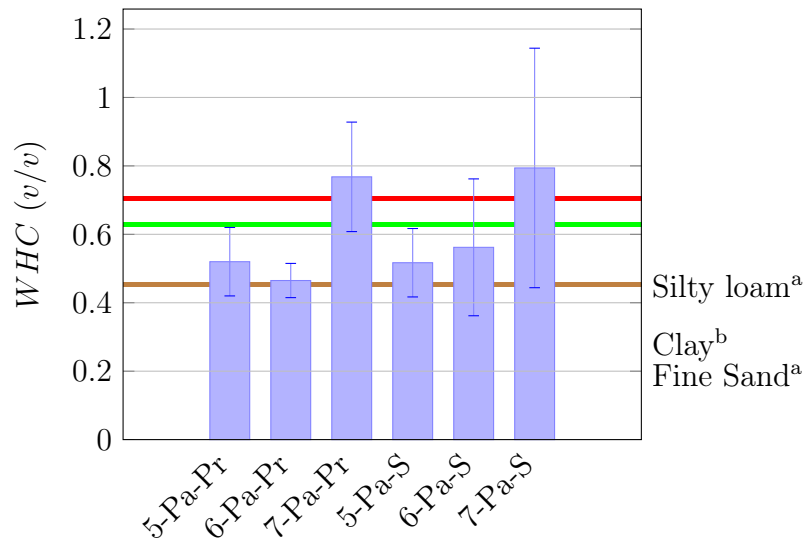
Figure 5.7: WHC at pressure of 0 kbar. Values are collected in Appendix (Table 7.5). The maximum WHC is reach at 700°C.

5.3.5 Comparison with soils

Comparing experimantal data with water retention curve of some soils, it can be inferred that biochars' water retention is comparable with the one of clay loamy soils, so it can be useful to improve WHC of sandy soils (Figure 5.8).
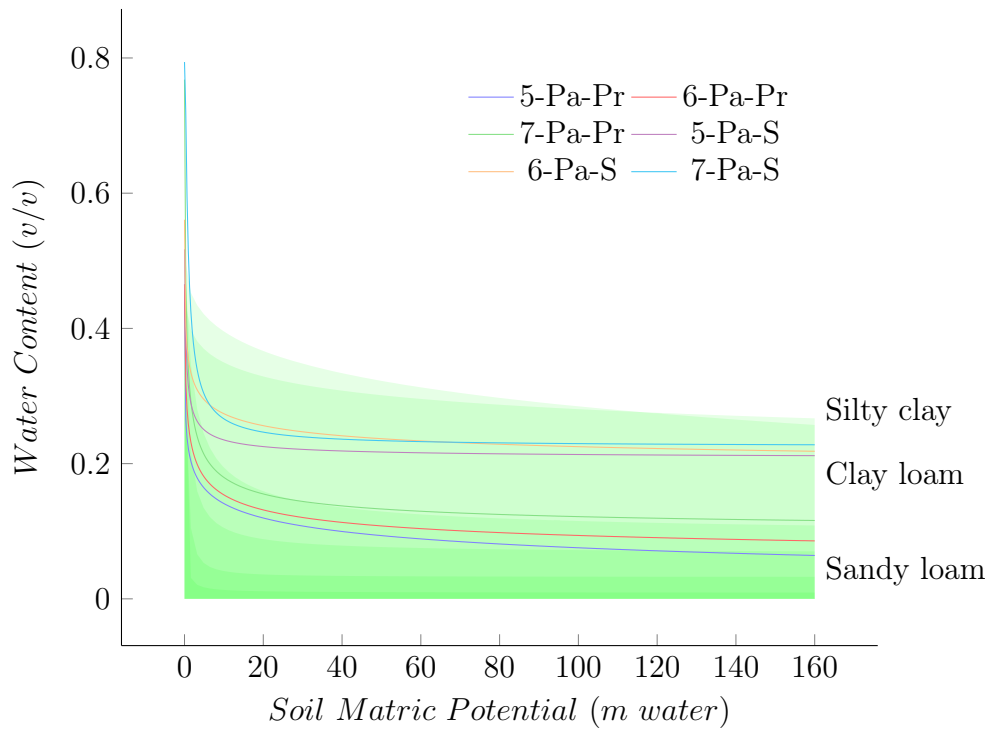
Figure 5.8: Biochar's water retention compared to other soils. Biochars have a water retention similar to loamy soils. Soil areas are drawn by using data from Grant et al. (2010).

In Figure 5.7 the WHC of biochars measured at pressure of 0 bar are shown. In the background are plotted the WHC of some other soils.

Biochar addition to soil could significantly increase WHC. Based on an unamended sandy loam soil with an average WHC of 0.16% [Yu et al., 2013], the addition of a layer of 10 cm of 7-Pa-Pr biochar (WHC = 0.75%) into a root zone of 100 cm depth, represents an increase of 3.7% in equivalent depth of water in the 100 cm soil depth. This 3.7% is the extra amount of water that will be available in the root zone for crops by adding biochar, and could represent the amount of irrigation water that a producer will save.

5.4   Conclusion

Biochars produced at 400ºC are hardly wettable. Biochars produced at temperatures higher than 400ºC have a good WHC, higher that some agricultural soils. They could be mixed in order to reduce water demand and irrigation needed.

Further studies are needed to clarify, whether adding biochar into soil will lead to enhanced plant available water content, and could thus be used to mitigate fluctuating water availability.

Chapter 6

Quo Vadis

"The greatest enemy of knowledge
is not ignorance,
it is the illusion of knowledge."
Daniel J. Boorstin, 1983

6.1 Other studies needed

Although much has been discovered about biochar in the last years, the knowledge is still poor. A lot of mechanisms are unclear and more should be investigated before its application.

The enthusiasm of the benefits of biochar are inhibited by the need to analyze and study in deep some critical aspects that can compromise its use, especially if applied to crops [Quilliam et al., 2013b]. Biochar is found to have high amount of dioxins and PAHs, dangerous for the environment and human health.

Dioxins (PCDD), Furans (PCDF) and Polycyclic Aromatic Hydrocarbons (PAH) are Persistent Organic Pollutants (POPs), chemicals able to persist in the environment for years because they are difficult to be degraded. They can result from natural processes (e.g. volcanic eruptions), but also by unintentional

reactions of high-temperature processes (e.g. incomplete combustion, pesticide production).

POPs generate alert because some compounds have been identified as carcinogenic, mutagenic and teratogenic [IARC, 2015]. They are considered to be one of the most difficult organic contaminants to treat [Zheng et al., 2007, Cerniglia, 1993, Weissenfels et al., 1992, Edwards, 1983], and for this reason current efforts are focused on banning their use and production.

Biochar, that is produced through thermal processes, contains varying levels of these organic pollutants [Gar, 2008, Hale et al., 2012b], often overcoming the limits imposed by Italian law (D.Lgs. 152/06) also if mixed in low amount into soil.

On the other hand, biochar can stimulate microbial activity in soil [Kolb et al., 2008, Steinbeiss et al., 2009, Quilliam et al., 2013a] and its addition could facilitate the degradation of naturally occurring PAHs [Quilliam et al., 2013b]. At the same time, the strong sorbing capacity of biochar could limit the leaching of PAHs from soils and could prove a significant management strategy for the reduction of PAH contamination of groundwater [Khan et al., 2013, Beesley et al., 2010, Hale et al., 2012a]. In both cases, the effects are still unclear, and possible mechanisms are greatly unknown.

The amount and kind of POPs into biochar varies widely, depending mainly on process conditions but also on the feedstock. Their values are dangerously close to the law limits and for this reason more studies are required to avoid the contamination of soils and the risk for human health.

6.2 Socio-Economic Prospectives

Biochar is an opportunity for a new market, but it is important to evaluate the economic feasibility and market potential. Lehmann et al (2009) developed a cost-benefit analysis for large- and short-scale pyrolysis plants for the production

of biochar as primary product.

The large-scale plant's products are devoted to industrial use for the profit, so the analysis is only economic. The short-scale pyrolysis is developed for household, farm and village level, so for the sustainability of small community which interest is not only financial but also social end environmental. The socio-economical aspects considered are collected in table 6.1.

Table 6.1: Variants that regulate plant decision

	Cost	**Benefit**
Economic	Plant Pyrolysis process Feedstock supply	Biochar value Energy produced GHG market effect
Social	Possible land competition Possible increase of extraction of wood from forest	Less air pollution Less medical expenses More labour available

To ensure profitability of exclusively biochar-focused enterprises, the revenues generated from biochar sales need to support all expenses associated with operations including equipment, labor, and capital costs for feedstock procurement and preparation; biochar production, post-processing, packaging and distribution; marketing activities; and others [Jirka and Tomlinson, 2014]. The profit margins on exclusively biochar sales may be slim or negative, but the business can be profitable if all products are considered (heat, syngas, energetic oil, tradability of CO_2 stored).
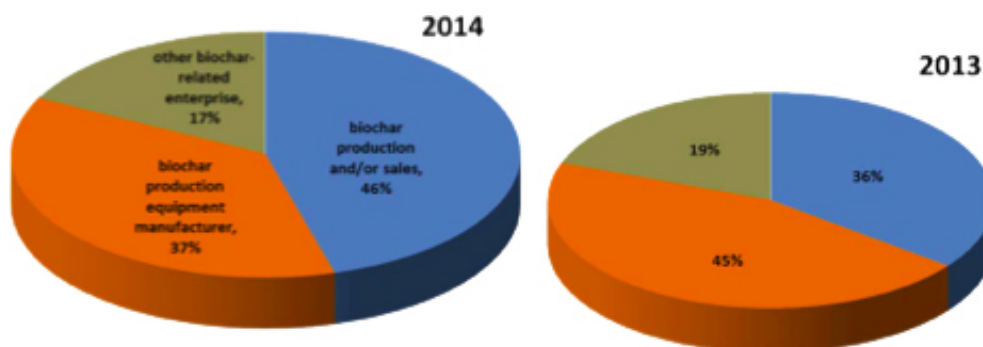
Figure 6.1: Companies in the biochar industry by sector in 2014 (n=200) compared to 2013 (n=175). Source: IBI, 2014

For these reasons the production of biochar is a fruitful market: in 2014 there were registered more than 200 companies (Figure 6.1) in which biochar represents primary or secondary product, an increase of 14% from 2013 [Jirka and Tomlinson, 2014]. Businesses are mainly located in developed countries (Figure 6.2) where the sell price range is wide, depending on the selling condition (wholesale or retail, pure or blend). The average price of wholesale pure biochar was roughly 2 USD kg^{-1} in 2014, but the dataset is not long enough to define a trend along the time [Jirka and Tomlinson, 2014].
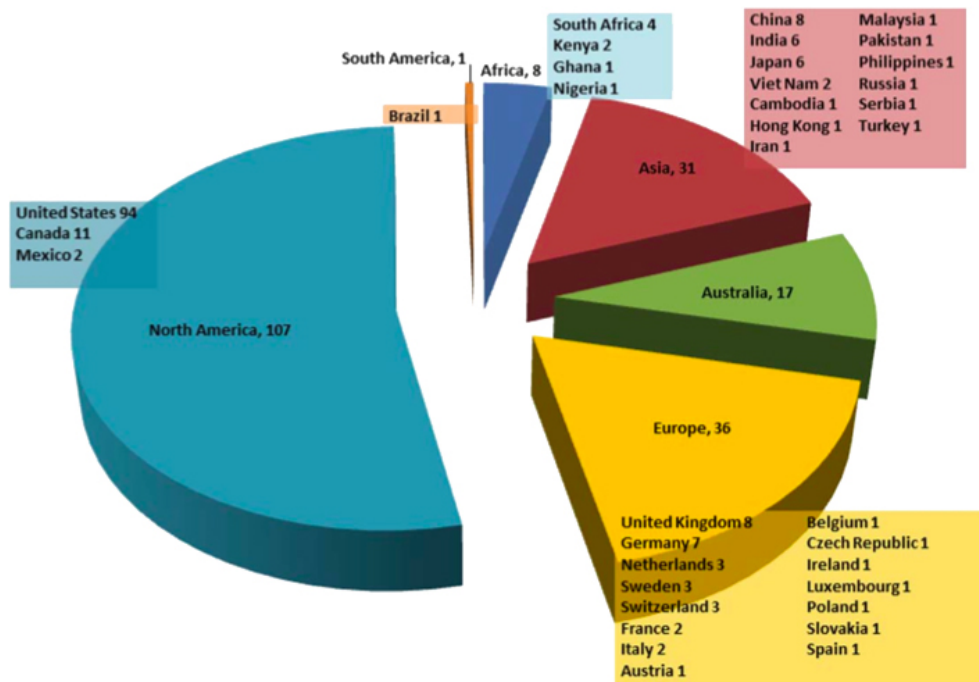
Figure 6.2: Geographic location of biochar businesses (n=200). Source: IBI, 2014

6.3 Biochar in Italy

In the Mediterranean area, water scarcity is the major limiting factor for agriculture, that is predicted to become more vulnerabile in the near future. The larger interannual rainfall variability and higher frequency and intensity of extreme events, such as droughts and heat waves, will seriously threaten agroecosystems [IPCC, 2013, p. 7]. The identification and implementation of adaptive measures aimed at enhancing the resilience of the agroecosystems to water scarcity is a key priority, in order to maintain both the quality and quantity of crop productions and protect water resources.

In Italy, biochar could become a powerful tool for the adaptation to climate change. The Italian Biochar Association (ICHAR), established in 2009, is the main promoter of biochar research and production in Italy. Thanks to an its instance, biochar was introduced in June 2015 in Italian law as a possible soil

improver[1]. In Italy, as in the rest of the Mediterranean area, biochar is a great opportunity to face with some of the major problems of the next future (water scarcity, climate change mitigation, green energy, circular economy). This new law is expected to be the starting point for opening the market for this technology.

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[1]Decreto 22/06/15. Aggiornamento degli allegati 2, 6 e 7 al decreto legislativo n. 75 del 29 aprile 2010 «Riordino e revisione della disciplina in materia di fertilizzanti, a norma dell'articolo 13 della legge 7 luglio 2009, n. 88». (GU Serie Generale n.186 del 12-8-2015)

Chapter 7

Appendix A

Table 7.1: Elemental analysis wt%

	Carbon	Hydrogen	Nitrogen	Oxygen[a]	pH
Feedstock	45.2	8.8	0.8	45.2	-
BC400	72.1	5.1	1.5	21.3	6.8
BC500	75.4	3.6	1.6	19.4	8.5
BC600	76.7	2.8	1.4	19.1	9.0
BC700	79.9	2.1	1.5	16.5	10.2
F-Pa-Pr	45.9	5.9	0.7	46.4	-
F-Pa-S	44.6	5.6	0.6	48.3	-
4-Pa-Pr	70.5	4.2	1.2	23.3	8.2
5-Pa-Pr	75.7	3.1	1.1	19.6	10.0
6-Pa-Pr	77.5	2.1	1.1	19.0	9.0
7-Pa-Pr	75.4	1.8	0.9	22.7	9.8
4-Pa-S	64.3	3.8	0.9	30.3	9.2
5-Pa-S	70.6	2.8	1.0	25.4	10.3
6-Pa-S	70.8	2.0	0.8	26.0	9.8
7-Pa-S	72.3	2.0	0.9	24.5	10.7

[a] calculated my difference

Table 7.2: Elemental analysis (mg kg^{-1})

Sample	Fe	Mn	B	Cu	Mo	Co	Ni	Zn	Ca	Mg	Na	K	P	S	Al	Ti	Cr	Cd	Pb	As	Se
F-Pa-Pr	26	16	17	36	<1	<0.9	<1	40	7,600	1,690	970	8,000	940	620	20	0.84	<0.4	<0.3	<3	<4	<7
F-Pa-S	20	21	29	19	<1	<1	<1	14	5,400	1,740	9,600	19,300	540	800	6.6	0.61	<0.4	<0.3	<3	<4	<8
4-Pa-Pr	89	47	43	74	1.2	<1	3.1	89	19,800	4,400	2,600	18,900	2,800	480	50	1.8	5.3	<0.3	<3	<4	<8
5-Pa-Pr	98	38	36	77	<1	<0.9	6	121	18,300	4,300	2,100	18,300	3,200	620	31	1.3	11	<0.3	<3	<4	<8
6-Pa-Pr	177	49	45	93	1	<0.9	14	123	21,000	4,900	2,100	21,000	3,500	780	38	2.2	27	<0.2	<2	<4	<7
7-Pa-Pr	149	56	60	133	<0.9	<0.9	7	124	26,000	6,000	2,900	26,000	3,700	1,220	58	3.7	13	<0.2	4.5	<3	<7
4-Pa-S	79	46	58	50	<1	<0.9	1.7	34	12,400	3,000	14,500	42,000	1,410	710	31	1.4	2.4	<0.2	<2	<4	<7
5-Pa-S	96	57	69	65	<1	<1	2.5	47	14,700	3,800	17,200	48,000	1,670	980	50	2.5	4.1	<0.3	<3	<4	<8
6-Pa-S	81	54	72	59	<1	<0.9	7.4	42	15,100	3,800	18,200	51,000	1,670	1,060	38	3.4	1.4	<0.3	<3	<4	<7
7-Pa-S	141	68	81	65	<1	<1	2.9	46	16,600	4,600	19,500	58,000	1,880	1,330	45	3.9	4	<0.3	<3	<4	<8

Table 7.3: Bulk Density (g/cm^3)

Sample	Mean	St dev
4-Pa-Pr	0.2	$6 \cdot 10^{-4}$
5-Pa-Pr	0.22	$6 \cdot 10^{-4}$
6-Pa-Pr	0.19	$3.7 \cdot 10^{-3}$
7-Pa-Pr	0.22	$1.9 \cdot 10^{-3}$
4-Pa-S	0.31	$2.4 \cdot 10^{-3}$
5-Pa-S	0.3	$1.4 \cdot 10^{-3}$
6-Pa-S	0.33	$5.3 \cdot 10^{-3}$
7-Pa-S	0.33	$1.1 \cdot 10^{-3}$

Table 7.4: Removal rate (%)

Concentration (mg/L)	400	500	600	700
120	75.9	89.1	90.3	99.8
245	71.7	90.3	86.6	98.6
370	65.4	70.7	82.4	96.2
490	44.3	60	50.1	95.3
735	35.1	21.8	29.5	79.3
860	29.7	24.3	16.8	44.1
980	35.6	24	15.4	32
1,230	23.1	18.6	12.4	15.4
1,470	11	9.2	7.8	6.7

Table 7.5: WHC (v/v) of biochar under different pressure.

Pressure (m water)	5-Pa-Pr	6-Pa-Pr	7-Pa-Pr	5-Pa-S	6-Pa-S	7-Pa-S
0	0.52	0.465	0.768	0.517	0.56	0.79
1	0.211	0.244	0.276	0.309	0.34	0.51
3	0.204	0.234	0.327	0.281	0.34	0.34
10	0.131	0.133	0.151	0.217	0.26	0.28
50	$8.4 \cdot 10^{-2}$	0.101	0.13	0.218	0.22	0.25
150	$7.3 \cdot 10^{-2}$	$9.6 \cdot 10^{-2}$	0.127	0.217	0.23	0.21

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