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Characterization of modified cactus pear (*Opuntia ficus indica* (L.) Mill) pruning waste as a sustainable and innovative solution to recycle phosphorus from agricultural streams

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Abstract

This thesis provides an overview of the most promising current solutions to recover lost phosphorus (P) fluxes in surface water, and focuses mainly on its recycling through the use of waste materials from agriculture. In this thesis, cactus pear pruning waste (henceforth, called biomass). The thesis evaluates *i)* the potential of biomass as an adsorbent biomass to remove P from an aqueous solution; *ii)* studies the hydraulic properties of soils in which this by-product is incorporated; *iii)* its use for growing potted plants.

Many intensively farmed soils show high P contents compared to the thresholds required for agricultural production; 0.084 Mt of P y^{-1} is leaving the European terrestrial system.

Given the global shortage of the primary resource of P, wastage and loss at every stage of the P cycle raise concerns about future supplies and especially about the resulting environmental problems, such as the eutrophication of surface water bodies and the reduction of biodiversity. The opportunity for P recovery with green and sustainable technology is, therefore, a great challenge for the next years. Waste materials or by-products of agricultural processing have been considered ecologically safe, low-cost, and highly selective with high pollutant adsorption capacities, which would enable sustainable P recovery, both environmentally and economically.

The removal P capacity in biomass enriched in Ca^{2+} , Fe^{2+} and Fe^{3+} was 2.27, 1.33 and 1.87 mg g^{-1} , respectively.

The desorption/regeneration process revealed that less than 8% P desorption in Ca or Fe-enriched biomass and showing strong stability of the biomass-cation-P system. Therefore, cactus pear pruning waste, previously reduced to powder, and enriched with ions, could be a cheap adsorbent with a good P removal performance, which could be used directly in agriculture as a soil conditioner/fertilizer. The amendment of biomass shows positive effects on soil water retention. However, observable benefits require very high amendment proportions, more than 20% by volume. These quantities make use in the open field unrealistic but offer perspectives in the horticultural and floricultural sectors. The addition of Fe^{3+} -loaded biomass to the growing media improves nutrient assimilation in basil, suggesting that the positive effects may be attributed to the presence of Fe in the biomass.

These findings provide insights into the potential of recycled cactus pear waste as a valuable resource for P recycling, and for improving soil health and plant growth in horticultural settings. This approach can be particularly useful in Mediterranean environments where this biomass is largely available.



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1. Introduction

Today, global society faces serious challenges due to scarcity, importance, unequal global distribution, and, at the same time, regional excess of phosphorus (P). Over the years, human activity through deforestation and soil loss has severely compromised the natural P cycle, leading to a more rapid P loss from soil to surface waters. Phosphorus is a resource that is as valuable for the development of animal and plant life as it is limited and being depleted globally. Its reckless use in agriculture has polluted the environment, creating harmful phenomena such as eutrophication which deplete the water of oxygen and decimate marine ecosystems (Withers et al., 2019).

In addition, phosphorite, the primary resource from which P is extracted, is a finite resource, subject to price volatility, with variable quality and unequal access around the world. The geopolitical aspects are of concern because P reserves are found in a limited number of countries and undoubtedly significantly affect the availability and price of P. In addition, although there is general vagueness as to when the peak will be reached, there is broad consensus that the remaining phosphate rock reserves are declining (Li et al., 2019). Thus, the growing perception of a global P crisis could lead to international tensions due to both the distribution of terrestrial reserves and their control and the growth of the world's population (Vaccari et al., 2018). These are strong arguments for pursuing a circular P economy now, regardless of the exact timing of phosphate resource depletion. Now it is clear how the future of phosphorus is linked to its recycling and reuse, so its recovery becomes essential. To date, the reuse of alternative P sources is not receiving the attention it deserves, but to improve sustainability, global agriculture must become less dependent on P-based mineral fertilizers by optimizing P use and production, minimizing direct losses such as those from mining and soil erosion, and above all by promoting the recovery and recycling of P streams that leave the cycle and reach surface waters. Scholars in recent years have proposed some adsorbents derived from waste materials from the agricultural sector with good properties that would enable sustainable P recovery, both environmentally and economically. These waste materials or by-products from agricultural processing, with or without further modification, are considered environmentally friendly, low-cost, and highly selective with high adsorption capacities (Alqadami et al., 2017; Mezenner et al., 2009). Agricultural by-products that can be used to adsorb P, and thus used as a fertilizer or substrate, are diverse (Bailey et al., 1999; Berecha et al., 2011). In addition, numerous attempts have been made to develop new anion exchangers by grafting positively charged amine groups onto the polymer chains of agricultural residues, such as sugarcane bagasse (Shang et al., 2018), corn bracts (Banu et al., 2019;



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Wandg et al., 2018), raw walnut and raw almond wood shells (Faraji et al., 2020), and wheat straw (Xu et al., 2009). These studies showed that the adsorption capacities of the chemically loaded materials were significantly increased compared to the raw materials.

1.1 Purpose of the thesis

This thesis aims to focus on potential P recovery strategies, addressing the problems associated with the reckless use of P in agriculture, which leads to excessive P losses and proposing a local solution to the global collapse of fertilizer supplies and the problem of eutrophication.

The proposed solution is the reuse of agricultural waste material from cactus pear (*Opuntia ficus indica* (L.)) pruning, a plant readily available in the Mediterranean area, known for its pronounced ability to retain large amounts of water, including ions dissolved in it. Its potential as a sustainable adsorbent for P recovery was studied, with the idea of reintroducing into the environment a portion of the P lost in surface waters and, at the same time, enhancing an agricultural waste material that, at present, has no specific utility. The thesis is based on the research, testing, characterization and transformation of cactus pear pruning waste into environmentally friendly substances and, therefore, reusable in agriculture in the form of fertilizers. Based on these assumptions, the main body of the thesis was structured according to the objectives set during the doctoral course. The objectives of the thesis, in detail, were as follows:

- to describe the current industrial alternatives for the recovery of lost P from nonpoint and point sources, such as municipal, livestock and agricultural wastewater, and propose biobased solutions for P recycling, paying particular attention to the reuse of materials derived from agricultural wastes, which would result in lower costs and environmental impact. This issue is discussed in Chapter 2, which focuses primarily on P fluxes and provides an overview of the most promising and sustainable solutions for P recycling, focusing on waste materials from agriculture. The chapter emphasizes the opportunity to recover P with green and sustainable technology, which, therefore, becomes a major challenge for the coming years. Waste materials or by-products of agricultural processing are ecologically safe, low-cost and highly selective with high pollutant adsorption capacities, which would enable sustainable P recovery, both environmentally and economically;
- propose an agricultural waste that can act as an adsorbent, to recover P from surface waters and reintroduce it into the system, combining productive development with environmental sustainability and through exploring technological innovation. Chapter 3 addresses this



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objective, the potential of natural or enriched in Ca or Fe cactus pear pruning waste (from here on called ‘biomass’) as low-cost adsorptive biomass to remove P. The P removal capacity, found in biomass enriched in Ca or Fe, increased compared to that found in natural biomass, which was almost zero. The chapter described P adsorption mechanisms using Langmuir and Freundlich isotherm models and pseudo-first-order pseudo-second-order kinetic models. Therefore, the natural or enriched biomass can be considered an economical adsorbent with good P removal performance, which could be used directly in agriculture as a soil conditioner/fertilizer;

- to study the physical behavior of two extreme benchmark soils in the Mediterranean area, after the addition of the biomass, and how this addition influences the physicochemical processes that occur in the water-soil system. Chapter 4 reports how, and to what extent, the use of biomass as a potential soil conditioner could affect the bulk density and water content of the soils and the relative water readily available to the plant;
- to study the biomass influence on the growth of a pot-grown plant and how it affects the physicochemical processes in the soil-plant system. In chapter 5 we evaluated the possible effects of modified biomass (Ca or Fe) enriched in P, added in different ratios to a commercial substrate, on the pot growth of basil plants. Parameters such as height, leaf area, number of leaves per plant, leaf chlorophyll content, and the amount of P available at the beginning and end of the experiment were monitored to determine the optimal biomass-commercial substrate ratio to promote basil growth.



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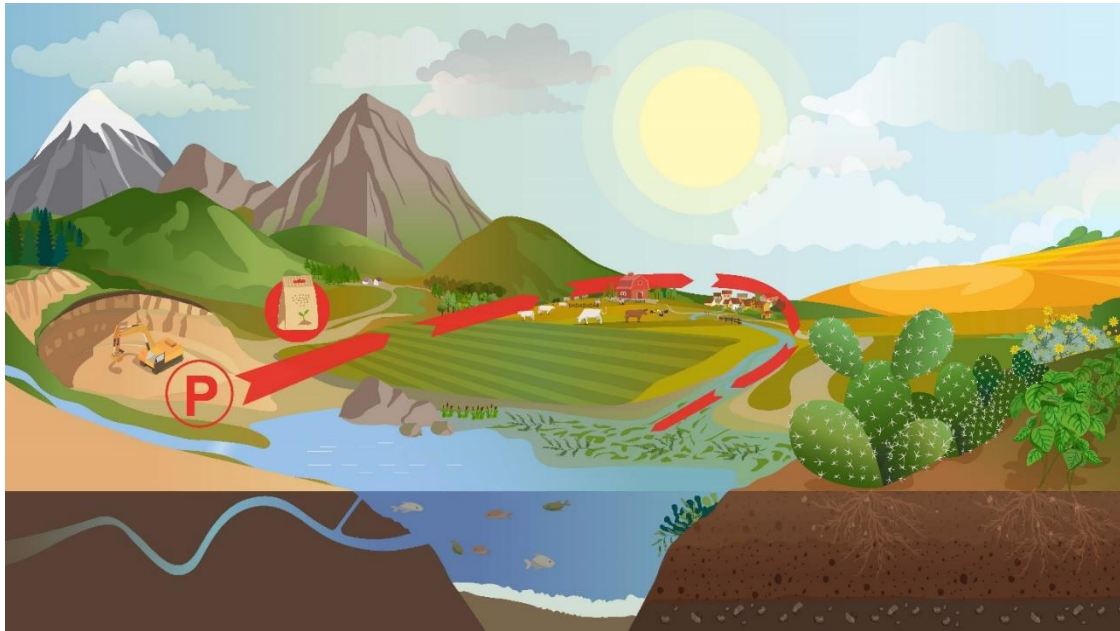
2. “RECYCLING PHOSPHORUS FROM AGRICULTURAL STREAMS: GREY AND GREEN SOLUTIONS

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Abstract

Many intensively farmed soils show high P contents compared to the thresholds required for agricultural production; 0.084 Mt of P y^{-1} is leaving the European terrestrial system. This paper focuses mainly on non-point flows of P and provides an overview of the most promising and sustainable solutions for P recycling, centered on waste materials from agriculture (Figure 1). Given the global shortage of the primary resource of P, its management is critical for its efficient use. Nowadays, wastage and loss at every stage of the P cycle raise concerns about future supplies and especially about the resulting environmental problems, such as the eutrophication of surface water bodies and the reduction of biodiversity. Recovering P costs more than EUR 640 per tons depending on the type of technique used. The opportunity for P recovery with green and sustainable technology is, therefore, a great challenge for the next years. Waste materials or by-products of agricultural processing have been considered ecologically safe, low-cost, and highly selective with high pollutant adsorption capacities, which would enable sustainable P recovery, both environmentally and economically. A realistic threshold for considering the reuse of P sustainably at the farm level is EUR 320 per tons.

Figure 1. The P cycle involves its movement through different forms and reservoirs. It begins with the weathering of rocks, which releases inorganic P. This P is then taken up by plants and used for growth. When the plants die and decompose, P is returned to the soil, where it can be taken up by other plants microbes or converted into an inorganic form, which can be transported to bodies of water through runoff. In aquatic environments, P is used by algae and other aquatic plants for growth and is eventually returned to the land through the death and decomposition of these organisms.



2.1. Introduction

The constant increase in the world's population poses a crucial risk to environmental emergencies, such as the supply of finite (limited) raw materials such as phosphorite, from which P, a key nutrient for ensuring global food support, is derived (Sutton et al., 2013).

In addition, today's society cannot imagine any production process scheme without considering waste, byproducts, and residues in order to meet the growing demand for raw materials worldwide. (Petruccioli et al., 2019). Phosphorus is a crucial element for producing crops and is widely used in both recycled manure and inorganic fertiliser (Bindraban et al., 2020; Withers et al., 2019). Its cycle has a high impact on the total environment, interfacing the hydrosphere and the pedosphere, and being heavily dependent on the biosphere and anthroposphere. Today, the global society faces serious challenges given the scarcity, importance, unequal global distribution, and, at the same time, regional excess of P. Phosphorite, the primary resource from which P is extracted, is concentrated in a few areas of the globe, with China, Morocco, the United States, Jordan, and Saudi Arabia being the leading producers, followed by ongoing capacity expansion projects in Brazil, Kazakhstan, Mexico,



Russia, and South Africa (Azam et al., 2019; U.S. Geological Survey, 2022). The approximate annual global consumption for P is 3 kg per capita, which has been rising over time for most regions (Manning and Theodoro, 2020). However, the amounts of P available and price volatilities, as occurred in 2008 and from 2020 on, have given rise to concerns about future supplies and water and soil pollution, encouraging moves toward the recycling of P (EC, 2013).

Ninety per cent of extracted P is used for food production (Cordell and White, 2013), mostly indirectly as fertiliser. Therefore, food production depends on a non-renewable resource, which, in recent decades, has become progressively expensive due to the growing global demand, with negative environmental impacts caused by constant mining (van Vuuren et al., 2010; Canziani and Di Cosmo, 2018, Reta et al., 2018).

Europe is the most import-dependent region, with 86% of P total demand (IFA, 2014). In EU agriculture, 1.1 million t of P fertiliser was used, a slight reduction of 6.5% in 2012 (Eurostat, 2020). Waste deriving from industrial processes, such as sludge, contains agronomical valuable P, so its application on cropland might decrease the necessity of mined fertilisers, but its risky downside is the content of potentially harmful organic and inorganic contaminants (Seleiman *et al.*, 2020). Given this dependence on P and the global shortage of the primary resource of P, management is critical for the efficient use of P resources. Considering that P risky downside management might not be low-cost but is the only option to maintain P supply, as P is not replaceable or renewable, we should be investing in sustainable strategies that will, on the one hand, increase productivity in the short term and, on the other hand, could be a probable low-cost guarantee for the future, supporting the food supply and farmers and safeguarding water quality (Villalobos et al., 2019). The Raw Materials Initiative of the European Commission addresses challenges related to access to raw materials by identifying materials with a high supply risk and economic importance, to which reliable and unhindered access is critical for industry and value chains (Table 1); they set the fundamental importance of phosphate rock. The list should help boost European production of critical raw materials by strengthening recycling activities and, if necessary, facilitating the launch of new recycled materials in line with environmental sustainability and the circular economy. Additionally, it provides a better understanding of how the security of the supply of raw materials can be ensured through diversification, the use of different geographic sources, mining, recycling, or substitution. Critical raw materials are a priority in the Circular Economy Action Plan of the European Union, which aims to promote their efficient use and recycling (EC, 2017).



Table 1. Major world producers and supply P sources and phosphorite, both considered essential raw materials. Data from European Commission (EC, 2017). Percentages refer to major producers/importers only.

Raw materials	Main world producers (average 2010-2014)	Main EU importers from (average 2010- 2014)	EU source of supply (average 2010-2014)	Rate of dependence on imports*
Phosphorite	China (44%)	Morocco (31%)	Morocco (28%)	88%
	Morocco (13%)	Russia (18%)	Russia (16%)	
	United States (13%)	Syria (12%)	Finland (12%)	
		Algeria (12%)	Syria (11%) Algeria (10%)	
Phosphorus	China (58%)	Kazakhstan (77%)	Kazakhstan (77%)	100%
	Vietnam (19%)	China (14%)	China (14%)	
	Kazakhstan (13%)	Vietnam (8%)	Vietnam (8%)	
	United States (11%)			

(*) The “Import Reliance Rate” takes into account global supply and actual EU sourcing in the calculation of Supply Risk, and it is calculated as follows: $EU\ net\ imports / (EU\ net\ imports + EU\ domestic\ production)$.

Phosphate rock is a finite resource for all practical purposes, subject to price volatility, with varying quality and unequal access across the globe. Additionally, although there is an overall vagueness as to when the peak will be reached, there is a large consensus that the remaining phosphate rock reserves are declining (Li et al., 2019). According to USGS data (2022), almost 220 million t of phosphate rock was extracted in 2021 from global mineral reserves, but only about 0.03 million t were marketable. Of this marketable phosphate rock, consumers used more than 99% in the same year for an estimated EUR 1940 million in sold products. Marketable phosphate rock contains less than 18% P. Therefore, the geopolitical situation can have a significant influence on the availability and price of P; the other dimensions of this issue (price, quality, access) seem more compelling to us currently. Thus, the growing perception of a global P crisis could lead to serious international tensions due to both the distribution of terrestrial reserves and their control, as well as global population growth (Vaccari et al., 2018). According to the European Sustainable Phosphorus Platform (ESPP), the annual world market for phosphate fertilisers is around EUR 45–60 billion. At the time of writing, the price of rock phosphate is EUR 300 per metric ton (+79% February to December 2022) (from <https://www.indexmundi.com/commodities/> accessed on 22 February 2023), while diammonium phosphate exceeds EUR 625 per ton, reflecting the fertiliser end-user price (from <https://www.agrarmarkt-nrw.de/duengermarkt.shtm>, accessed on 22 February 2023). These are strong arguments for pursuing a circular P economy now, regardless of the exact timetable of



phosphate rock resource depletion. Given these issues, P recovery strategies represent the solution to collapsing fertiliser supplies and the growing problem of eutrophication. Economically, P recovery is also beneficial when compared to the potential economic loss due to its release (Martín-Hernández et al., 2022).

The current literature on P reuse and recycling has increased dramatically in the recent decade, according to both Scopus and Web of Knowledge, and Elsevier's and Clarivate's abstract and citation databases. This review describes the current industrial alternatives for recovering lost P (grey removal) and proposes bio-based solutions for P recycling (green removal). P recycling from both non-point sources and point sources, such as urban and livestock wastewater, focusing on the reuse of materials derived from agriculture waste, would result in lower costs and environmental impact and could lower P excess.

2.2 P in the soil environment

2.2.1 Overfertilized soils

The presence of P is essential for modern agriculture. However, fertiliser efficiency varies between regions, and in general, less than 20% of the P absorbed by the plants is then harvested (Bhattacharya, 2018). Globally, farmers apply about 25 Mt P year⁻¹, and about 14 Mt P year⁻¹ is not used by crops, becoming a pollutant. This means that more than half is lost to the environment and can create ecological imbalances in ecosystems and water bodies. Therefore, it is crucial to provide crops with the correct amounts of fertilisers to avoid excesses (FAO, 2006). In Europe, Panagos et al. (2022) estimated the total P in agricultural topsoil (0–20 cm) at a mean of 1412 kg ha⁻¹. A high soil P concentration, conferring no direct agronomic advantage, has resulted in inefficient resource use (Withers et al., 2017). When considering European agricultural soils (171 million ha; not considering set-aside agricultural land), P input with inorganic fertilisers is estimated to be a total of 1.3 Mt P y⁻¹. Of this about 11% is estimated as a P y⁻¹ surplus, and total P losses in river basins and outlets have been estimated to be about 0.1 Mt P y⁻¹ (Panagos et al., 2022). Therefore, best practices should be to estimate the recommended threshold values for soil P testing (STP), a good indicator for the potential risk of phosphorus movement at the edge-of-field into downstream waters, based on routine soil sampling and analysis that have been identified to help assess the likely yield response to P applied on-farm (Nawara et al., 2017). Once you have estimated the threshold, you need to develop guidelines to guide fertilisation based on suspending fertiliser supply when the soil available P is above that threshold. However, many regions with intensive agriculture have STP values above the threshold



values required for optimal agricultural production (Gourley et al., 2015; IPNI, 2015; Tóth et al., 2014).

2.2.2 P losses

As a fundamental element of plant nutrition, P excess does not cause problems for the crop itself but exposes the environment to the risk of P leakage and the consequent eutrophication of water bodies (Carpenter and Bennett, 2011; Steffen et al., 2015). Although we can consider transfer into the oceans a natural process resulting from erosion and runoff, it is nevertheless accelerated by human activities such as arable farming, concentrated animal husbandry, and direct anthropogenic discharges, with losses in the range of 19–31 Mt P year⁻¹ (Compton et al., 2000). Total P losses to European river basins and sea outlets are estimated to be around 100,000 t P year⁻¹ (Panagos et al., 2022). In general, preventing nutrient losses is more beneficial in energy and economic terms than recycling (Cordell and White, 2014).

Losses from agricultural soils occur in both dissolved and particulate forms, and their transport depends on the soil type, the extent of soil P accumulation, erosion vulnerability, and hydrological connectivity to the waterbody (EEA, 2012; Liu et al., 2015; Soranno et al., 2015; Schröder et al., 2016; Withers and Bowes, 2018). For instance, a negligible decrease in pH (from 7.47 to 7.34 pH value) is enough for the mobilisation of significant quantities of P (Wollmann and Möller, 2022). Several studies have shown the influence of catchment characteristics and changes in land use on water quality and the integrity of ecosystems downstream (Table 2).

Agricultural areas contain very P-rich soils and it play an important role in P losses, as they are the main areas subject to erosion, which facilitates the loss of significant P flows. Their impacts are obvious not only on a local scale but also on a much larger scale (Fischer et al., 2017; Latinopoulos et al., 2016; Mavromati et al., 2018; Sandstrom et al., 2020). Thus, the goal of eutrophication control would be more achievable if P concentrations in soils were kept at or below the recommended threshold values for improved fertiliser response (Diaz et al., 2013; Ekholm et al., 2015; Jarvie et al., 2008, 2010; Manovrati et al., 2018; Tattari et al., 2017; Vuorenmaa et al., 2002; Withers et al., 2019), including strategies to mitigate the transfer of P by erosion (Dodd and Sharpley, 2016).

Mockler et al. (2017) calculated 0.39 kg ha⁻¹ as the annual average value of P export to the Irish national territory, of which 51% comes from wastewater and 49% from grazing and agricultural land (0.19 kg ha⁻¹). Van Dijk et al. (2016) suggested that emissions from runoff and erosion to the hydrosphere from the 27 EU member countries account for 41% of total P losses. With over 191



million hectares of agricultural land in Europe, 0.084 Mt of P from runoff and erosion is leaving the system each year, values comparable with those estimated by a recent study by Palagon et al. (2022).

Table 2. General characteristics of the catchments global area. The quantities of P lost from soils entering surface waters or the P content in the surface waters of the basin are also reported.

Catchments ID	Coordinates	Soils ^a	Land use ^b	MAP mm y ⁻¹	Clay %	OC g kg ⁻¹	pH	P loss kg ha ⁻¹	P loss mg L ⁻¹	Ref ^c
<i>cereals</i>										
Robe (IR)	53°41'32" N 9°03'45" W	PZ, UM	CPAH	1150	19	50	6.0	1.09		[4]
Wye (UK)	52°03'16" N 3°10'32" W	PZ, CM	CMGFHP	1000	13	132	5.5	0.52		[1]
Chesapeake (US)	37°31'15" N 76°06'18" W	AL, AC, LV	CSWHDP	890	13	25	5.0	0.84		[1]
Paimionjoki (FI)	60°28'02" N 22°40'56" E	GL, PZ	CLDA	680	35	19	4.9	0.88		[1]
Odense (DK)	55°13'00" N 10°18'36" E	CM, LV	CPAH	580	15	17	6.5	0.75		[4]
Palma del Río (ES)	37°41' N 5°18' W	VR	CDWLS	570	47	15	7.2	1.07		[2]
Palma del Río (ES)	37°41' N 5°18' W	LV	CDWS	570	22	15	7.8	0.67		[2]
<i>pasture</i>										
West (IR)	53°46'40" N 9°04'34" W	PZ, GL	PPF	1100	22	55	6.1	0.21		[5]
North-West (IR)	54°36'18" N 8°01'15" W	PZ, CM	PPF	1100	20	130	5.4	0.21		[5]
South-West (IR)	51°56'51" N 08°52'11" W	PZ, GL	PPF	850	18	70	5.3	0.20		[5]
Neagh-Bann (IR)	53°31'04" N 6°43'34" W	CM, LV	PPFAL	800	20	30	6.7	0.16		[5]
South-East (IR)	52°45'21" N 6°54'28" W	PZ, GL	PPF	800	21	40	6.1	0.18		[5]
Shannon (IR)	53°16'30" N 7°57'29" W	PZ, CM	PPF	750	20	50	6.2	0.16		[5]
<i>forestry</i>										
F26 (SE)	57°13'45" N 13°38'24" E	PZ, CM	FAL	1070	5	60	4.3		0.12	[3]
N33 (SE)	56°36'01" N 13°03'28" E	CM, LV	FAL	820	21	20	6.2		0.16	[3]
N34 (SE)	56°34'46" N 13°03'45" E	CM, LV	FAL	820	14	25	6.8		0.10	[3]
Schuitenbeek (NL)	52°15'07" N 5°32'20" E	PZ	FMCFP	780	15	26	5.0	1.59		[4]
M36 (SE)	56°08'36" N 13°04'51" E	CM, FL	FAL	720	26	30	6.3		0.20	[3]
M42 (SE)	55°20'27" N 13°48'04" E	FL, PZ	FAL	710	16	50	6.4		0.15	[3]
O18 (SE)	58°26'42" N 12°54'25" E	PZ, CM	FAL	660	35	40	4.5		0.50	[3]
C6 (SE)	59°42'48" N 17°18'52" E	PZ, CM	FAL	620	42	65	4.8		0.21	[3]
I28 (SE)	57°30'14" N 18°42'58" E	FL, CM	FAL	590	20	28	6.5		0.18	[3]
Flakkensee Locknitz (DE)	53°26'27" N 14°13'24" E	CM, LV	F CPAH	550	13	21	7.1	0.27		[4]
U8 (SE)	59°20'45" N 16°33'33" E	PZ, CM	FAL	540	50	45	4.7		0.26	[3]
E21 (SE)	58°24'36" N 15°20'57" E	PZ, CM	FAL	510	16	44	4.6		0.06	[3]

^a Soils: VR Vertisols, FI Fluvisols, GL Gleysols, PZ Podzols, AL Alisos, AC Acrisols, LV Luvisols, UM Umbrisols, CM Cambisols. The soil classification is according to the World Reference Base for Soil Resources (this information was obtained from SoilGrids.org platform, which contains soil information on a global scale), and any adaptations from other reference systems were made using a conversion table developed by Buol et al. (2006).

^b Land use: CDWLS durum wheat, linseed and sunflower; CDWS durum wheat and sunflower; CLDA cereal and a low animal density; CMGFHP mixed grassland and cereals, fruit, hops and potatoes; CPAH cereals, potatoes and animal husbandry; CSWHDP corn, soybeans and wheat and a high density of poultry locally; FAL forest and agriculture land; FCPAH forest, cereals, potatoes



and animal husbandry; FMCFP forests, moors, cereals, fruits and potatoes; PPF pasture, peatlands and forestry;

PPFAL pasture, forestry, peatlands and arable land;

°References [1] Withers et al. (2019); [2] Diaz et al. (2013); [3] Sandstrom et al. (2020); [4] De Klein and Koelmans (2011); [5] Mockler et al. (2017)

2.2.3 Catchment level estimation of P requirements to prevent P loss

The estimate of P potentially lost by a catchment has been a topic of research but also of management for some time. One approach has been to simplify the number of key parameters by modeling the P flows with empirical functions. Pedotransfer functions serve to predictively extrapolate certain unmeasured soil properties using measured data from soil surveys. Pedotransfer functions that use indicators are included in the software developed to be utilised directly at the farm level by farmers, calculating the seasonal need for nutrients that could be used to reduce the use of fertilisers and thus avoid P accumulation in soils. Such software was developed to calculate the seasonal demand for P and the best cost–benefit combination of commercial fertilisers (Villalobos et al., 2019). In this way, farmers should have the information necessary to apply the required doses to increase the yield of their crops, gaining benefits in both economic and environmental terms thanks to the reduction of fertilisers used, and consequent reduced P loss.

At the management level, however, even if P concentrations in the soil are kept to the agronomic optimum, it is not clear whether this would be sufficient to reduce P concentrations in the runoff enough to avoid eutrophication problems (Cassidy et al., 2017; Duncan et al., 2017). Based on the optimal soil P threshold test (STP), which provides information on the maximum P threshold required for optimal agricultural production on farms (Nawara et al., 2017), Vadas et al. (2018) used the Annual Phosphorus Loss Estimator (APLE) model to predict the impact of STP reductions and erosion control measures on the transfer of soil P contents (current and drawdown) and P transport (runoff and soil erosion) in three contrasting catchment areas.

On average, each year, about 90% of P flows to rivers, lakes, oceans, or non-agricultural land, so optimising soil management and the efficient use of P would reduce nutrient pollution in intercepting waterways (Gilbert, 2009). Overall, livestock production contributes the most to total P releases into water bodies, and the phenomenon is magnified in areas where the soils are naturally submerged or by farming practices (Liu et al., 2022).

2.3 Technologies to remove P from water



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Technologies developed to remove and recover P from P-rich waste streams, such as municipal wastewaters ($5\text{--}25\text{ mg total P L}^{-1}$) (Henze et al., 2008), are basically of two types: physical–chemical, such as membrane filtration, precipitation, adsorption, ion exchange, or crystallisation, and biological processes (Table 3). These technologies target different P sources, using different engineering approaches that differ significantly in the P recycling rate, pollutant removal potential, product quality, environmental impact, and cost (Di Capua et al., 2022; Ehama et al., 2016; Egle et al., 2016).



Table 3. Technologies to remove phosphorus from water.

Technologies		Pros	Cons	Constriction	Operative costs ^a EUR per 10 ⁶ L of treated water	Cost of 1 kg of P recovered ^a
Membrane filtration	semi-permeable selective separation wall	low energy cost, low capital investment, high productivity	membrane fouling	membrane cleaning	42 to 744	-
Ion exchange	functionalized polymeric matrices	suitable for all ions, high productivity	economic viability	pre-treatment	42 to 330	-
Precipitation	salt added	removal of suspended and dissolved solids	sodium carbonate management or H ₂ S emissions	plant maintenance	32 to 330	1.59
Crystallisation	Ca and/or Mg added	produce granular hydroxyapatite or struvite	-	-	148 to 305	0.64
Coagulation/flocculation	adding polymers or metal ions	-	-	-	32 to 330	-
Thermochemical treatment of sewage sludge	mixes the ash with sodium-based salts	produce P-enrich ash	-	heavy metal-rich ash	28 to 180*	-
Biological treatment	selected bacteria	cost, low; high productivity	additional treatment before P recovery	high concentrations of organic substrate	32 to 330	-
Adsorption	surface phenomenon of molecular interaction	cost, low; high productivity	reduced ability to remove organic P	surface area and selectivity of adsorbent; contact time	42 to 130	-

^aThe costs expressed in different currencies were converted into euros and discounted (<http://rivaluta.istat.it:8080/Rivaluta/>).

*Expressed in EUR t⁻¹ treated sludge

The scarcity of raw material coupled with environmental problems are related to the overuse of phosphate fertilisers. Therefore, it is essential to consider not only point sources of P, such as



phosphate rocks, but also non-point sources. These sources contain dissolved P, such as surface water, agricultural runoff channels, or surface rainwater, from which the needed P can be drawn to sustain global needs (Malagò et al., 2019; Mockler et al., 2017). Though progress has been made using strategies for the general management of fertilization and irrigation to decrease the amounts of P losses (Martinez and Pellerin, 2016), these themselves, although smaller than before, continue to reach the receiving waters (Xia et al., 2020). However, removing P from agricultural surface wastewaters and its reuse as fertiliser could only meet one-fourth of the annual European demand and at least 3% of the global demand for P fertilisers (Bouwman et al., 2013; Fertilizers Europe, 2020). However, EU agricultural strategies suggest replacing and supplementing mineral fertilizers with nutrients from organic sources would significantly expand the range of tools for farmers and make European agriculture less dependent on fertilizer imports from third countries. In the long term, the European commission aims to accelerate the decarbonization process and use fossil-free and recycled nutrients to produce fertilizers (EC, 2018). For this reason, even agricultural waste, which evidently abounds only in some areas (where the productions that generate them are concentrated), can be local solutions to the global problem of recovering lost P.

2.3.1 P adsorption

As mentioned above, it is important to recover P from agricultural runoff channels, but as it is not easy to intercept in that context, it is necessary to capture P directly from watercourses, where its concentration is low. One of the most suitable techniques to recover these P from low concentrated solutions is physicochemical adsorption, a surface molecular interaction that occurs on contact between a solid phase (the adsorbent) and a fluid (liquid or gaseous) phase (the adsorbate). The adsorption process in a solution–adsorbate system occurs because of two factors: the affinity between a solute and solvent and a higher affinity between a solute and solid. The chemical species of the adsorbates establish chemical–physical interactions through Van der Waals forces or intermolecular chemical bonds with groups of adsorbents. The adsorption process, classified among the more advanced treatments, is suitable for the removal of suspended, dissolved, and colloidal forms still present in wastewater treatment plants. The adsorption of P ions depends on different adsorbent factors, such as the surface area, charge, and physicochemical properties of the solution, P concentration, temperature, pH, and presence of other competing ions or molecules (Mia et al., 2017; Weng et al., 2012; Zhu et al., 2013). The selectivity of an adsorbent, i.e., its ability to remove P preferentially from competing ions, is another factor in adsorption studies and depends on the type of



interaction formed by the ions competing directly for the active sites of the adsorbent surface. In general, ions such as chloride and nitrate show little or no competition, while ions such as arsenate and silicate show high competition (Lů et al., 2013; Xie et al., 2014; Zhang et al., 2016; Kumar et al., 2019). Phosphate adsorption usually reaches an optimal level when the pH promotes its electrostatic attraction to the adsorbent, i.e., when the pH of the solution is lower than that of the zero-charge point (ZPC) of the adsorbent, making it electropositive. Since several adsorbents have a ZPC near neutral pH, optimal P adsorption is often in the acidic range (Wen et al., 2014; Fang et al., 2017; He et al., 2017; Zhou et al., 2018; Ostram and Davis, 2019; Liu and Hu, 2019; Jiang et al., 2019).

2.3.2 P adsorbent industrial materials: “grey removal”

In this thesis, I have considered as “grey removal”, wastes, residues, or by-products of the metallurgical industry sometimes modified proposed as solutions to P recovery from surface waters. In the beginning, the circular economy, and the possibility of recycling fertiliser elements, such as P, was not a research priority given the low cost of the materials. Studies on possible biosorbents started in the 1990s, intending, essentially, to remove metal ions, organic molecules, or dyes from wastewater (Wang et al., 2021). Since these experiments also studied the behaviour of different anions, the extension of these findings to the phosphate ion is certainly plausible. Different materials have been used for P removal from waste streams through an adsorption mechanism (Arenas-Montano et al., 2021; Gubernat et al., 2020). The materials most used and reported in the literature have been wastes, residues, or by-products of the metallurgical industry sometimes modified (Table 4), identified grey removal. Cusack et al. (2019) used adsorption to remove P from agricultural waters, employing bauxite residue, a sedimentary rock that is the source of aluminum, resulting in a potential low-cost adsorbent. They treated two freshwaters: low-P forest runoff (FR; pH 7.6 and 1 mg P L⁻¹) and high-P dairy-soiled water (DSW; pH 7.8 and 11 mg P L⁻¹). From the experiments conducted on three columns of different heights (20, 30, and 40 cm), bauxite residue had P removal capabilities in both the low and high ranges of P-concentrated waters (FR: 0.34 mg g⁻¹ of P; DSW: 2.75 mg g⁻¹ of P) due to the strong interaction between Al and orthophosphate anions. The estimated service times of the column media, based on the largest column studied, were 1.08 min per g of P removed for the FR and 0.28 min per g of P removed for the DSW.



Table 4. Phosphorus removal with adsorption using adsorbents derived from agricultural wastes, metal industry wastes and by advanced biological P removal with microorganisms. The table also shows the minimum concentration of the treated aqueous solution and the pH at which the highest removal efficiency has been achieved.

Material ^a	P ₀ ^b mg L ⁻¹	pH	Recovery %	Ref ^c
Bauxite residue	1	7.7	95	[1]
HPMM	1	5.9	85	[2]
Zr@MCS	2	5.0	97	[3]
<i>Chlorella vulgaris</i>	3	7.0	93	[4]
BS	5	5.0	93	[5]
Lanthanum-based hydrogel beads	5	4.0	92	[6]
RMA	5	7.0	85	[7]
Microalgae	5	7.0	90	[8]
PAO	7	7.0	83	[9]
ZSFB	10	4.4	99	[10]
Steel chips bed	10	7.0	83	[11]
CSH	13	7.0	97	[12]
Oil shale ash	22	7.1	99	[13]
ZrMCB	40	2.0	94	[14]
JP	50	7.0	96	[15]
CH	50	7.0	83	[15]

^aMaterial HPMM= High Permeability Media Mixture; RMA= red mud akaganeite; ZSFB = composite fibre constituted of steel slag, zeolite, fly ash, basalt; BS = sugarcane bagasse; JP jack fruit peel; CH corn husk; Zr@MCS Zr immobilized on modified corn straw; ZrMCB Corn bract modified (Zr); Microalgae = *Dunaliella* sp., *Nannochloropsis* sp. and *Tetraselmis* sp.; PAO = biofilm of phosphorus accumulating organisms; CSH= hydrated calcium silicate adsorbent;

^bP₀, P initial concentration

^cReferences [1] Cusack et al., 2019; [2] Ostram and Davis, 2019; [3] Hu et al., 2020; [4] Li et al., 2013; [5] Shang et al., 2018; [6] Zhou et al., 2018; [7] Pepper et al., 2018; [8] Sacristan de Alva et al., 2018; [9] Wong et al., 2013; [10] Liu and Hu, 2019; [11] Sellner et al., 2019; [12] Kuwahara and Yamashita, 2017; [13] Kasak et al., 2015; [14] Jiang et al., 2019; [15] Banu et al., 2019

Another high-volume by-product produced in the steel industry, blast furnace slag, was used to prepare a hydrated calcium silicate adsorbent (CSH) to remove phosphate from aqueous solutions. CSH showed a maximum P adsorption capacity of 53 mg g⁻¹ in a solution with an initial P concentration of 13 mg L⁻¹, at pH 7.0 and 25 °C. CSH showed excellent adsorption performance related to abundantly present Fe and Ca ions, even from phosphate solutions with a wide range of initial concentrations (2–26 mg L⁻¹) and pH conditions (pH 3–9) (Kuwahara and Yamashita, 2017). Sellner et al. (2019) conducted laboratory experiments on fixed bed columns with recycled steel chips of different sizes using alkaline solutions. It was found that adsorption was initially rapid, followed



by a stable removal step with a contact time of 3 minutes and an initial P concentration of 10 mg L^{-1} (the desorption depended on the NaOH concentration). Kasak et al. (2015) treated wastewater in submerged cells with an experimental horizontal filter filled with well-mineralised oil shale ash and peat. Comparing peat and oil shale ash, the latter removed 99% of the 22 mg L^{-1} of P present in the wastewater, whereas peat removed 63%. However, oil shale ash increased the pH value and the Ca^{2+} concentration in the runoff. Ostram and Davis (2019) treated simulated rainwater with a 5 cm expanded shale aggregate, based on aluminium, and a psyllium binder (*Plantago psyllium* L., a herbaceous plant that contains aucubin glycoside, polyphenols, mucilage, and other substances, with high-permeability media mixture, HPMM). P retention increased as the simulated rainfall intensity decreased, and the pH was acid. Additionally, iron oxides have been widely used; examples include fly ash and red sludge modified by FeCl_3 (Wang et al., 2016), where the adsorption capacity increased at pH 7. Another adsorbent is akaganeite, ($\text{FeO}_{0.833}(\text{OH})_{1.167}\text{Cl}_{0.167}$) derived from red sludge waste, which was not affected by the pH range of the solution tested (pH 5–9) due to the zero-charge point on the sorbent and the capacity to release hydrogen and chloride ions (Pepper et al., 2018).

Liu and Hu (2019) used a composite fibre composed of steel slag, zeolite, fly ash, and basalt (ZSFB) in a fixed bed reactor; the best P removal occurred at pH 4 and an initial concentration of 10 mg L^{-1} . Afterwards, the fibre was regenerated with sulfuric acid. Zhou et al. (2018) synthesised, characterised, and tested P removal/recovery in novel wastewater poly(vinyl alcohol)/sodium alginate/lanthanum hydroxide (PVA-SA-LH) hydrogel beads with an interpenetrating network (IPN) structure. They demonstrated a high P absorption capacity under acidic conditions due to the influence of the Lewis acid-base interactions between lanthanum hydroxide and phosphate. After five absorption–desorption cycles, the P absorption capacity of the adsorbent remained above 75% of the first cycle. Many studies have tested the reusability of the adsorbent in 5 to 10 cycles.

2.4. P adsorbent bio-based materials: “green removal”

All the studies above reported, based on the “grey” removal of P using adsorbents derived from by-products or the waste of the industries of steel, aluminium, or other material, or by their modifications, were carried out because of the availability of these materials and their chemical affinity with phosphate ions. Additionally, if often very efficient in P removal, P recovery by the adsorbent is carried out with strong acids or hydroxides. Therefore, many of these adsorbents, also meeting the criteria of a “circular economy” because the adsorbent is fully recovered and reusable several times, do not fit exactly with the concept of a “green treatment” (Altamira-Algarra et al., 2022). In this



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thesis, I have considered “green removal” agricultural waste products proposed as bio-based solutions to recover and reuse directly on farmland soils. On the other hand, relatively few works have described typical adsorption processes and the ability of adsorbents derived from agricultural waste to recover important anions such as P anions, or as arsenic (As), and chromium (Cr) (VI) anions that, in oxidation states (CrO_4^{2-} and AsO_4^{3-}), they behave similarly as phosphate anions (PO_4^{3-}). Indeed, the feasibility of using the recovered materials in agriculture has not received much attention, however, due to their low cost, adsorbents from recovered agricultural materials deserve further study and still need major research. The great advantage in the removal of the P anions consists of the possibility, in the eventuality of a strong bind that does not allow for the recovery of P and reuse of the adsorbent, to use the product obtained as a fertiliser or a substrate. This opportunity, evidently, is not conceivable in the case of Cr or As. Table 5 lists some agricultural waste materials on which experiments have been conducted to evaluate their Cr(VI) and As(V) removal capabilities. As (V) and Cr (VI) are only considered because, in these oxidation states, they behave as anions, CrO_4^{2-} and AsO_4^{3-} , as well as P (PO_4^{3-}), and thus, these three elements behave similarly in adsorption processes. The adsorption mechanisms of other PTEs (Pb, Fe, Zn, ...) were not considered because their behaviours are essentially those of cations.

Biosorbents tested to recover Cr(VI) work under extremely acidic pH conditions (pH 2). Therefore, the development of this solution is a challenge from an economic and chemical point of view because maintaining a pH 2 in an actual plant is far from the concept of a “low-cost and green solution”. The same cannot be said for the biosorbents that have been tested to remove arsenate, which work in a pH range between 4 and 9, ensuring the promising performance of the biosorbent. Certainly, works such as those of Fox et al. (2012), Gandhi et al. (2013), and Asha et al. (2014) will help in the development of new sustainable adsorbents for P removal, given the chemical affinity of the latter to arsenate ions.

Table 5. There are not many works in the literature that describe the adsorption of P by biomass *sensu lato*, however there are many that describe anions which are chemically analogous to the phosphate anion. The adsorption capacity of biosorbents that can remove anion Cr (VI) and As (V), and the conditions under which adsorption processes occur.

Adsorbent	Modification	Pollutant removed	Adsorption capacity mg g ⁻¹	Removal %	pH	T °C	References
<i>Ficus auriculata</i> leaves	Unmodified	Cr (VI)		94.3	2.0	30	[1]
Milled olive stones	Unmodified	Cr (VI)	2.3		2.0	-	[2]
Olive stone	-	Cr (VI)	53.3		2.0	30	[3]
Date pit	-	Cr (VI)	82.6		2.0	30	[4]
Cellulose derived by rice husk	Treated with alkaline humic acid	Cr (VI)	19.3		5.0	25	[4]
Exhausted coffee waste	Unmodified	Cr (VI)	686		3.0	25	[5]
Raw rice straw	Unmodified	Cr (VI)	8.0		2.0	30	[6]
Date palm trunk	Graft with diethylenetriamine and triethylamine	Cr (VI)	129.8		3.5		[7]
Sludge Biomass	Immobilised with Ca-alginate	Cr (VI)	116.1		5.0	25	[8]
Sugarcane bagasse pith	Immobilised with Na-alginate	Cr (VI)	52.8		2.0	25	[9]
Black wattle tannin	Immobilised with nanocellulose	Cr (VI)	104.6		2.0	25	[10]
Cactus mucilage	Unmodified	As (V)	2.8		5.0–9.0	-	[11]
Powder of stem of <i>Acacia nilotica</i>	Unmodified	As (V)	50.8		4.0–7.0	-	[12]
Sorghum biomass	Unmodified	As (V)	2.8		5.0		[13]
Cactus pear fruit powder	Unmodified	As (V)		85–92	6.0–7.0	-	[14]
Mucilage cactus	Unmodified	As (V)		98		30	[15]
Cactus mucilage (non-gelling extract)	Mixed with sodium alginate and CaCl ₂	As (V)	97.1				[16]
Cactus mucilage (gelling extract)	Mixed with sodium alginate and CaCl ₂	As (V)	101.6				[16]

References [1] Fox et al., 2012; [2] Rangabhashiyam et al., 2015; [3] M. Ben Amar et al., 2020; [4] Mangwandi et al., 2020; [5] Basu et al., 2019; [6] Fiol et al., 2008; [7] Elmolla et al., 2016; [8] Yadav et al., 2015; [9] Ramteke et al., 2016; [10] Ullah, et al., 2013; [11] Xu et al., 2017; [12] Baig et al., 2010; [13] Haque et al., 2007; [14] Gandhi, et al., 2013; [15] Asha et al., 2014; [16] Vecino et al., 2016

To consider the environmental sustainability of the adsorbent and its usefulness and easiness for reintroducing P into the environment, over recent years, researchers have proposed some adsorbents from waste materials of the agricultural sector with good properties that would enable sustainable P recovery, both environmentally and economically. These waste materials or by-products of agricultural processing, with or without further modification, are considered environmentally



friendly, low-cost, and highly selective with high adsorption capacities (Alqadami et al., 2017; Shahat et al., 2015; Mezenner and Bensmaili, 2009; Xue et al., 2009; Yuan et al., 2015; Zeng et al., 2004). The agricultural by-products that can be used to adsorb P, and then used as fertiliser or substrate are various: apple and black currant pulp, tea scraps, banana pith, sugar cane pith, coffee pulp (Bailey et al., 1999; Berecha et al., 2011, Hernández et al., 2003; Laufenberg et al., 2003), orange peel, potato peel, tangerine peel, onion peel, palm peel, hazelnut peel (Laufenberg et al., 2003; Quisperima et al., 2022; Petruccioli et al., 2019; Akinbile et al., 2018), exhausted coffee, corn cobs, rice hulls, corn straw and sawdust, rice straw and husk, sugarcane bagasse (González Bautista et al., 2019, Ozdemir et al., 2017; Sharmin et al., 2021; Xiong et al., 2021), almond shells, palm shell charcoal, hazelnut shells, peanut shells, eggshell or apricot kernels, and sunflower seed shells (Imamoglu and Tekir, 2008; Kobya et al., 2005; Wilson et al., 2006; Fang et al., 2020). Numerous attempts have been made to develop new anion exchangers by grafting positively charged amino groups onto the polymer chains of agricultural residues, such as sugar cane bagasse (Shang et al., 2018), corn bracts (Wang et al., 2018; Banu et al., 2019), raw walnut wooden shells and raw almond wooden shells (Faraji et al., 2020), and wheat straw (Xu et al., 2009). These studies have shown that the absorption capacities of the charged materials were significantly increased compared to raw materials. The reuse of agricultural waste in the form of classic fertilisers (pellets, for example) is not yet sustainable, either economically or agronomically. The main problem is the elemental composition: all the elements of plant nutrition should be present and in balanced relative quantities (Brod et al., 2008; Müller-Stöver et al., 2018).

A non-alternative but potentially synergistic approach, when P concentrations are high, is to precede the bio(ad)sorption phase with growing duckweed (Roman and Brennan, 2019).

Using vegetable material (corn bracts) modified by zirconium (Zr), Jiang et al. (2019) observed an adsorption rate of organic P faster than that of inorganic phosphorus. Complexation and electrostatic attraction were probably the main adsorption mechanisms. The highest removal efficiency occurred at pH 2, highlighting the limitations of this material. Another limitation of this work was the pre-treatment with Zr; the corn bract by itself cannot remove P because it lacks anion-binding sites in its original surface structure. Hu et al. (2020) anchored the Zr(IV) oxide nanoparticle on maize straw grafted with quaternary ammonium groups. The resulting composite Zr@MCS showed excellent performance for P removal in terms of adsorption capacity, selectivity, and regeneration, higher than that of raw maize straw and maize bract. Again, as with the corn bract of Jiang et al. (2019), the treatment of corn straw with Zr oxides made it an excellent P adsorbent but, at the same time, was a



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limitation for the biosorbent itself since it could not be directly used as a fertiliser or soil conditioner. The strong selectivity of the adsorbent medium was also due to the high affinity between the Zr and P, especially at an acidic pH.

Other studies have been conducted in order to increase the sustainable recovery and reuse of waste resources by evaluating the potential use of compost in combination with locally available crop residues (Table 6). This table shows the extreme variability of P adsorption values related to materials that are taken as is or used successive more or less complex contractions. It can be seen that the initial P content is variable, going from rice husk containing 0.4 % P to rice hull containing 6 % P. In addition, the minimum concentration at which biomass can act to remove P is 1 mg L⁻¹. While the maximum adsorption of P is extremely variable ranging from 1 to 300 mg P per g of biomass. The table also emphasize the degree of biomass sustainability according to the type of treatment received. However, the potential use of compost in combination with available crop residues can be considered a feasible option to improve the performance of the vermicomposting process judging from the aspects of organic matter destabilisation efficiency, microbial and earthworm activity, and the fertiliser value of the final product. This can help develop alternative and environmentally friendly economic strategies for the nutrient recovery of resource-rich crop residues (Lim et al., 2012; Kalemelawa et al., 2012; Khatua et al., 2018; Mago et al., 2021; Li et al., 2020; Ozdemir et al., 2017; Quisperima et al., 2022).

Above all, as a final consideration, with the use of materials that provide nutrients to the soil, site-specific consideration should be given to their most suitable rates and types (Withers et al., 2016). From this analysis of P recovery solutions, the most promising feasibility lies in direct use as a soil amendment or composting. The cost-effectiveness of P recycling, independently from the availability of a waste, depends largely on the costs of transportation, storing, and management.

Table 6. Alternative, environmentally friendly, economic strategies for nutrient recovery of resource-rich crop residues.

Production By-Product	P Content % ^a	P Rem Min mgL ⁻¹ ^b	P Ads Max mg g ⁻¹ ^c	Use	Suitability ^d	Extra Treatment ^e	References
Banana Fruit			1.0	Soil conditioner	+++	Compost	[1]
Peels	0.2			Soil conditioner	+++	Compost	[2]
Stem	0.5			Soil conditioner	+++	Vermicomposting	[3]
Leaves	0.2			Soil conditioner	+++	Vermicomposting	[4]
Fruit and vegetables				Soil conditioner	+++	Vermicomposting	[4]
Clover Crop residues	0.6			Soil conditioner	+++		[5]
Hazelnut Husk				Soil conditioner	+++	Compost	[6]
Poultry Feather waste	0.5			Soil conditioner	+++		[7]
Eggshell			180	Soil conditioner	+	High temp	[8]
Potato Peel		15	190	Soil conditioner	++	Compost	[9]
Rice Husk		1		Soil conditioner	++	High temp	[10]
	0.5			Soil conditioner	++	High temp	[10]
			12	Soil conditioner	+	Low pH	[11]
Hull	6.0			Soil conditioner	+	Compost	[12]
Rice Husk	0.04			Soil conditioner	+	High temp	[13]
			300	Soil conditioner	+	High pH	[14]
Almond Shell		2		Soil conditioner	+	High pH	[15]
Sugarcane Molasse		4.0		Soil conditioner	++		[16]
Bagasse	0.30	10	250	Soil conditioner	++	High temp	[17]
			3.0	Soil conditioner	++	P added	[18]
Vinasse	0.01			Irrigation	+		[19]
Sugarbeet Root	0.5			Energy, fertiliser	+	Digestion	[20]
Orange Peel	0.2			Fertiliser	+++		[21]
Palm Kernel shell		1		Fertiliser	+	High temp	[22]
Peanut Shell			30	Fertiliser	+	High temp, low pH	[23]
Coffee Ground exhausted	0.2			Growth media	+++		[24]

^aP content

^bP removal min concentration

^cP adsorption maxima

^dSuitability +++ reasonable use at farm both economically and technologically; ++ economically sustainable use at farm; + reasonable use at farm technologically only

^eExtra treatment, at least one further treatment is required for re-use in agriculture

References; [1] Lim et al., 2012; [2] Kalemelawa et al., 2012; [3] Khatua et al., 2018; [4] Mago et al., 2021; [5] Li et al., 2020; [6] Torma et al., 2018; [7] Ozdemir et al., 2017; [8] Gurav et al., 2013; [9] Quisperima et al., 2022; [10] Melia et al., 2019; [11] Pasquali et al., 2018; [12] Wan et al., 2016; [13]



Tabinda et al., 2021; [14] Xiong et al., 2021; [15] Sharmin et al., 2021; [16] Faraji et al., 2020; [17] Liao et al., 2022; [18] Manca et al., 2020; [19] Yin et al., 2019; [20] Shilpi et al., 2019; [21] Guerrero et al., 1995; [22] Akinbile et al., 2018; [23] Fang et al., 2020; [24] Ma et al., 2020.

2.5. Recycling phosphorus from agricultural streams: Concluding remarks

One of the key socio-economic and environmental impacts of agriculture concerns the use of fertilizers. Phosphorus, in particular, being crucial for producing our food, can be relatively easily reinserted into crop cycles before it becomes harmful to the total environment, via the hydrosphere. The most effective solutions pass through the economic enhancement of its recovery from water bodies and its reuse in the soils. The easiest, cheapest, and closest to farm solutions can be adopted by farmers before a specific policy recommends them. Current adsorbents that recover P based on adsorption phenomena are mainly waste materials from the steel industry, which ensure a high rate of P removal, but which do not allow direct reuse as fertilizer. On the other hand, relatively few studies have been carried on agricultural wastes. Vegetable waste materials are abundant, locally available, low-cost, and eco-sustainable, but the bottleneck is certainly their transport.

At the time of writing the thesis's chapter, rock P costs 320 EUR per ton, while diammonium phosphate exceeds 1000 EUR per ton, as the fertilizer end-user price. Recovering P from the surficial water can cost as much as 640 EUR per ton, depending on the type of technique used. If cheap agricultural waste adsorbents were used, the cost-effectiveness of recycling P would be even more apparent, but would also need to take into account the availability of the waste, the cost of transport and the possible cost of storing such waste.

There are many studies available on the use of agricultural by-products for the recovery of P. Most, however, consist of small-scale or laboratory studies, so the real applicability of positive findings, at farm level, has not been demonstrated. A further limitation of the approaches to the reuse and recycling of agricultural by-products is seeking reuse at all costs, without evaluating its technical and economic feasibility: extra interventions are frequently proposed (i.e., applying high temperatures or adding expensive synthetic molecules to modify the pH). In general, the most promising feasibility is given by the direct use as a soil conditioner or composting as a by-product, as the only pre-treatment.



3. P removal from aqueous solutions using cactus pear pruning wastes

Abstract

The potential of cactus pear pruning waste (CPPW), as low-cost adsorbent biomass to remove P from aqueous solution, was studied in batch mode. Biomass from cactus pear, natural and enriched in Ca or Fe, was used. The removal capacity of phosphorus in biomass enriched in Ca^{2+} , Fe^{2+} and Fe^{3+} was 2.27, 1.33 and 1.87 mg g^{-1} , respectively.

The Langmuir isotherm was found to be the best model in the study of P adsorption, for biomass enriched in Ca^{2+} , Fe^{2+} and Fe^{3+} . Pseudo-first-order, pseudo-second-order, and intraparticle diffusion models were applied to describe the kinetic data. The best fit was obtained for the pseudo-second-order model. The desorption/regeneration process was also studied revealing less than 8% desorption of phosphorus in Ca or Fe-enriched biomass and showing strong stability of the biomass-cation-phosphorus system. Therefore, cactus pear pruning waste, previously reduced to powder, and enriched with ions, could be a cheap adsorbent with a good P removal performance, which could be used directly in agriculture as a soil conditioner/fertilizer.

3.1 Introduction

In recent years, there is a growing interest in methodologies to remove P from water bodies, particularly using natural or waste materials, fitting a sustainable cycle of P recovery. To take into account the environmental sustainability of the adsorbent and its usefulness and ease of reintroduction of P into the environment, researchers in recent years have proposed some adsorbents made from waste materials from the agricultural sector, with or without further modification, which are considered environmentally friendly, low-cost and highly selective with high adsorption capacities, with good properties that would enable sustainable P recovery (Auteri et al., 2022). Several studies investigated the potential of adsorbents such as corn bracts (Jiang et al., 2019; Wang et al., 2018; Banu et al., 2019), sugar cane bagasse (Shang et al., 2018) and wheat straw (Xu et al., 2009). Recently, the potential of dried cactus pear was also evaluated; the powder of its cladodes (modified branches, photosynthetic flattened shoots, synonymous with phylloclades) was used for the removal of heavy metals and synthetic dyes from aqueous solutions (Nouri et al., 2021; Aziam et al., 2021). Cactus pear grows, today, in all semi-arid countries of the world and is particularly cultivated in the Mediterranean basin and Central America. Annual pruning results in the disposal of 13-15 tons ha^{-1}



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of biomass (Enea, 2017). This plant produces a hydrocolloid, a 'mucilage', able to form a network trapping large amount of water.

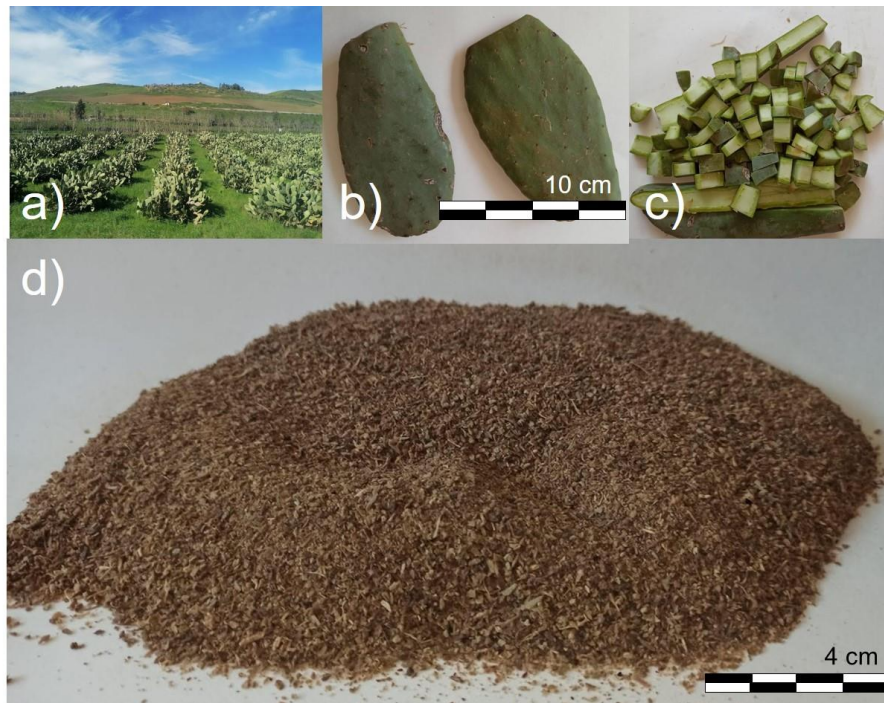
The present study discusses the potential of dried cactus pear cladodes as a low-cost and environmentally friendly adsorbent of P present in water. The main objective is to investigate P adsorption by untreated and chemically modified pruning waste (cladodes) of cactus pear. Chemical modification, such as enrichment of Ca or Fe in the chemical composition of the biomass, should result in a higher P removal efficiency.

3.2 Materials and Methods

3.2.1 Cactus pear, *Opuntia ficus indica* (L.) Mill.

Cladodes from cactus pear were collected during the fall season in Roccamena (IT) (37°50'17"88 N, 13°9'20"16 E; 472 m a.s.l.). We collected cladodes (*cv* Gialla) of different ages (1-3 years) and sizes (34.2±2.1 x 21.3±3.7 x 2.2±0.3 cm), which would be removed in normal annual pruning. The spines were removed with a knife after harvesting, and the cladodes were washed with tap water followed by deionized water and air-dried. Sequentially, the cladodes were manually dissected and then dried at 105°C for 48 hours (Figure 2). The dried cladodes were ground with a laboratory blender, sieved into different sizes, $\emptyset \leq 0.250\text{mm}$; $0.250\text{mm} < \emptyset \leq 2\text{mm}$; $\emptyset > 2\text{mm}$, and stored in an airtight container at room temperature.

Figure 2. Cactus pear, *Opuntia ficus-indica* (L.) Mill.: a) the cactus pear production chain is, at the European level, exclusive to Sicily which holds the monopoly of the Italian market and over 90% of the EU market. The total area involved in the cultivation of cactus pear in Sicily is about 4000 hectares. The most important area in terms of surface and degree of specialization of the plants are the areas of San Cono (37°17'24"N, 14°22'02"E), Santa Margherita Belice (37°41'34"N, 13°01'16"E) and Roccapalumba (37°48'01"N, 13°38'02"E); b) cladodes *cv* Gialla 2 years old; c) cladodes manually dissected; d) biomass.



3.2.2. Material characterization

Lewis basic sites determination

Lewis basic sites make it possible to determine the binding sites available in the biomass surface and allow the formation of chemical bonds between biomass-ions. Information on the number of Lewis basic sites on the sorbent material was obtained and used as a guideline for adsorption studies in evaluating the experimental molar ratio with metal ions. In brief, a suspension of 5 g of biomass was treated in 0.1 M KOH solution, and then in 30 mL of 0.5 M HCl solution. Afterwards, it was stirred for 24 h. After this period, 5 mL of filtered solution (0.45 μ m) was taken and titrated with 0.1 M NaOH solution. The differences in hydrogen ion (H^+) amounts in solution provide the basic Lewis site equivalents in biomass.



Treatments of biomass

The biomass treatments were carried out with the addition of metal ions, which could improve the ability of biomass to uptake P, and at the same time were not toxic or potentially polluting for the soil in its use as a soil conditioner or fertilizer. For these reasons we have selected Ca and Fe ions. Initially, 5 g of biomass was added directly in 50 mL of a solution containing 50 mmol of $\text{Ca}(\text{OH})_2$, shaking them together for 24 hours. Other attempts were made by carrying out a treatment that would allow us to introduce more calcium ions into the chemical composition of the biomass. This treatment involved putting 5 g of the biomass in 50 mL of solution with 10 mmol of KOH for 24 hours and, sequentially, with 50 mmol of CaCl_2 for 24 hours.

We tried to improve the P adsorption capacity of the biomass with iron ions. The first attempt was by treating 5 g of biomass put in direct contact with 50 mL, of 50 mmol of FeSO_4 solution and another 5 g of biomass, instead, was treated with 50 mmol FeCl_3 . and Both solutions were stirred for 24 hours. As seen above with calcium, the second attempt was to treat 5 g of biomass in contact with 10 mmol of KOH for 24 hours and, successively, with both 50 mL of a solution containing 50 mmol of FeSO_4 and 50 mL of a solution containing 50 mmol of FeCl_3 and shaking them for 24 hours. After treatment with the three cations, the solid residue was separated from the solvent by centrifugation (7000 rpm for 10 min) and rinsed with ultrapure water two times. The solids were then placed in an oven at 105°C for 24 hours.

All these materials (biomass + Ca^{2+} ; biomass + KOH + Ca^{2+} ; biomass + Fe^{2+} ; biomass + Fe^{3+} ; biomass + KOH + Fe^{2+} ; biomass + KOH + Fe^{3+}) have been used for subsequent batch P adsorption tests. The initial P content of the biomass used for the experiments was measured by mineralization of the sample and determination of the P content with UV-Vis spectrophotometry. On the treated materials, release tests of Ca^{2+} , Fe^{2+} and Fe^{3+} in ultrapure water, to verify the stability of the chemical interaction between the biomass and cations, were performed by immersing 1 g of the treated biomass in 30 mL of ultrapure water for 24 hours. All tests were performed in duplicate.

Together with Fe and Ca, the content of heavy metals, such as Zn, Cu, Cd, Ni, Pb, Mn and Cr, on the biomass was determined. Analyses of total amounts of metals were performed with an Agilent ICP-MS 7500ce instrument in quantitative mode with an external calibration in the range of 50-5000 ng mL^{-1} , and with ^{103}Rh , 1000 ng mL^{-1} , as internal standard. Three replicates were always performed. All solutions were obtained by diluting the corresponding ICP grade standard (1000 ng mL^{-1}).



Infrared measurements

To get a more complete view of the characteristics as a possible P adsorbent, biomass chemically treated with Ca^{2+} , Fe^{+2} and Fe^{3+} , as well as biomass itself, was analysed using the Fourier-transform infrared spectroscopy both before and after contact with the phosphate ions. Infrared spectra were recorded in the range $4000\text{-}400\text{ cm}^{-1}$ on a Perkin Elmer FT-IR spectrometer Spectrum Two. Every spectrum was recorded acquiring 64 scans at a resolution of 4 cm^{-1} . The Perkin-Elmer software allowed the acquisition and manipulation of spectra.

Point zero charges (PZC)

We performed electrophoretic mobility measurements to check the proposed competitive adsorption mechanism relying on the Doppler velocimetry technique (Bellini et al., 1995). The electrophoretic mobility was obtained from the measured frequency shift between the incident and scattered light. We derived the zeta potential from the electrophoretic mobility using a numerical approximate solution (O'Brien and White, 1978). The kinetic zero charge of the particles (PZC) value was calculated using the solid addition method. Accordingly, solutions of HCl and NaOH were mixed in six different vials at varied proportions to adjust the initial pH values in the range of 3.5 - 9.0. About $0.300\text{ }\mu\text{g}$ of the biomass was added to 20 mL of ultrapure water and shaken on an orbital platform shaker at 300 rpm for 24 h. At 0.200 mL of the resulting suspension, 2.5 mL of ultrapure water was added to the chosen pH and resuspended for 12 h at the final volume of 5 mL, and, finally, the Z potential (mV) was measured using a Coulter DELSA 440 SX instrument. From a plot of pH against mV, the PZC was obtained.

3.2.3. Batch experiments to test adsorption biomass ability

Two solutions of about 1 mmol with, respectively, hydrogen phosphate and dihydrogen phosphate ions in ultrapure water, were prepared. These were chosen because they are the principal inorganic phosphate species present in a range of pH between 5 and 8, typical of freshwater runoff.

Adsorption batch experiments were set up by immersing 1.5 g of three biomass types (Ca^{2+} , Fe^{+2} and Fe^{3+} biomass) in 50 mL of phosphate solutions, which were stirred together (250 rpm) overnight. The experiments were conducted at room temperature ($\approx 22^\circ\text{C}$). Then, the adsorbent matrix was separated by centrifugation at 7000 rpm for 10 minutes, and the concentration of phosphate ions in the solution was determined by UV-Vis spectrophotometry. All adsorption experiments were conducted in triplicate and averaged results were reported.



3.2.4. Kinetic modelling

The contact time chosen in the batch experiments to test adsorption biomass ability was 1 and 24 hours. Subsequently, to study the kinetics of adsorption, the selected contact times were 15, 30, 45, 60 minutes, 5 and 24 hours.

Pseudo-first and pseudo-second-order kinetic models were utilized to test the experimental data, and intraparticle diffusion was considered to examine the controlling mechanism involved in the biosorption of ions onto biomass, such as mass transfer and chemical reactions.

The pseudo-first-order equation follows the Lagergren theory of adsorption of soluble substances, and is given as:

$$q_t = q_{eq} (1 - e^{-k_1 t}) \quad [1]$$

where q_{eq} and q_t are the amounts in $mg\ g^{-1}$ of adsorbed ions on the biomass at equilibrium at time t and k_1 is the first-order biosorption rate constant in min^{-1} .

The pseudo-second-order equation is also based on the sorption capacity of the solid phase and is given as (Ho, 1999):

$$q_t = q_{eq}^2 k_2 t / (1 + k_2 q_{eq} t) \quad [2]$$

where k_2 is the second-order biosorption rate constant ($g\ mg^{-1}\ min^{-1}$), and q_{eq} is the biosorption capacity at the equilibrium ($mg\ g^{-1}$).

When intraparticle diffusion is the rate-limiting step, the adsorbate uptake varies with the square root of time. The intraparticle equation can be described as (Ho, 2000):

$$q_t = K_s t^{0.5} \quad [3]$$

where q_t is the amount of adsorbed ions ($mg\ g^{-1}$) at the contact time t (min) and K_s is the intraparticle diffusion constant ($g\ mg^{-1}\ min^{-1}$).

3.2.5. Equilibrium isotherm models

The adsorption isotherms can use to predict the adsorption capacity of a particular substance. The adsorption isotherm data of P onto biomass, both in the single and multi-component system, were analysed using both Langmuir and Freundlich equations. The Langmuir model, monolayer sorption of a solute from a solution, is given by:

$$q_{eq} = Q_{max} k_1 C_{eq} / (1 + k_1 C_{eq})^{-1} \quad [4]$$

where:

q_{eq} = equilibrium adsorbate loading on the biomass ($mg\ adsorbate\ g^{-1}$ of biomass);

C_{eq} = equilibrium concentration of the adsorbate ($mg\ adsorbate\ L^{-1}$);



Q_{\max} = ultimate capacity (mg adsorbate g^{-1} of biomass);

k_1 = relative energy (intensity) of adsorption ($L\ mg^{-1}$), also known as binding constant.

The Langmuir isotherm considers sorption as a chemical phenomenon. It was first theoretically examined in the adsorption of gases on solid surfaces. The smaller k_1 , the higher is the affinity of the sorbent for the sorbate.

Q_{\max} can also be interpreted as the total number of binding sites that are available for biosorption, and q_{eq} as the number of binding sites that are in fact occupied by the sorbate at the concentration C_{eq} . Although the Langmuir model sheds no light on the mechanistic aspects of sorption, it provides information on uptake capabilities and can reflect the usual equilibrium sorption process behavior. Langmuir assumed that the forces that are exerted by chemically unsaturated surface atoms (total number of binding sites) do not extend further than the diameter of one sorbed molecule and therefore sorption is restricted to a monolayer. The Freundlich model, based on sorption on a heterogeneous surface, is represented as:

$$q_{eq} = K_2 C_{eq}^{1/n} \quad [5]$$

where:

q_{eq} = equilibrium adsorbate loading on the biomass (mg adsorbate/g of biomass);

C_{eq} = equilibrium concentration of the adsorbate (mg adsorbate L^{-1});

K_2 = Freundlich adsorption constant;

n = Freundlich exponent.

K_f and n are the Freundlich constants indicative of adsorption capacity and adsorption intensity, respectively. Values of n between 1 and 10 are favourable for adsorption.

The Freundlich relationship is an empirical equation. It does not indicate a finite uptake capacity of the sorbent and can thus only be reasonably applied in the low to intermediate concentration ranges.

The fundamental difference between Freundlich's and Langmuir's adsorption isotherms is that Freundlich's adsorption isotherm is empirical, while Langmuir's is theoretical.

The Langmuir adsorption isotherm gives us an idea of how the solute is adsorbed onto the surface of a solid in a monolayer structure, while the Freundlich isotherm is associated with multilayer adsorption onto the surface of the solid.

Langmuir's isotherm is more satisfactory than Freundlich's for explaining the adsorption of solutes onto solids and explains the mechanism of chemisorption.



3.2.6. The batch experiments desorption

Desorption tests were performed on biomass enriched in Ca and Fe by immersing 1 g of treated biomass in 30 mL of ultrapure water for 24 hours to evaluate the Ca and Fe content stably bound to the biomass. The same conditions were repeated to assess P desorption from the biomass previously used for the P adsorption tests.

3.3 Results

3.3.1 Biomass characterization

Lewis basic sites determination

Lewis basic sites for our biomass were 2.31 ± 0.08 mmol H^+g^{-1} . These values are important because they define the maximum amount of calcium and iron that, added to biomass, could affect the adsorption of dissolved phosphate ions in the solution. In the case of bivalent (Ca^{++} , Fe^{++}) or trivalent cations (Fe^{+++}), the maximum adsorption capacity could be 1.16 ± 0.04 and 0.77 ± 0.03 mmol g^{-1} , respectively.

Determination of PZC

The pH value at which the functional groups of the adsorbent surface do not affect the pH of the solution during adsorption is the pH at the point of zero charge. The zeta-potential measurements of our biomass in water, enriched and not, indicate that the point of zero charges occurs in a pH range of 5.5-5.8. Consequently, when the pH value was lower than the pH at PZC, the surface charge of the enriched biomass was found to be slightly negative and for pH values higher than the pH at PZC the surface charge of the modified biomasses was found highly negative.

Calcium and iron determination on natural and treated biomass

The Ca and Fe content in the chemical composition of the biomass, obtained from the mineralization of the solid material and subsequent measurement, was about 57.5 mg Ca and 4.6 mg Fe in 1 g of biomass. The attempt of enrichment using $Ca(OH)_2$ increased calcium content to 166.6 mg g^{-1} . With the second treatment, a promising increase in calcium content of 184.0 mg g^{-1} was found (Table 7). Also with Fe ions, the attempt using directly both $FeSO_4$ and $FeCl_3$, obtained 9.7 and 7.1 mg Fe g^{-1} of biomass, respectively. With the second attempt, the iron content increased significantly and 60.8 and 103.1 mg Fe g^{-1} for Fe^{++} and Fe^{+++} respectively were measured (Table 8). All these materials (biomass + Ca^{2+} ; biomass + KOH + Ca^{2+} ; biomass + Fe^{2+} ; biomass + Fe^{3+} ; biomass + KOH + Fe^{2+} ; biomass + KOH + Fe^{3+}) have been used for subsequent batch P adsorption tests. The initial P content



of the biomass used was 0.45 mg P g^{-1} . The content of other metals, such as Zn, Cd, Cu, Ni, Pb, Mn and Cr, in the chemical composition of the biomass, obtained from the mineralization of the solid material and subsequent measurement values, expressed in $\mu\text{g g}^{-1}$, were found to be low (Table 9) and in any case lower than the threshold concentrations of contamination for soils in agricultural areas reported in Italian legislation (Decreto Legislativo, 152/2006). It may be relevant if the use of P-enriched biomass is intended for direct incorporation within the soil as a soil conditioner or substrate.

Table 7. Ca (mg g^{-1}) content in biomass after Ca enrichment

Samples	non-treated	Ca(OH) ₂	KOH+CaCl ₂ (10mmol)	KOH+CaCl ₂ (50mmol)
Ca (averaged)	57.5	166.6	125.9	184.0
<i>st. dev.</i>	17.9	2.2	2.7	1.2

Table 8. Fe (mg g^{-1}) averaged content in biomass after various Fe enrichment

Samples	non-treated	FeSO ₄	FeCl ₃	KOH+ FeSO ₄	KOH+ FeCl ₃
Fe-biomass	4.3	9.7	7.1	60.8	103.1
<i>st. dev.</i>	1.6	1.8	0.7	8.2	32.4

Table 9. Zn, Cd, Cu, Ni, Pb, Mn and Cr ($\mu\text{g g}^{-1}$) averaged content in natural biomass (dry weight)

Elements ($\mu\text{g g}^{-1}$)	Zn	Cd	Cu	Ni	Pb	Mn	Cr
Natural biomass	8.6	< 0.1	3.2	< 1.0	< 1.0	18.0	0.2
<i>st. dev.</i>	1.4		1.13			0.6	0.3

The pH value phosphate solutions in contact with the biomass

For the adsorption test, all the sizes of the biomass matrix were used and no substantial difference in the P adsorption phenomena, using the different particle sizes, was noticed. The pH of the KH₂PO₄ solution started from a value of 5.1 and, after being in contact with the untreated biomass, attained pH 5.7 after 1 hour, then lowered and stabilized to pH 5.3 after 24 hours. The pH of the K₂HPO₄ solution started at pH 8.8 and, after contact with the biomass, slowly dropped to a sub-acidic pH stabilizing at pH 5.3. The pH of both solutions in contact with the biomass attained a stable value in both cases at a sub-acidic pH of around 5.5, the same pH measured by immersing the biomass in ultrapure water, both after 1 hour and 24 hours. Regarding the pH values from the contact of the chemically modified biomasses with the phosphate solutions in K₂HPO₄ and KH₂PO₄, they are both

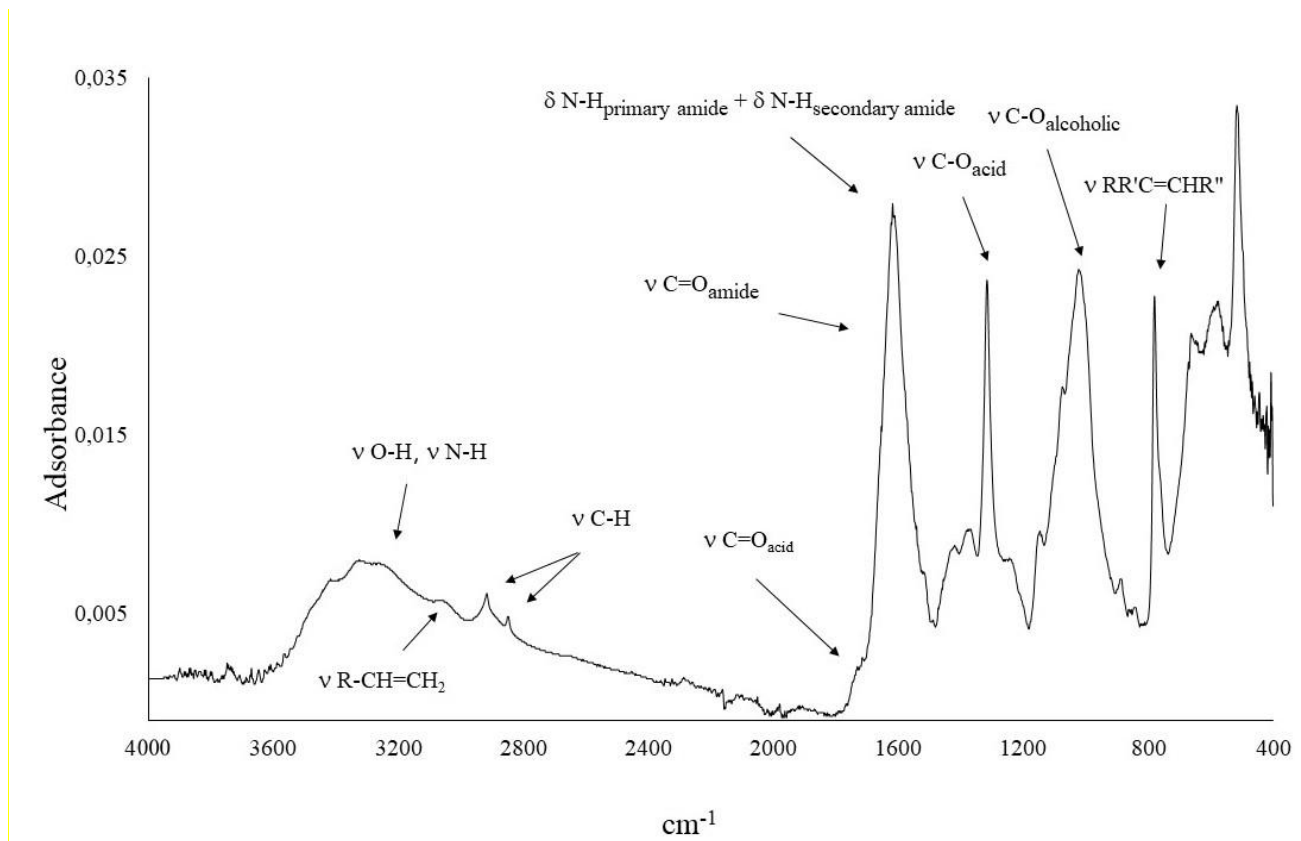
5.8 ± 0.1 after 24 hours. The different particle sizes of the biomass do not affect the pH of the solutions (data not shown).

FT-IR spectra

FT-IR spectral study of natural biomass (Figure 3) shows different absorption peaks. In the treated biomass samples, no new signal was evidenced by FT-IR spectra (data not shown). The characteristic peaks of phosphate ions usually appear at $1000-1100\text{ cm}^{-1}$ (Sowmya and Meenakshi, 2014), but in our case, the broad and strong bands between 1180 and 950 cm^{-1} , related to the C-OH and C-O-C groups of alcohol or ether, hide phosphate ions' features.

The broad absorption band in the range $3700 - 2500\text{ cm}^{-1}$ corresponds to the intramolecular vibrational stretching of the -OH groups, which are extensively involved in hydrogen bonding, and weak peaks at 2842 and 2932 cm^{-1} related to the symmetric and asymmetric C-H bond stretching vibrations of the CH_3 and CH_2 groups (Anirudhan et al., 2012).

Figure 3. FT-IR spectra of dry biomass





Below 2000 cm^{-1} , broad bands, between 1730 and 1500 cm^{-1} , can be seen. A medium-intensity shoulder can be seen at 1720 cm^{-1} attributable to C=O stretching of non-ionized carboxylic acid groups or other carbonyl-containing compounds; the bands at 1645 , 1618 and 1520 cm^{-1} can be attributed to Amide I, Amide II, C=C bands and asymmetric stretching of the $-\text{COO}^-$ group. The bending vibrations of -OH and -CH in the $-\text{CH}_2$ groups were found to be 1634 cm^{-1} and 1427 cm^{-1} , respectively. The absorption peaks between 1480 and 1300 cm^{-1} are assigned to the C-H bending of the CH_3 and CH_2 groups plus symmetric stretching of $-\text{COO}^-$ and stretching of the C-N group. The vibrational peaks at 1241 cm^{-1} are due to C-O-H bending and 1143 cm^{-1} due to asymmetric stretching of the C-O-C glucosidic bond. The bands between 1180 and 950 cm^{-1} are related to the C-OH and C-O-C groups of alcohol or ether, and finally, the bands at 888 and 780 cm^{-1} could be assigned to the out-of-plane deformation of C-H groups of $\text{RR}'\text{C}=\text{CHR}''$ type or similar.

3.3.2. Batch experiment on P adsorption

The results of the experimentations on the pure biomass, even regardless of the use of one of the three different particle sizes, showed no significant chemical interaction of adsorbent with the different phosphate anions. P adsorption tests conducted with the solution containing H_2PO_4^- ions did not produce any positive result: the biomass, Ca-enriched or not, did not show any significant ability to remove H_2PO_4^- ions present in the solution, more precisely, the adsorption was 5%, after one hour with Ca-enriched biomass, with particle size $0.250\text{mm} < \varnothing \leq 2\text{mm}$. This sorbed P, within 24 hours, was released into the solution, highlighting no adsorption capacity. The batch experiments conducted using a solution containing HPO_4^{2-} ions showed different results: a removal capacity of about 46% was measured after 1 hour, stabilizing at 43% after 24 hours (Table 10). This behaviour was recorded with all sizes of biomass. Even after 24 hours, the P removal capacity of the three particle sizes remained almost unchanged. No substantial difference in the P adsorption phenomena, using the different particle sizes, was noticed, therefore intermediate particle size ($0.250\mu\text{m} < \varnothing \leq 2\text{mm}$), was used for the subsequent experiments.

Tables 10 and 11 show that P adsorption tests produced different results, depending on the type of Fe-enriched sample used and, on the solution used, H_2PO_4^- or HPO_4^{2-} . The samples of biomass, directly enriched in Fe^{2+} and Fe^{3+} , showed no ability to remove either H_2PO_4^- or HPO_4^{2-} ions present in the solution, and the contact time did not influence this result. Samples of biomass prepared by double treatment, first in KOH and then in FeSO_4 or FeCl_3 , produced better results when in contact with both solutions containing H_2PO_4^- and HPO_4^{2-} ions. Samples treated with KOH and Fe^{2+} , after 1



hour, adsorbed 6% and 14%, respectively from H_2PO_4^- and HPO_4^{2-} solution, both reaching about 25% after 24 hours. Samples treated with KOH and Fe^{3+} , after 1 hour, adsorbed 26% and 28%, respectively from H_2PO_4^- and HPO_4^{2-} solution, reaching 44% and 37% after 24 hours.

Table 10. P adsorption of Ca-enriched biomass, after 1 and 24 hours, in H_2PO_4^- and HPO_4^{2-} solutions

H ₂ PO ₄ ⁻ solution						
Samples	Ø	C ₀ mg P 50mL	C _{1h} mg P g ⁻¹	P _(1h) removal	C _{24h} mg P g ⁻¹	P _(24h) removal
Ca-biomass <i>st. dev.</i>	2000µm	5.1	<0.1	2%	<0.1	3%
Ca-biomass <i>st. dev.</i>	250- 2000µm		0.3	5%	<0.1	0%
Ca-biomass <i>st. dev.</i>	<250µm		0.3	6%	<0.1	0%

HPO ₄ ²⁻ solution						
Samples	Ø	C ₀ mg P 50mL	C _{1h} mg P g ⁻¹	P _(1h) removal	C _{24h} mg P g ⁻¹	P _(24h) removal
Ca-biomass <i>st. dev.</i>	2000 µm	4.8	2.0	42%	1.9	40%
Ca-biomass <i>st. dev.</i>	250- 2000µm		2.2	46%	2.1	43%
Ca-biomass <i>st. dev.</i>	<250µm		2.1	44%	2.1	44%

Note: Ø= size particle of biomass; C₀ = initial content P in solution; C_{1h} = P content in biomass after 1h; C_{24h} = P content in biomass after 24h.

Table 11. P adsorption from H_2PO_4^- and HPO_4^{2-} solutions

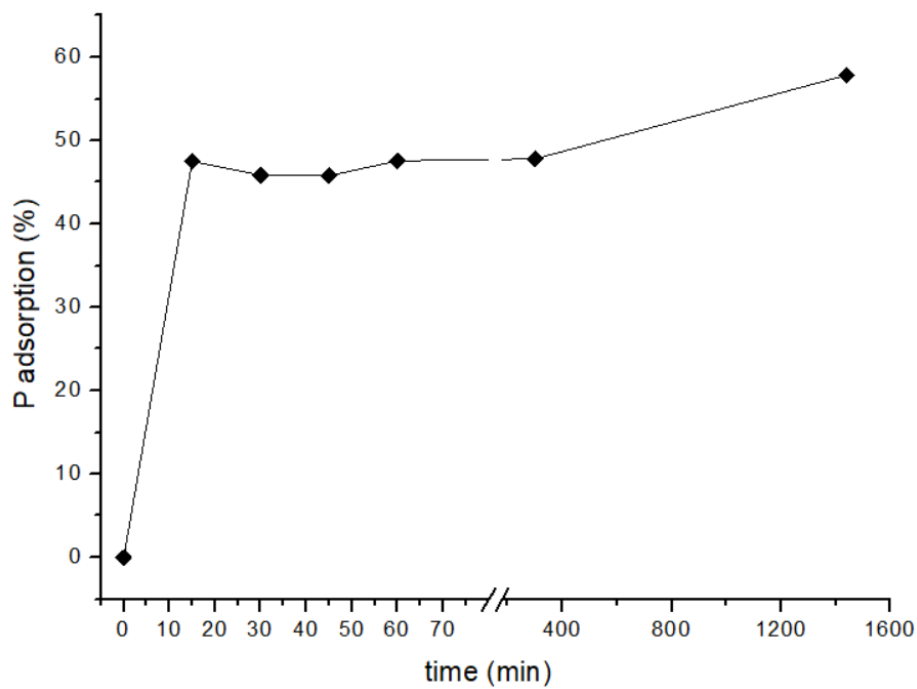
H ₂ PO ₄ ⁻ solution							
Samples	C ₀	15'	30'	45'	60'	5h	24h
	mgP/50 mL	mg g ⁻¹	mg g ⁻¹	mg g ⁻¹	mg g ⁻¹	mg g ⁻¹	mg g ⁻¹
biomass+KOH+Fe ²⁺	5	<0.1	<0.1	0.2	0.3	0.6	1.2
st. dev.		-	-	0.3	0.2	0.1	0.2
% adsorption		<1	<1	4	6	12	24
biomass+KOH+Fe ³⁺	5	0.2	0.9	1.2	1.3	1.8	2.2
st. dev.		0.1	0.1	0.1	0.1	0.1	0.1
% adsorption		4	17	23	26	36	44

HPO ₄ ²⁻ solution							
Samples	C ₀	C _{15'}	C _{30'}	C _{45'}	C _{60'}	C _{5h}	C _{24h}
	mgP/50 mL	mg g ⁻¹	mg g ⁻¹	mg g ⁻¹	mg g ⁻¹	mg g ⁻¹	mg g ⁻¹
biomass+KOH+Fe ²⁺	5	0.3	0.5	0.6	0.7	0.9	1.3
st. dev.		0.1	0.1	0.1	0.1	0.1	0.1
% adsorption		5	9	12	14	17	27
biomass+KOH+Fe ³⁺	5	0.8	1.1	1.4	1.4	1.7	1.9
st dev..		0.1	0.2	0.1	0.2	0.2	0.2
% adsorption		16	22	28	28	35	37

3.3.3 P adsorption kinetics

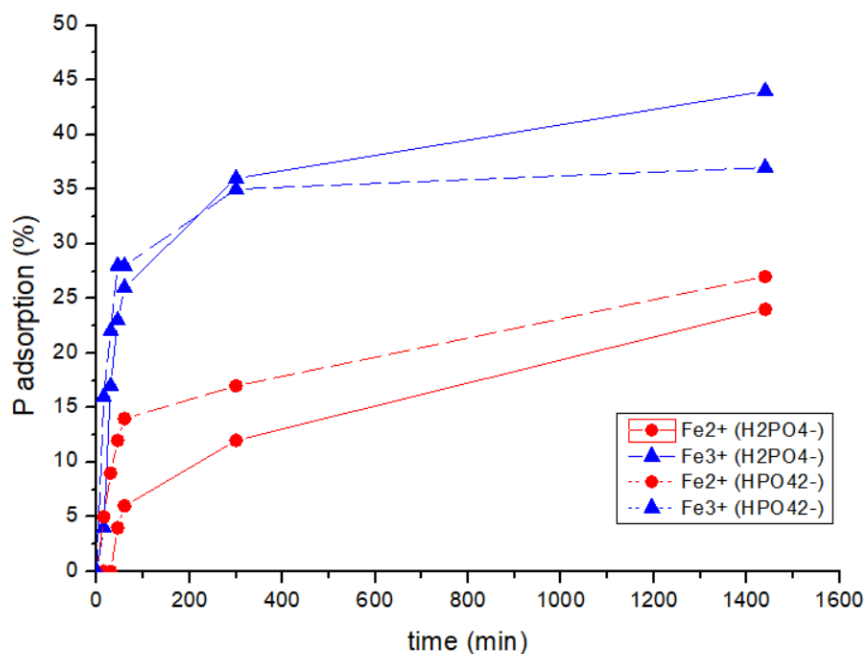
From the data collected on the P content in solution after each predetermined time, it appears that approximately 48% of P is adsorbed within the first 15 minutes after contact. For subsequent samplings, the removal capacity of the biomass remains almost unchanged, reaching the maximum adsorption after 24 hours with the adsorption of 58% of P present in the solution. In quantitative terms, 1 g of biomass adsorbs about 1.9 mg of P from the solution after 1 hour and reaches 2.3 mg of P after 24 hours (Figure 4).

Figure 4. P adsorption kinetics of Ca-biomass



From the study of adsorption kinetics, the physicochemical interaction between the Fe-biomass and P occurs slowly, reaching just 16% of P removal within the first 15 minutes only in the biomass samples enriched in Fe^{3+} immersed in the HPO_4^{2-} solution (Figure 5).

Figure 5. P adsorption kinetics of Fe-enriched biomass





Adsorption kinetics model

Data on P uptake rates on biomass were tested with the pseudo-first-order and pseudo-second-order models and Table 12 summarizes the parameters of the kinetic models applied.

The pseudo-first-order model did not fit our data. Conversely, the pseudo-second-order model well described the adsorption mechanisms ($R^2 > 0.94$, Q_e calculated in comparison with Q_e experimental) and both Q_e calculated and K_2 values was coherent with others reported in the literature (Faraji et al., 2020; Fang et al., 2020).

Although the experimental data of our samples gave a good fit to the pseudo-second-order model, it should be kept in mind that the model is based on chemisorption, which involves the sharing or exchange of electrons between adsorbent and adsorbate, and homogeneity of all adsorption sites, not considering the heterogeneous character of the biomass and the existence of other processes such as intraparticle diffusion, mass transfer, or ion interaction. Therefore, to test whether intraparticle diffusion is the limiting step, regression analysis between Q_t and $t^{0.5}$ is usually performed (Ginestra et al., 2009). The application of this analysis showed that this model did not fit our experimental data, so intraparticle diffusion is not the limiting factor (Nharingo et al., 2016), and phosphate ion uptake is essentially limited to adsorption occurring on the biomass particles' surfaces.

Table 12. Parameters of the applied kinetic models

Kinetics models	Parameter	Ca-biomass	Fe ⁺⁺ -biomass in HPO ₄ ²⁻	Fe ⁺⁺⁺ -biomass in HPO ₄ ²⁻	Fe ⁺⁺ -biomass in H ₂ PO ₄ ⁻	Fe ⁺⁺⁺ -biomass in H ₂ PO ₄ ⁻
	Q_e experimental (mg g ⁻¹)	2.27	1.33	1.87	1.22	2.20
Pseudo 1 st order	Q_e (mg g ⁻¹)	1.48	1.02	1.04	1.25	1.67
	K_2 (g μmol ⁻¹ min ⁻¹)	37.40	31.99	11.73	38.25	17.26
	R^2	0.15	0.68	0.83	0.85	0.84
Pseudo 2 st order	Q_e (mg g ⁻¹)	2.01	1.24	1.89	1.63	2.24
	K_2 (g μmol ⁻¹ min ⁻¹)	13.54	0.93	1.62	0.08	0.52
	R^2	0.96	0.94	0.99	0.97	0.96

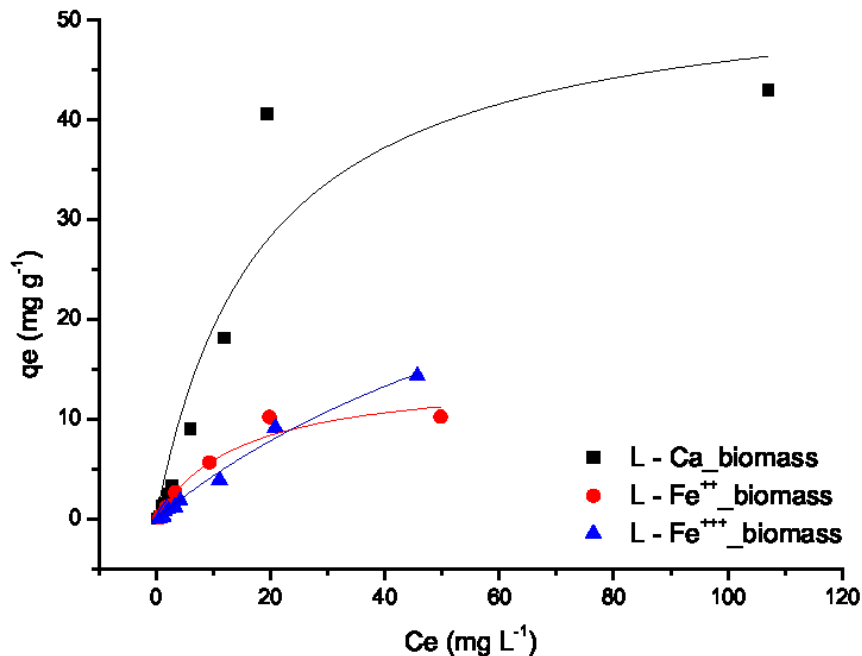
3.3.4 Equilibrium isotherm models

The results of the adsorption studies show a rapid increase in P adsorption by the biomass with the concentration increasing to a plateau.

The collected data were studied according to the Langmuir and Freundlich models. The isotherm that best fits our data was found to be the Langmuir isotherm, as shown in Figure 6, and its parameters are expressed in Table 13. The Freundlich isotherm failed to describe the adsorption phenomenon

that occurred and the parameter values of K_f and n ($n > 1$) did not suggest a favourable adsorption intensity.

Figure 6. Langmuir isotherm type for Ca-biomass, Fe^{++} -biomass and Fe^{+++} -biomass



The adsorption isotherms of P on biomass were studied at ambient temperatures (20°C) and are shown in Table 13.

Table 13. Description of fitting parameters applied to Langmuir and Freundlich isotherm models.

Isotherm models	Parameter	Ca-biomass	Fe^{++} -biomass in HPO_4^{2-}	Fe^{+++} -biomass in HPO_4^{2-}
	Q_e experimental ($mg\ g^{-1}$)	42.973	10.23	14.3
Langmuir	Q_{max} ($mg\ g^{-1}$)	54.31	14.58	44.21
	K_l (min^{-1})	0.054	0.067	0.01
	R^2	0.90	0.95	0.99
Freundlich	K_f (min^{-1})	1.67	1.35	0.50
	n	0.45	3.78	1.69
	R^2	0.62	0.56	0.77

3.3.5 The effect of pH values and pH_{pzc}

P mobility in variable charge (v-c) materials is dominated by the orthophosphate ligand exchange with surface hydroxyl groups on v-c minerals (Sollins et al., 1988). In our biomass, at low pH (< 5.0), the zeta potential versus pH curve for the sorbent surface is slightly negative, at higher pH (> 6.0),



strongly negative and values around zero at pH = 5.5-5.8 were measured. It is generally accepted that anions should be adsorbed more effectively at pH values lower than pH at PZC because, at these pH values, the functional groups on the adsorbent surface could have adopted a positive net charge form (Anirudhan et al., 2009). On the other hand, the surface charge will be negative if the pH is higher than the pH at PZC, allowing cations to be adsorbed. Thus, when the ion exchange process occurs, phosphate adsorption is closely related to the pH of the medium. P exists as neutral species, H_3PO_4 , at pH below 2.0 and as species $H_2PO_4^-$, the predominant species in aqueous solutions with pH values between 2.0 and 3.5 (Aryal et al., 2011), and HPO_4^{2-} at pH between 7.0 and 9.0. After the contact with the untreated biomass, the pH of the $H_2PO_4^-$ solution increased from 5.1 to 5.7 after an hour, then to 5.3 after 24 hours. The pH of HPO_4^{2-} solution initially was at 8.8, but after the contact with the biomass, gradually decreased to a sub-acidic pH until it stabilized at 5.3. After one hour and after 24 hours, the pH of both solutions in contact with the biomass in both situations stabilized at a sub-acidic pH of around 5.5, the same pH obtained by immersing the biomass in ultra-pure water. The biomass's various particle sizes have no impact on the solutions' pH (data not shown).

3.3.6 The batch experiments desorption

Ca-biomass

The Ca release, assessed on biomass previously enriched, is $91.6 \text{ mg Ca g}^{-1}$, compared with the 143 mg Ca g^{-1} initially present. The content of stably bound Ca in the chemical composition of the biomass, therefore, is about 52 mg Ca g^{-1} , an amount that is found to positively influence the interaction between biomass and P. In contrast, the desorption of P conducted on the biomass previously used for the P adsorption test is found to be minimal. Only $0.2 \text{ mg of P g}^{-1}$ was released after the first hour, rising to $0.3 \text{ mg of P g}^{-1}$ after 24 hours. Considering that, from the study of adsorption kinetics, the biomass adsorbed 1.9 and $2.3 \text{ mg of P g}^{-1}$ after 1 and 24 hours, respectively, it follows that about 88% of the P is stably retained by the biomass.

Fe-biomass

The Fe release, evaluated on biomass previously enriched in Fe^{2+} and Fe^{3+} , is 0.6 and $3.1 \text{ mg of Fe g}^{-1}$, respectively, compared with the 100.2 and $100.5 \text{ mg of Fe g}^{-1}$ initially present. The Fe content is almost totally stably bound in the chemical composition of the biomass and is found to positively influence the interaction between biomass and P. In contrast, the desorption of P, conducted on the biomass previously used for the P adsorption test, is found to be minimal. Only 0.15 and $0.24 \text{ mg of P g}^{-1}$ were released after the first hour, respectively, from Fe^{2+} and Fe^{3+} enriched biomass, confirming



the same data after 24 hours. Considering that, from the study of adsorption kinetics, biomass enriched in Fe^{2+} and Fe^{3+} adsorbed 0.3 and 1.3 mg of P g^{-1} and 0.8 and 1.9 mg of P g^{-1} , respectively, after 1 and 24 hours, it follows that about 90% of the P is stably retained by the biomass.

3.4 Discussions

3.4.1 Biomass characterization

Lewis basic sites and PZC

The estimation of the Lewis basic sites, corresponding to the number of accessible complexing sites for biomass gram, both ionic and non-ionic has been essential to a proper plan of adsorption studies with Ca and Fe metal ions to enrich the biomass itself. The results obtained have been promising, when compared to other biosorbents (e.g. biochar, Melia et al., 2019), to improve, with enrichment operations, the ability of biomass to uptake P-negative ions.

Theory predicts that adding phosphate to soil should affect cation retention in v-c soils (Sollins et al., 1988). Because P adsorption depends both on electrostatic attraction and chemical interactions (Özacar, 2003; Yan et al., 2010), when the surface of biomass, enriched or not, for $\text{pH} > 6.0$ were strongly negative, then P adsorption was essentially impeded by the increasing electrostatic repulsions with multivalent P anions in the solution. Similarly, for $\text{pH} < 5.0$, though the surfaces of biomasses were only slightly negative. Therefore, these determinations suggest only a pH value of about 5.0-6.0 as the possible value to have a chemical interaction. The obtained results are explained by the presence in significant amounts of partial or entire negatively charged binding sites on the surface area of our biomass, making difficult any possible chemical affinity with the P, or any other negatively charged ions. However, P sorbed and zeta potential have no strict relationship, although P sorption may be influenced by surface charge (Zhou et al., 2005).

Metal determination on natural and treated biomass.

As expected, KOH treatment, followed by 50 mmol of CaCl_2 , has ensured the greatest increase in Ca content (Table 7). The treatment first in KOH and after in FeSO_4 or FeCl_3 has higher effectiveness in binding more iron ions on biomass (Table 8), favouring a more significant chemical interaction with Fe^{3+} than with Fe^{2+} ions.

As phosphate rock normally contains heavy metals (e.g., Scholz et al., 2013), the use of mineral fertilizers must however consider this co-factor of potential pollution. The content of other metals, Cr, Mn, Ni, Cu, Zn, Cd and Pb, in our biomass, due to their extremely low concentrations, suggests its possible direct application in agriculture.



3.4.2 Batch experiment on P adsorption

The obtained results could be explained because on the surface area of our biomass, partial or entire negatively charged binding sites are present in significant amounts, making difficult any possible chemical affinity with the P, or any other negatively charged ions. Furthermore, the calcium amount naturally present in the biomass was not enough to influence the mutual interaction with phosphate ions. From this consideration the decision followed to increase the binding sites on which P could bind by increasing the calcium and iron content in the biomass. The choice of these two ions was closely related to our starting goal, to use a natural, or develop a modified, sorbent to apply directly in agriculture practices, and as such, without adding substances, and in every case without leaving residues from the modifying treatment that could pollute the soil or cause undesirable effects on plant growth (use of zirconium as a bridge between natural biomass and phosphate is an example, Jiang et al., 2019). Ca-enriched biomass, in contact with H_2PO_4^- fails to establish chemical-physical interaction, which is what happens between Ca and HPO_4^{2-} ions. Probably the reason is due to the high solubility values of $\text{Ca}(\text{H}_2\text{PO}_4)_2$, which tends to remain in solution rather than bind stably to the biomass surface unlike CaHPO_4 (solubility: CaHPO_4 0.1g L^{-1} , $\text{Ca}(\text{H}_2\text{PO}_4)_2$ 18g L^{-1}). The Ca increase influenced the P adsorptive capacity: 45% after one hour, remaining constant after 24 hours. This behaviour agrees with the adsorptive capacity of different Ca-enriched biomass (Wang et al., 2018). Comparing the behaviour of the four Fe-biomass samples, we see that the ones treated in KOH and Fe^{2+} have a lower P removal capacity than the samples treated in KOH and Fe^{3+} . Indeed, samples treated in KOH and Fe^{3+} offer a higher removal capacity manifested as early as 1 hour after contact with the two phosphate solutions, but its best performance was obtained in contact with the solution containing H_2PO_4^- ions.

3.4.3 P adsorption kinetics

The adsorption kinetics (Figure 4) show that the phenomena of chemical-physical interaction between the Ca-enriched biomass and P occurs very quickly, reaching almost 48% of P removal within the first 15 minutes. This result is very significant in planning to use this modified biomass solution to a scale where large quantities of water are to be treated allowing a relatively short contact time and consequently fast flows. The positive interaction in the presence of Ca ions is also confirmed in other environmental contexts (Arias et al., 2001), suggesting the coexistence between adsorption and co-precipitation phenomena with P.



Also interesting are the results obtained with iron ions. The theory calls for the formation of a coordination bond between the anionic ligand (Lewis acid-base interaction) accompanied by the electrostatic attraction (Sengupta and Pandit, 2011). Our four kinetics (Figure 5) show a slower and more gradual pattern of adsorption: in time the biomasses increase the removal efficiency, reaching, after 24 hours, a 44% of P removal in the case of the Fe^{3+} -enriched sample in contact with the solution containing H_2PO_4^- ions. Also here, however, we have a good possibility of application on a real scale, considering that after 30 - 45 min we have a removal of about 20%. The adsorption kinetics of Ca- and Fe-treated biomass suggest different adsorption times, highlighting very fast mechanisms of biomass-P interactions for Ca-enriched biomass compared to Fe, which instead has a slower trend; on the other hand, there are no major differences in adsorption capacity between the different materials. Therefore, both can provide a good P removal capacity, choosing to use Ca-biomass or Fe-biomass appropriately depending on the application and contact time required.

3.4.4 Equilibrium isotherm models

The L isotherm type is usually associated with the adsorption of ionic substrates with weak competition from solvent molecules. Between the L isotherms, Langmuir and Freundlich ones are the more commonly used to fit experimental data hypothesizing a monolayer interaction (e.g., Rehman and Qayyum, 2020; Zhou et al., 2005). Our results (Table 13) find that the Langmuir model, compared to the Freundlich model, provided a better fit of the equilibrium data. The Langmuir equation described the equilibrium conditions of adsorption behavior in the sorbate-sorbent system, where low values of K_1 , suggest high sorbent affinity for sorbate, while the Freundlich model was not effective in describing the collected data. Based on the Langmuir model, the theoretical maximum adsorption capacities were 54.31 mg P per g of biomass. In our system, the adsorption rate increased over time due to the presence of enough quantities of binding sites and abundant P in solution, so that instantaneous adsorption (boundary layer diffusion on the external surface) and film diffusion (external surface adsorption) might be the P immobilizing mechanism. Afterwards, the decreased adsorption rate might imply an intraparticle diffusion mechanism as a rate-limiting step (Zhu et al., 2020).

3.4.5 The desorption experiments

The batch desorption experiments were conducted on the enriched biomass to verify the stability of calcium or iron within the adsorbent chemical composition. Generally, lower desorption values indicate a strong interaction between adsorbent and adsorbate (Nardis et al., 2022). Calcium stably



bound in the chemical composition of the biomass (52 mg Ca g^{-1}) positively influences the interaction with biomass: 88% of the P is stably retained by the biomass. Iron is stably bound within the chemical composition of the biomass, as less than 3% is released in the desorption test: 90% of the P is retained by the biomass. Therefore, our attempts to recover P from biomass, and reuse both the P and the biomass itself for new P adsorption cycles from water, failed. Especially since, in the soil, under oxic environmental conditions, inorganic P in solution would be rapidly adsorbed by intracellular polymeric substances of soil biota, and taken up as internal P and, thus, would not be available to plants (Zhou et al., 2017).

Indeed, the P desorption test in HCl required a too-high amount of acid to remove almost all of the adsorbed P, or Ca or Fe with phosphate ions, so as to make the recovery and reuse of the biomass itself impractical because of the costs of this unsustainable process. These data support the idea of using an agricultural waste product to recover dissolved P in water and replenish both in the soil-plant system. The use of amendments resulting from the recycling of waste materials is a priority for soil health while valuing the total environment (Zhao et al., 2021). The applicability of this new material (Ca or Fe biomass) in a real system, in the form of a soil conditioner or plant substrate, at this point, can be quite simple and straightforward, without the need to make additional economic efforts. This agrees with De-Bashan and Bashan (2004) suggesting an adsorbing filter material that retains P efficiently, and after P saturation, uses the discarded filter as a fertilizer.

3.5 P removal from aqueous solutions using cactus pear pruning wastes: Concluding remarks and synopsis

Cactus pear pruning wastes (dried, ground, and enriched in calcium or iron) have been successfully used as an environmentally friendly and efficient alternative adsorbent for P removal from aqueous solutions (Figure 7). The maximum P adsorption capacities from Ca-biomass, Fe^{2+} -biomass and Fe^{3+} -biomass obtained were 2.16 ± 0.02 mg P per g of biomass, 1.3 ± 0.16 and 2.0 ± 0.3 , respectively. The experimental adsorption data were well described using Langmuir isotherm models, suggesting equilibrium conditions of adsorption behavior in the sorbate-sorbent system, where low values of K_1 , suggest high sorbent affinity for sorbate, while the Freundlich model was not effective in describing the collected data.

The adsorption kinetics show that there is a rapid chemical-physical interaction between the Ca-biomass and P, with almost 48% of P being removed within the first 15 minutes. On the other hand,



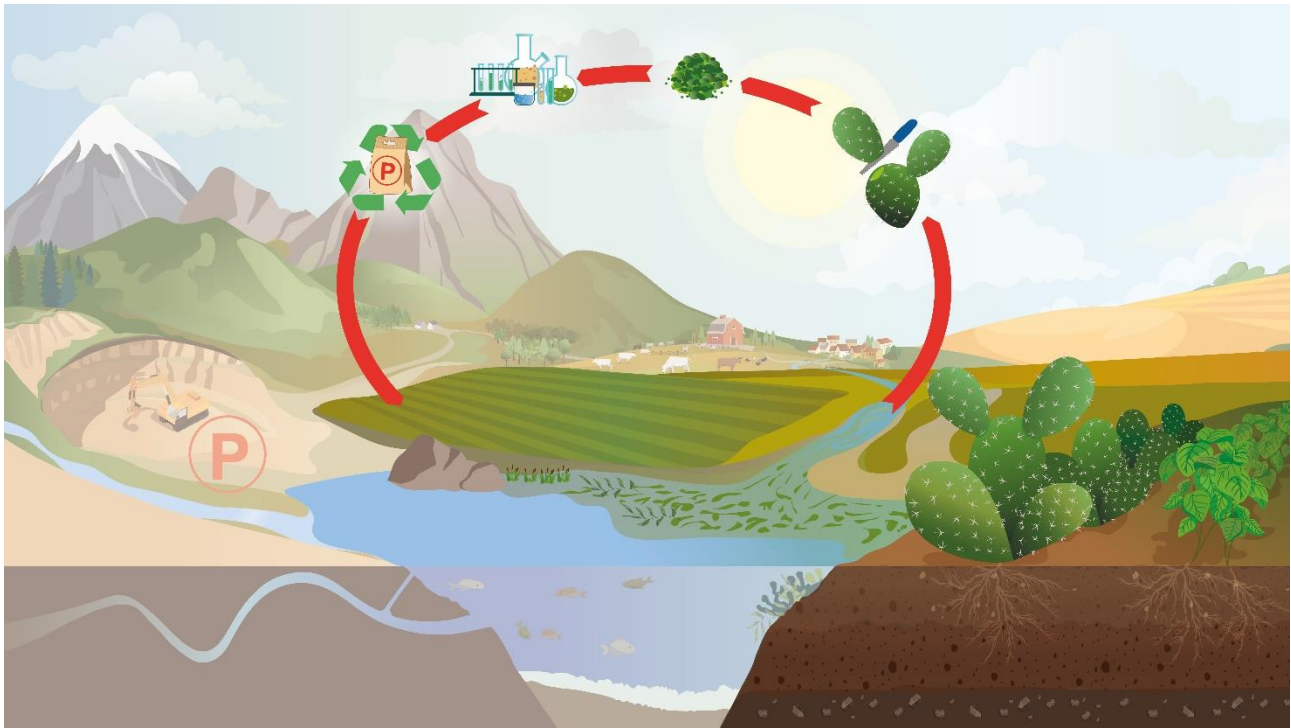
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the adsorption kinetics of Fe-enriched biomass reveal different adsorption times, showing mechanisms of biomass-P interactions slower compared to Ca-biomass.

The information on desorption was important to support the starting idea of the work: using an agricultural waste product to recover dissolved P in water and reintegrate both into the soil-plant system. The applicability of this new material in a real system, in the form of a soil conditioner or plant substrate, at this point, can be straightforward and simple, without the need to make additional economic efforts.

Figure 7. The potential of cactus pear pruning waste, as low-cost adsorbent biomass to remove phosphorus (P) from aqueous solution, was studied in batch mode. Biomass from cactus pear, natural and enriched in Ca or Fe, was used. Therefore, cactus pear pruning waste, previously reduced to powder and enriched with ions, could be a cheap adsorbent with a good P removal performance, which could be used directly in agriculture as a soil conditioner/fertilizer.





4. Evaluation of cactus pear powder amendment on the water content of two typical Mediterranean soils

Abstract

This section aims to investigate the hydraulic properties of benchmark soils in which this by-product is then incorporated. Here we show that amendment of powdered pruning waste of cactus pear shows positive effects on soil water retention. However, observable benefits require very high amendment proportions, more than 20% by volume. These quantities make use in the open field unrealistic but offer perspectives in the horticultural and floricultural sectors. These results reveal agreement with expected decrease in soil bulk density, increase in plant available water capacity or increase in swelling potential. These results add to previous knowledge an agronomic application: biomass addition at low amounts improves the drainable water capacity only in the case of not very clayey soils where their use becomes useless. The principles of the circular economy are important, but they must not be pursued a priori. For example, in the use of soil amendments, the behavior in the different soils conditions the suitability of their use.

4.1. Introduction

Arid and semi-arid regions, more than forty per cent of the global land surface, are key production areas for grains, fruits, and cash crops. Unfortunately, in these regions, agricultural development is limited by water shortages and low soil fertility (Myers et al., 2017). Water management in these soils is the key to agronomic success. In this regard, the use of amendments might be one of the most effective agronomic practices (Diacono and Montemurro, 2010, Kranz et al., 2020, Leogrande and Vitti, 2019, Ullah et al., 2021). For instance, biopolymers are ecologically friendly soil improvers that have been commonly employed to increase soil quality (Wang et al., 2023). Organic amendments increase soil organic matter (SOM) content, improving soil fertility and consequently crop yield (Bastida et al., 2012, Larney and Angers, 2012). They also indirectly improve hydrological functions and soil structure (Dong et al., 2021; Reynolds et al., 2007b) ameliorating the spatial arrangement, shape, and size of solid particles, voids, and SOM (Almendro-Candel et al., 2018). In particular, amendments modify soil water status, flow, evaporation, and retention (Jury and Horton, 2004). Organic amendments can be residues or by-products from both agricultural and industrial processes. However, by-product availability cannot be the only selection criterion to use as several factors,



including quality, applicability, sustainability, cost, and beneficial effects on the soil system, should be considered (Siedt et al., 2021). A variety of organic wastes have been proposed as soil amendment materials, with various characteristics and locally available in different regions (Larney and Angers, 2012). Types of organic materials include sewage sludge and municipal waste (Sadeghi et al., 2014; Paradelo et al., 2019), corn and sewage sludge (Głab et al., 2020), gardening waste (Arthur et al., 2011; Curtis et al., 2009), agricultural crop residues (Ibrahim et al., 2021), pruning waste (Benito et al., 2006; Auteri et al., 2022), or mixtures of these materials. Among the different types of soil improvers, pruning waste from agricultural activities is interesting as they are locally available and therefore generally sustainable in terms of costs. However, the large variability in the composition of pruning makes results hardly generalizable and studies conducted for a specific waste composition in each pedoclimatic condition should be transferred with caution.

Among the low-cost and large-available pruning waste, the residues of cactus pear, which grows in most semi-arid countries and is particularly widespread in Central America and the Mediterranean basin, currently leads to the disposal of 13-15 t ha⁻¹ of biomass per year (Enea, 2017). Cactus pear cladodes are succulent plant organs consisting of chlorenchyma, the outer layer in which photosynthesis occurs, and parenchyma, the innermost layer whose main function is to retain water. Both are composed of mucilage, which is a hydrocolloid forming stable (honeycomb-like) lattices capable of retaining large amounts of water. The presence of hydrocolloids explains the ability of Cactaceae to grow even in the most unfavorable climatic conditions. This characteristic makes it an interesting agricultural by-product. In addition to its potential as a soil amendment, some authors have evaluated dried and powdered cladodes of cactus pear as adsorbents for the removal of heavy metals or synthetic dyes from aqueous solutions (Nouri et al., 2021; Aziam et al., 2021).

Soil water retention (SWR) is the relationship between the volumetric soil water content and soil water suction, describing the ability of a certain soil to store and release water. Its knowledge is important for agro-environmental modelling or irrigation scheduling and optimization (*e.g.*, Hillel, 1998; Angulo-Jaramillo et al., 2016). The experimental assessment of the SWR is extremely time-consuming, thus attention has increased towards pedotransfer functions (PTFs) (Bouma, 1989). PTFs have the merit of predicting SWR from easily measured and/or routinely surveyed soil data, such as particle size distribution (PSD), SOM and bulk density (BD) (Arya and Paris, 1981; Weynants et al., 2009; Vereecken et al., 2016; Castellini and Iovino, 2019). The extreme simplification with which the hydraulic properties are estimated by the existing PTFs considers soils mostly composed by mineral fraction only while the effects of large amount of SOM added as soil conditioners is not



specifically accounted for. Furthermore, PTFs neglect the presence of plants and the rhizospheric environment. With these experiments, in fact, the intention is to provide useful information to be incorporated into PTFs, to improve their predictivity. Considering that, the global average distribution of root mass for all biomes and vegetation types is 75% in the upper 40 cm (Schenk and Jackson, 2002), neglecting the different properties of this layer of soil, especially in an agricultural environment, could be misleading.

The main purpose of this study was to investigate the effects of the amendment of powdered pruning waste from cactus pear on the water retention characteristics of two contrasting soils widely diffused through the Mediterranean basin.

4.2 Materials and Methods

4.2.1 Benchmark Mediterranean soils

The Mediterranean Sea basin covers a surface of seven million square kilometres, encompasses latitude 30° to 40°N and extents from longitude 10°W to 40°E. Its soils are a quite disordered layer of evaporitic deposits originated during the Messinian Salinity Crisis, five and seven million years ago. These soils show analogous characteristics, a specific climate in which the seasonal distribution and not the total amount of precipitation is the main determinant, a contour of mountains, an abundance of desert dust, accumulations of secondary calcium carbonate or more soluble salts, and a millennial anthropogenic setting. Such a climate provokes the re-precipitation, in the form of nodules, of the partially dissolved carbonates (Carrubba and Scalenghe, 2012; Yaalon, 1997). Two categories of soil are archetypal of the Mediterranean landscapes: *terra rossa* (from modern Italian, red soils) and *terra fusca* (from Latin, black soils). Red soils derive from the process of rubefication of iron oxides, while black soils originate from the weathering of silicates (from which originates new inter-layered phyllosilicates) and the simultaneous dissolution of calcareous parent material (Peña and Torrent, 1990). Furthermore, a continuous supply of allochthonous fine particles works together with pedogenesis, imparting a high water-holding capacity (Bilsel, 2004; Nettleton, 1991; Simonson, 1995).

We have chosen two contrasting soils, well-studied previously. The red soil (RS) is an Ap horizon from a Terric Chromic Cambisol (Loamic) (IUSS WG WRB, 2022; Alagna et al., 2018). The black soil (BS) is a Byss horizon from a Calcic Gypsic Vertisol (Hypereutric) soil (IUSS WG WRB, 2022; Laudicina et al., 2013 and 2021; Scalenghe et al., 2016) (Table 14). The rationale for this choice



depends on the different purposes of organic amendment with soil texture. In coarse soils, organic amendments are most commonly used to enhance the humus content of the soil and improve its physical and chemical properties. The use of organic amendments on clayey or fine-textured soils improves their permeability, reduces the risk of soil surface crusting, improves soil air-water relations, and reduces surface runoff from agricultural areas (Garbowski et al., 2023).

Table 14. Main features and characteristics of the selected soil horizons

	RS	BS
Coordinates	38°06'25" N, 13°21'06" E	37°60'58" N, 13°90'47" E
Climate	MAT 18.3 °C, MAP 803 mm	MAT 17.8 °C, MAP 460 mm
Current land use	Citrus orchard	Eucalyptus wood
Management practices	No tillage	No tillage
clay-silt-sand ^a (% fine earth)	15-36-48	46-28-26
Texture classification ^a	Loam	Clay
OC ^b	3.1	0.6
pH	7.8	7.8
BD ^c (Mg m ⁻³)	1.032	1.260

^a Particle Size Distribution according to USDA

^b OC: organic carbon (percentage)

^c Dry soil BD (Mg m⁻³) of the laboratory compacted soil samples

Not dispersed soil samples of biomass, BS and RS were sieved through a sieve pile with mesh between 2000 and 75 µm and the percentage by weight of material retained in each sieve was attributed to the mean geometric diameter of the upper and lower sieves of the pile.

4.2.2. Characteristics of cactus pear

The biomass used was characterized as in section 3.2.1.

4.2.3. Determination of soil water retention curve (SWRC)

The air-dried biomass was mixed with air-dried 2-mm sieved soil, in twelve different percentages by weight: 1, 2, 4, 6, 8, 10, 12, 15, 20, 30, 40, and 50%. Two control samples, i.e., not amended soil samples (100% RS and 100% BS), were also considered, thus resulting in a total of 26 repacked soil samples. No replications were performed because the number of samples was large for the type of measurement and the available instruments. Each sample was prepared by compacting, to a height of



4 cm, a dry mass of the two constituents (soil and biomass), into 5 cm diameter cylinders, a dry mass of the two constituents (soil and biomass) calculated by the following expressions:

$$M_s = \frac{V BD_c BD_s}{BD_c + r BD_s} \quad M_c = r M_s \quad r = \frac{M_c}{M_s} \quad (1)$$

in which M_c (g) and M_s (g) are, respectively, the oven-dried mass of biomass and soil, BD_c (g cm^{-3}) and BD_s (g cm^{-3}) are the oven-dry bulk densities of the two constituents, V (cm^3) is the sample volume ($V = 78.5 \text{ cm}^3$), and r is the ratio between the oven-dry mass of biomass and the oven-dry mass of soil. The initial water content of both constituents was taken into account to calculate the corresponding oven-dried mass. Sample compaction was conducted in four successive steps by beating the mixture with five strokes from a height of 5 cm followed by five rotations with a pestle at each increment (Bondi et al., 2022).

Laboratory determination of the water retention curves was conducted by the hanging water column apparatus, for matric head values, h , ranging from 0 to -1 m, and by the pressure extractor method for lower h values down to -150 m.

Soil samples were placed on the surface of the porous plate of a glass funnel and saturated from below by applying four successive equilibrium steps of $h = -0.20$, -0.10 , and -0.05 m followed by submersion (i.e., $h = 0$). From saturation, soil samples were desorbed by imposing a sequence of twelve decreasing matric head values: -0.025 , -0.05 , -0.075 , -0.10 , -0.15 , -0.20 , -0.25 , -0.30 , -0.40 , -0.50 , -0.70 and -1 m. At each equilibrium h value, the volume of water drained into the burette was recorded and these volumes backwards added to the equilibrium volumetric water content, θ ($\text{m}^3 \text{ m}^{-3}$), determined at the end of the drainage sequence ($h = -1$ m) by oven-drying the sample at 105°C for 24 h.

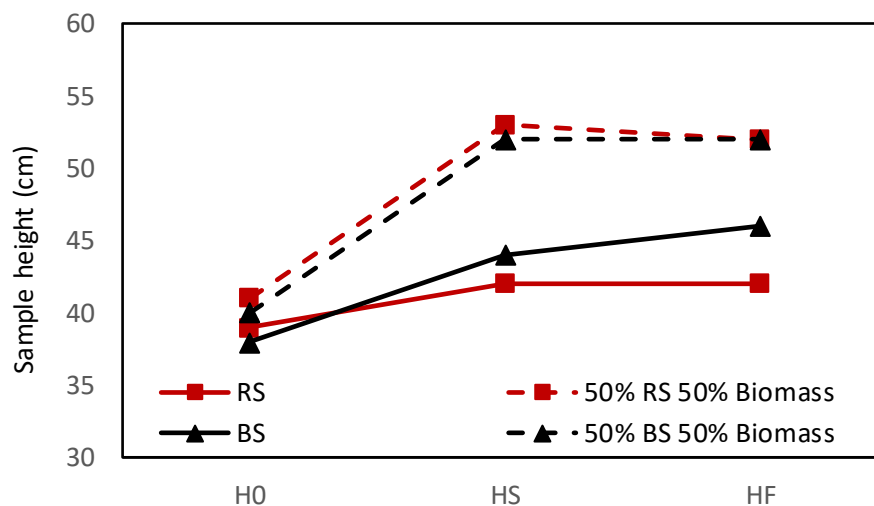
Variations in the bulk density of the samples were monitored during the whole process by measuring the height of the samples by a gauge after preparation, i.e., under initial air-dried condition (H0), at the end of the saturation process (HS), and at the end of the drainage (HF). Water retention data, at matric heads of -1 , -30 , and -150 m, were determined in pressure plate extractors on three replicated samples of 5-cm-diameter by 1-cm-height having the same BD as the 5 cm by 4 cm samples. Determination of volumetric water content at $h = -1$ m was included in pressure plate experiments for comparison with the θ value measured at the same matric head in the tension apparatus. All the measurements were conducted under temperature-controlled conditions at 22 ± 1 °C.

4.3 Results

4.3.1 Swelling and soil bulk density

Following saturation, the sample height increased for both the RS and the BS (Figure 8). As expected, the increase of sample height was more marked for the BS due to the higher clay percentage that promoted soil swelling. In particular, the sample height increased from 39 to 42 mm for the RS and from 38 to 44 mm for the BS. During the subsequent drainage process (from saturation to $h = -1$ m), the height of the RS did not change (HF = 42 mm) whereas continued to increase for the BS (HF = 46 mm). Saturation promoted a more marked increase in the sample height when the different mixtures with variable proportions of biomass were considered. In Figure 8 the effect for the 50% biomass addition to soil is reported only, with the notation that all the intermediate biomass percentages determined swelling heights between the pure soil (i.e., 100% RS or 100% BS) and the corresponding 50% biomass mixtures. For the latter, following saturation, the height of the amended samples increased to 52-53 mm. Once saturated, the amended samples maintained the swelling height, or a little reduced it, during the following drainage phase. It is worth noting that the two mixtures (50% RS 50% biomass and 50% BS 50% biomass) followed a similar trend thus showing that the characteristics of the amended soils are mostly controlled by the properties of the biomass.

Figure 8. Sample heights for the initial air-dried conditions (H0), at the end of the saturation process (HS), and at a water content corresponding to matric head $h = -1$ m (HF) for the red soil (RS) and the black soil (BS) and the mixtures of 50% soil and 50% biomass.



For both RS and BS, the soil dry BD significantly decreased at increasing the percentage of biomass (Figure 9a). The dry BD of biomass was 0.515 kg m^{-3} , which is 2.0 and 2.5 times lower than the dry



BD of RS and BS, respectively (Table 14). Therefore, the dry BD decreased from 1.032 to 0.698 kg m⁻³ for RS and from 1.260 to 0.689 kg m⁻³ for BS, when the percentage of biomass increased from 0 to 50% by weight (Figure 9a). In other words, the dry BD decrease is an expected consequence of the lower weight of the amended soils when an increasing percentage of lighter material is added. Furthermore, decreasing the content of the two soils, Rs and Bs, in the samples also cancels out the difference in BD between the two soils, initially attributed to the different clay content.

Under wet conditions, the BD was always lower than under dry conditions. Furthermore, no perceivable difference was observed for wet BD measured at saturation ($h = 0$) and field capacity ($h = -1$ m) (Figure 9b) (Assouline and Or, 2014). Under saturated conditions, BD decreased from 0.958 to 0.540 kg m⁻³ for RS and from 1.088 to 0.530 kg m⁻³ for BS. At field capacity ($h = -1$ m), BD decreased from 0.958 to 0.550 kg m⁻³ for RS and from 1.041 to 0.530 kg m⁻³ for BS. Significant linear regressions with the percentage of biomass were found also for wet BD (Figure 9). It is worth to be noted that, for both soils, the wet BD decreased to a greater extent than the dry BD at increasing the percentage of biomass, as can be observed in Figure 9.

The difference between dry and wet bulk densities can be considered as an index of the swelling potential of the biomass. Indeed, if the swelling potential of biomass were lower or equal to that of the amended soils, the substitution of an increasing fraction of swelling soil with biomass would determine less total swelling potential. Therefore, the wet BD would decrease less than the dry BD at increasing the amending dose and the differences between the two BDs tend to reduce. The opposite is if the swelling potential of biomass is greater than that on the considered soils.

Figure 9. Sample bulk density under dry (a), and wet (b), conditions as a function of percentages of biomass. For wet BD, filled and open symbols represent saturated ($h = 0$) and field ($h = -1$ m) conditions, respectively. (c) Relative differences between the dry and wet BD for soil mixtures with different percentages of biomass. RS = red soil; BS = black soil. Regression lines are shown for saturated conditions only.

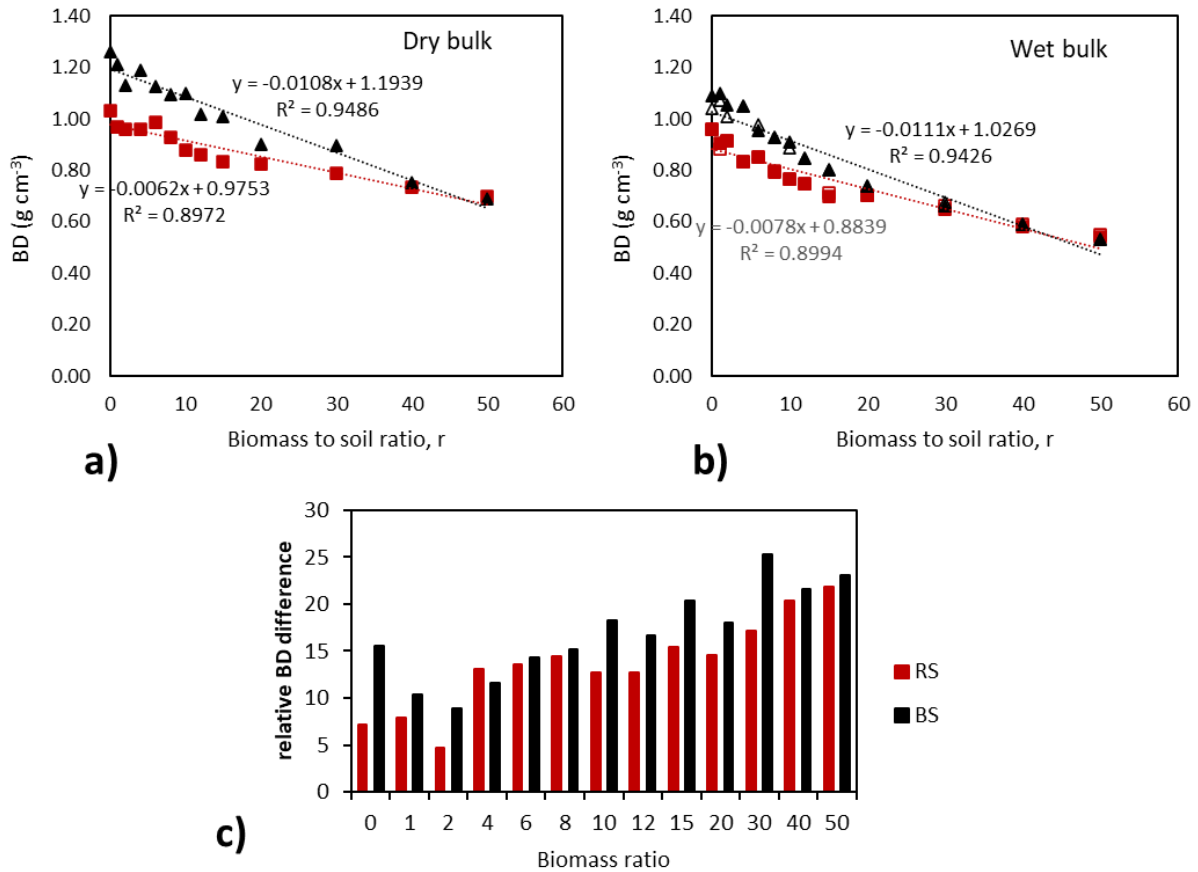
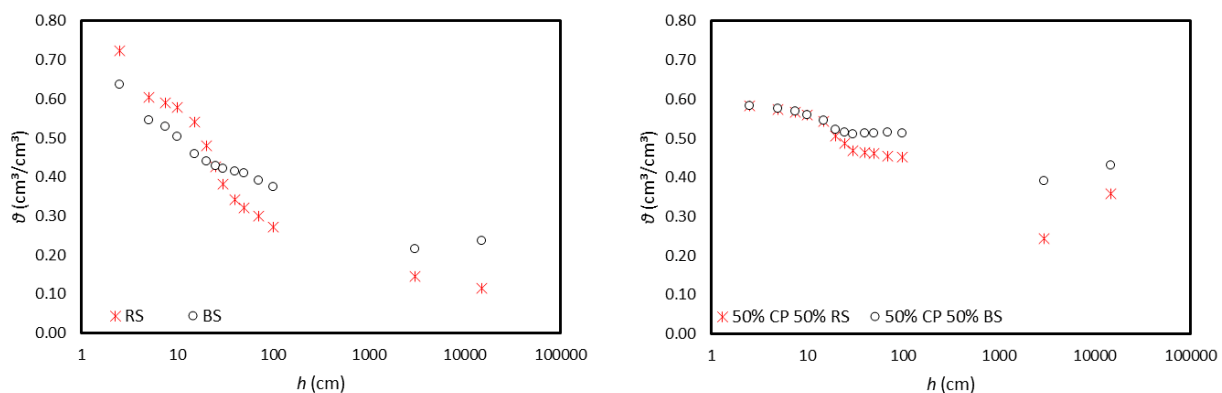


Figure 9c shows that the relative differences between dry and wet bulk densities were always positive and generally increased with increasing the biomass proportion. For both soils, relative BD difference was significantly correlated ($P < 0.0001$) to biomass ratio ($R^2 = 0.780$ for RS and $R^2 = 0.679$ for BS). Compared to the control (biomass ratio = 0), for which the differences between wet and dry BDs are exclusively due to swelling of clay particles, addition of biomass promoted additional swelling that can be attributed to hydration of the biomass. According to a paired t-test, the BS mixture showed larger relative differences between dry and wet BD than the RS likely as a consequence of larger clay content. However, these differences tended to reduce for the highest values of the biomass ratio given the sample swelling was mostly controlled by the cactus pear hydration.

4.3.2. Soil water retention

The water retention data of the RS and BS soils provided different information (Figure 10a). The two soils showed equivalent volumetric water content, θ , values for $h = -0.25$ m. For higher values of h , i.e., relatively wet conditions, the volumetric water content of BS was lower than that of RS. An opposite trend was observed at lower h values, i.e., relatively dry conditions, as BS exhibited a greater water retention capacity than RS (Figure 10a). The observed behavior agrees with the different PSD of the two non-amended soils as BS, having a higher clay fraction, is likely characterized by a pore size distribution shifted towards relatively smaller diameters (Table 14). Thus, more water is retained in small pores than in large ones in BS. The opposite is for RS where the large pores predominate over the small ones (Nasta et al., 2009).

Figure 10. Soil water retention data for **a)** the not amended RS and BS soils and **b)** the 50% biomass to 50% soil mixtures.



Comparison between the not amended soils and the corresponding biomass-soil mixtures showed a behavior in the retained volumetric water contents that differed with biomass dose and soil type (Figure 10). In particular, the addition of 50% of biomass to the RS, resulted in increased θ values for $h < -0.15$ m whereas for lower matric head values, the volumetric water content retained by the mixture slightly decreased. The maximum increase of θ ($0.0182 \text{ m}^3\text{m}^{-3}$) was observed for $h = -1$ m. For the 50% biomass to 50% BS mixture, a more general increase in the capacity to store water was observed as, compared to the not-amended BS, the volumetric water content increased from $0.032 \text{ m}^3\text{m}^{-3}$ at $h = -0.05$ m to $0.196 \text{ m}^3\text{m}^{-3}$ at $h = -150$ m. The biomass improve the water retention capacity for relatively dry soil moisture conditions, which is for soil water content corresponding to the above field capacity down to the wilting point. However, the two soils did not show the same susceptibility to the effects of biomass addition. Indeed, for the RS both a decrease and an increase of the water



content corresponding to a given matric head was observed whereas, for BS, the addition of biomass increased the stored water.

Amending effects were confirmed by Pearson's correlation coefficients between θ values at a given matric head and the biomass dose (Table 15). Significant negative correlations were observed for RS at matric heads close to the upper range of matric pores ($h = -0.1$ m). For low h values ($h < -0.25$ m) an opposite sign of the correlation was observed with θ values that always increased at increasing the percentage of biomass. For BS, the volumetric water content always significantly increased with biomass in the range from $h = -0.1$ to -150 m.

Table 15. Pearson's correlation coefficients and corresponding p-values for the regression between volumetric water content at a given matric head and the proportion of biomass. Bold values indicate significant correlations ($n = 13$).

h (m)	RS		BS	
	Pearson <i>r</i>	<i>p</i> -value	Pearson <i>r</i>	<i>p</i> -value
-0.025	-0.5487	0.0525	-0.1577	0.6085
-0.05	-0.6216	0.0235	0.3510	0.2396
-0.075	-0.6393	0.0187	0.5424	0.0555
-0.10	-0.6357	0.0197	0.7103	0.0065
-0.15	-0.4165	0.1574	0.8014	0.0010
-0.20	0.1531	0.6178	0.7677	0.0022
-0.25	0.5736	0.0404	0.8052	0.0009
-0.30	0.6712	0.0120	0.8347	0.0004
-0.40	0.7156	0.0060	0.8657	0.0001
-0.50	0.7241	0.0051	0.8788	0.0001
-0.70	0.7441	0.0035	0.8736	0.0001
-1.0	0.7476	0.0033	0.8643	0.0001
-30	0.8816	0.0001	0.9798	< .00001
-150	0.9749	< .00001	0.9847	< .00001

For both soils, correlations were significant at the matric head values of -0.1 , -1.0 , and -150 m, which correspond, respectively, to the volumetric water content equivalent to matrix capacity, θ_m , field capacity, θ_f , permanent wilting point, θ_w , yielding the following regression lines:

Matrix capacity, $h = -0.10$ m

$$\text{RS: } \theta_m = 0.584 - 0.00121r$$

$$\text{BS: } \theta_m = 0.517 + 0.00101r$$

Field capacity, $h = -1.0\text{ m}$

RS: $\theta_f = 0.350 + 0.00286r$

BS: $\theta_f = 0.424 + 0.00227r$

Wilting point, $h = -150\text{ m}$

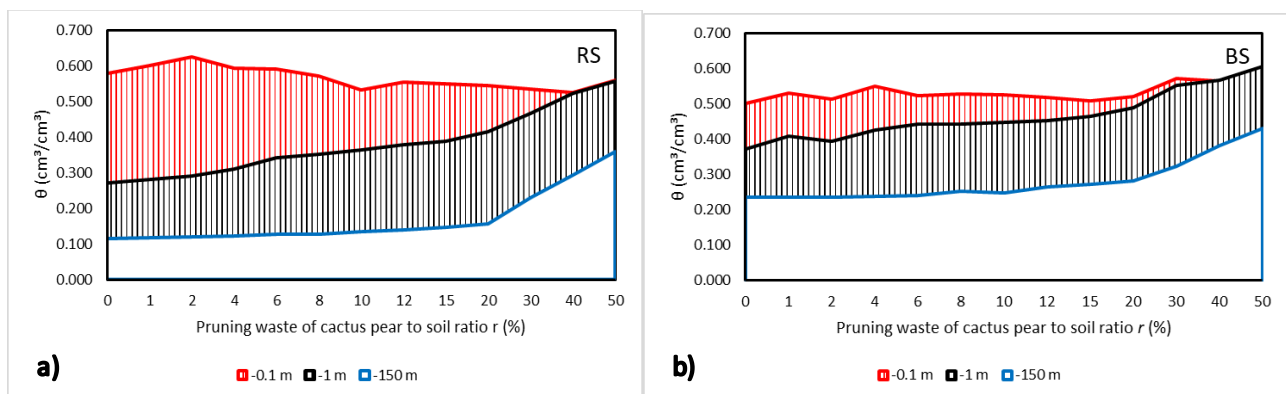
RS: $\theta_w = 0.095 + 0.00478r$

BS: $\theta_w = 0.221 + 0.00390r$

where r is the ratio of biomass mass to soil mass.

A representation of the observed trends is given in Figure 11, which shows how soil matrix capacity is distributed between drainable water capacity (DWC) and plant available water capacity (PAWC). The first, given by difference $\theta_m - \theta_f$, is the water retained in pores that, according to the capillary law, have pore diameters in the range from 30 to 300 μm . Such fraction corresponds to the soil water that is expected to drain below the root zone due to the combined effect of capillary and gravity flows. The latter, given by difference $\theta_f - \theta_m$, is the water retained in pores with a diameter from 30 down to 0.2 μm , and corresponds to the soil water readily available for crop growth (Reynolds, 2002).

Figure 11. Volumetric water content retained by biomass-soil mixtures for matric head values of -0.1 m (matrix capacity), -1 m (field capacity) and -150 m (permanent wilting point). Red soil (a) and back soil (b).



For both soils, DWC tended to decrease at increasing the percentage of biomass, thus showing that amendment is expected to slow down the drainage below the root zone. A contrasting result (increasing DWC) was observed for RS only for very limited amending doses (*i.e.*, few percent of biomass). The PAWC was to a less extent affected by biomass addition (Figure 11). For the RS, PAWC tended to increase from $0.15\text{ m}^3\text{ m}^{-3}$ for $r = 0$ to a maximum of $0.26\text{ m}^3\text{ m}^{-3}$ for $r = 20\%$ and then it decreased to $\text{PAWC} = 0.20\text{ m}^3\text{ m}^{-3}$ for $r = 50\%$. A similar trend was observed for BS with the only difference that the maximum $\text{PAWC} = 0.23\text{ m}^3\text{ m}^{-3}$ corresponded to $r = 30\%$.



To explain the reasons for these unexpected results, further investigations were made. Preliminary, the water repellency of the biomass was tested. If existing, water repellency would increase at increasing the biomass dose thus resulting in difficult saturation and lower water content, especially at low matric head. The water drop penetration time test (Bisdorn et al., 1993), conducted on the biomass, shows a slight repellency occurrence as the applied droplets ($N = 5$) infiltrated in time between 12 and 17 s. No repellency was detected for RS and BS, thus appears unlikely that the water repellency could justify the different behavior between the two soils.

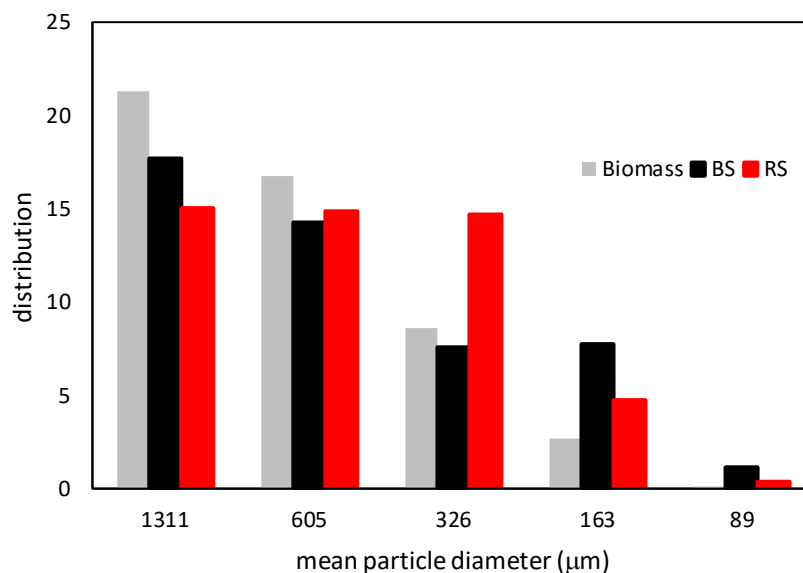
4.4 Discussion

Addition of biomass to a loamy red soil and a clay black soil determined a decrease in soil BD under dry conditions. Significant negative correlations were found between dry BD and the biomass dose indicating that BD decreases at a rate of $0.062 - 0.078 \text{ kg m}^{-3} \% \text{ v biomass}^{-1}$. Arvidsson (1998), similarly, showed that BD was largely dependent on SOM, with which it exhibited a strong negative correlation. Decreasing dry BD could be beneficial in fine-textured compacted or degraded soils showing BD values $> 1.3 \text{ Mg m}^{-3}$ in which root elongation may be impeded and soil aeration reduced (Reynolds et al., 2007). On the other hand, BD values below $0.8\text{-}0.9 \text{ Mg m}^{-3}$ may provide insufficient root-soil contact and plant anchoring (Fan et al., 2021). Despite the present investigation was conducted on laboratory repacked soil cores with limited compaction compared to natural soils, the observed relationships appear usable to predict the effect of the addition of a given quantity of biomass on soil BD. Furthermore, the two considered soils are widely diffused in the Mediterranean environment and, thus, the range defined by the two linear regression lines can be considered representative of the benefits expected when medium to fine-textured Mediterranean soils are amended with biomass.

Being a closed system, the biomass had a relatively high swelling potential as, when added to the RS and BS, determined additional decrease of the wet BD besides that determined by the soil clay particle swelling. Swelling capacity of the biomass is a consequence of the chemical structure of polysaccharides of the cactus pear (Amaya-Cruz et al., 2019). Cactus pear cladodes contain mucilage with a high content of galacturonic acid, which favors water retention (Matsuhiro et al., 2006). The high swelling capacity that characterizes the biomass-soil mixtures should be considered with attention given that under constrained conditions, i.e., when the soil is not free to swell, may determine reduced soil porosity with negative effects on air and water circulation. For a limited percentage of biomass, the observed increase in wet BD is probably positive as it increases the SWR.

Indeed, a significant positive correlation was found for water content at a given matric head and the biomass dose with the only exception of the matrix capacity for the RS. Figure 12 shows that in the range of larger diameters ($d \geq 605 \mu\text{m}$) biomass percentages prevailed over those of the two soils. The opposite occurred for $d \leq 163 \mu\text{m}$. The only exception is for $d = 326 \mu\text{m}$, for which the proportion of RS aggregates clearly prevailed over biomass ones. Given such particle diameter is very close to the sizes of pores that are saturated when $h = -0.1 \text{ m}$, it could be speculated that biomass addition reduced the number of soil pores falling in that class thus determining the reduction of θ_m at increasing the biomass dose. On the contrary, an increasing trend could be justified for BS. Plausible at the scale of the bulk pore volume sampled during water retention measurements (approximately 80 cm^3), this behaviour has been by the analyses analyses conducted at the micrometric pore scale (i.e., porosimetry).

Figure 12. Particle size distribution among selected diameter sizes in the range of 2000 to $75 \mu\text{m}$.



In terms of retained water, a limited addition of biomass (few percent units) seemed to increase the drainable water capacity (DWC) of the RS and did not affect BS. For higher biomass doses a decrease of DWC was observed for both soils, thus confirming that amending medium- to fine-textured soils with swelling biomass may hamper soil capacity to drain water and limit air circulation. The PAWC was also influenced by biomass addition, but observable benefits require very large biomass proportions (unlikely under field conditions), up to 20% v in RS and 30% v in BS. More in general, a redistribution between drainable and plant available water content can be supposed with the average



energy level of the retained water that becomes more and more negative and drainable water is transformed in plant available water up to a transition threshold of biomass dose of around 20% at which PAWC is maximum. Behind that threshold, DWC disappears, and PAWC reduces while most of the soil water is retained below the minimum soil matric head ($h = -150$ m) applicable by crops. For agronomic purposes, that threshold should be not overpassed, at least for these benchmark Mediterranean soils, rather fine textured.

The significant linear regressions deduced for BD, and the characteristic water retention points could help in selecting the most appropriate biomass dose to be applied to these soils. Despite the absolute values of BD, θ_m , θ_f and θ_w can be affected by the empirical setup that made use of laboratory-repacked soil samples, it could be supposed that the relative effects, that is the gradient by which the selected soil property changes as a consequence of biomass addition, is not affected by the sample preparation. Therefore, if soil properties under field conditions are known from other investigations, the short-term effect of a given biomass dose can be predicted. In particular, the proposed relationships offer a large potentiality to be embedded into PTFs specifically developed for Mediterranean soils with the aim to predict the effects of biomass amending on the SWR curve (Castellini and Iovino, 2019).

In soil, the rhizospheric environment is complex and difficult to model, so overlooked. And yet, it is precisely at the level of the rhizosphere that it would be useful to be able to know, for example, the dynamics of water through the porous medium of the soil. Currently, the knowledge of soils is extended to all parts of the world. Although with different accuracy, using a smartphone it is possible to know the properties of the surface on which we are walking. This has also been made possible with the introduction of pedo-transfer functions. Pedotransfer functions (PTFs) are used for converting existing data into data that we need but do not have available (Bouma, 1989), e.g., to deliver irrigation scheduling (Liang et al., 2016). In the case of soil hydraulic properties, PTFs are generally based on PSD, BD, SOM, and cation exchange capacity (Tóth et al., 2015; Román Dobarco et al., 2019). For example, in Europe, EU-SoilHydroGrids offers data on soil hydraulic properties up to 2 m depth at 250 m resolution (Tóth et al., 2017). A powerful tool for planning and land management (agriculture). The question is that most databases use the percent of clay and sand only as PTFs predictor variables (e.g., Román Dobarco et al., 2019). They necessarily simplify the complexity of the soil in an extreme manner, excluding the presence of plants. With these results, we believe that the roots should also be considered. I will not go too far here, being outside the scope of the thesis, to enter into the merits with specific suggestions. Evidently, the information must necessarily be simplified in order to be



used. But it must be able to differentiate rhizospheric soil from that in which there are no roots. Roots which, with our results, impart hydraulic behaviors which differ greatly from those hypothesized for soils without. Plants that live in the soil, anchored by their root architecture, modify their intrinsic properties, the dynamics of liquids and gases, in particular. For example, roots secrete mucilage. Mucilages are polymeric gels secreted from the cap cells of the root tip, playing a crucial role in root-soil interactions (Ahmed et al. 2015). Interactions of the chemical and physical properties of mucilage determine its unique and broad functions and are crucial for hydraulic processes in the rhizosphere (Benard et al. 2019; Roskopf et al. 2021). Addition of plant biomass improves soil physical properties by the development and stabilization of aggregates (Ansari et al., 2022). Soil macroaggregates (i.e., > 0.250 mm) are stabilized by roots, hyphae, and mucilages, particularly polysaccharides (Machado Vezzani et al., 2018).

The mucilage contained in cactus pear pruning, examined in this work with their potential as a soil conditioner, certainly mimic a rhizospheric environment, albeit oversimplified. Our results, limited to a Mediterranean environment, having chosen two extreme soils, can be used to improve the predictivity (particularly in three-dimensional models) of PTFs, considering the presence of plants.

4.5 Evaluation of cactus pear powder amendment on the water content of two typical Mediterranean soils: Concluding remarks and synopsis

The amendment of powdered pruning waste of cactus pear showed positive effects on the water retention characteristics of two contrasting soils widely spread in the Mediterranean basin (red soil, RS, and black soil, BS) (Figure 13). In both soil types, the addition of the amendment resulted in a decrease in soil BD under dry conditions, which could be advantageous in fine-textured compacted or degraded soils, having BD values > 1.3 Mg m⁻³, in which root elongation may be prevented and soil aeration reduced. However, biomass has a relatively high swelling potential because, when added to RS and BS, it resulted in a further decrease in wet BD, in addition to that caused by swelling of soil clay particles. The high swelling capacity that characterizes biomass-soil mixtures, when the soil is not free to swell, can lead to a reduction in soil porosity, which negatively affects air and water circulation. Regarding soil water retention, a limited dose of biomass (a few percentage units) seemed to increase the drainable water capacity (DWC) of RS and did not affect BS. Instead, for higher doses of biomass, a decrease in DWC was observed for both soils, thus confirming that the emendation of



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medium to fine-textured soils with swelling biomass can hinder the soil's ability to drain water and limit air circulation. Plant available water capacity (PAWC) was also found to be affected by the addition of biomass; however, observable benefits require very high biomass proportions, up to 20% in RS and 30% in BS. It is reasonable to assume that a redistribution between DWC and PAWC occurs, with the average energy level of retained water becoming increasingly negative and drainable water converting to available plant water up to a transitional threshold of the biomass dose of about 20%, at which PAWC is maximum. Beyond this threshold, DWC disappears and PAWC also decrease, since most of the water is hygroscopic ($h > -150$ m), not available for plants. For agronomic purposes, this threshold should not be exceeded, at least for these rather heavy textured Mediterranean reference soils.

Overall, the results showed that the addition of biomass, in both soil types, could trigger benefits on hydrological processes and agronomic services by promoting the increase of PAWC, while maintaining the biomass content below 20%, and the infiltration of plant roots (in the absence of swelling constraint conditions) due to the observed swelling phenomena. Therefore, biomass application, as a soil improver, can contribute to efficient water management in arid and semi-arid regions, which are characterized by limited water availability and low soil fertility.

Figure 13. The amendment of powdered pruning waste of cactus pear showed positive effects on the water retention characteristics of two contrasting soils, (red soil, RS, and black soil, BS). In both soil types, the addition of the amendment resulted in a decrease in soil BD under dry conditions. However, biomass has a relatively high swelling potential because, when added to RS and BS, it resulted in a further decrease in wet BD. Higher doses of biomass, a decrease in drainable water capacity was observed for both soils, however, and observable benefits require very high biomass proportions, up to 20% in RS and 30% in BS. Therefore, biomass application, as a soil improver, can contribute to efficient water management in arid and semi-arid regions, which are characterized by limited water availability and low soil fertility.



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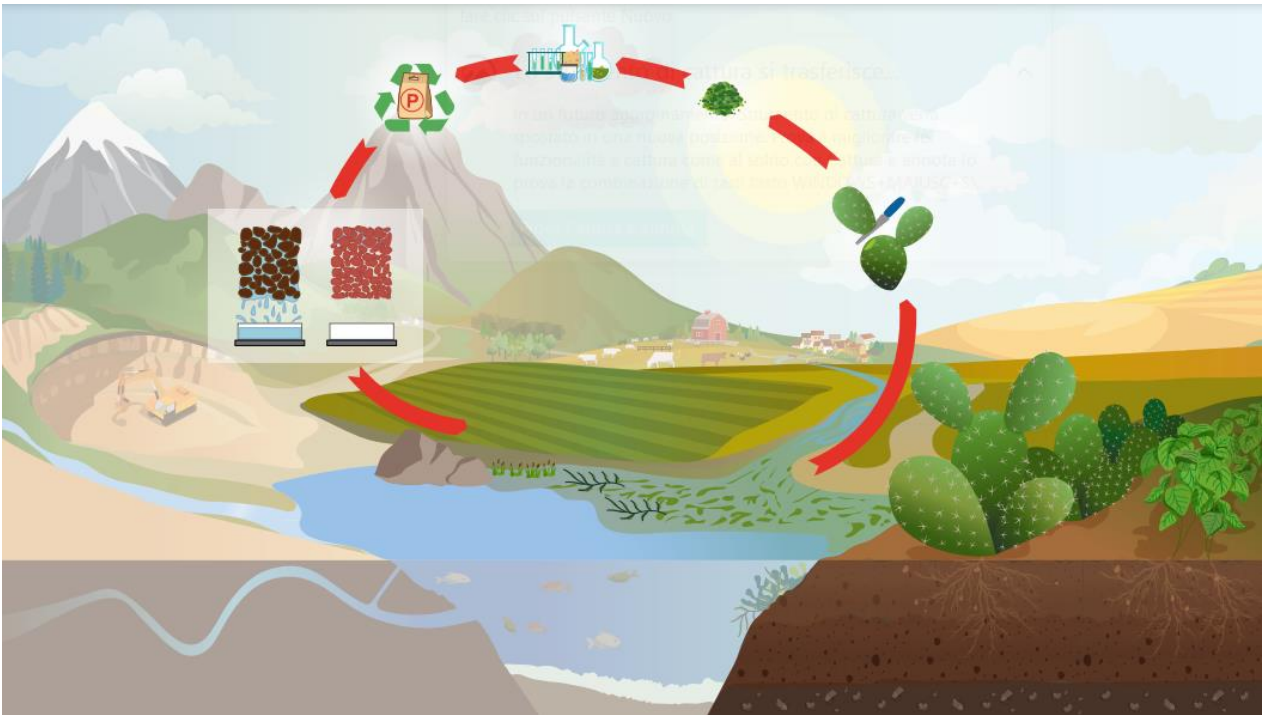


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5. Influence of cactus pear pruning waste on the growth of basil plants

Abstract

This chapter investigates the use of recycled organic substrates from cactus pear pruning waste as a sustainable and economical option for container plant cultivation, specifically basil. The results show that substrate with 5% content of biomass positively influenced plant growth, with better responses in terms of height, leaf area, and number of leaves per plant. The addition of Fe³⁺-loaded biomass to the growing media improves nutrient assimilation in plants, suggesting that the positive effects may be attributed to the presence of Fe in the biomass. This approach can be particularly useful in Mediterranean environments where cactus pear pruning waste is largely available.

5.1. Introduction

Growing media (GMs) are a crucial component for supporting the growth and development of horticultural and ornamental crops. Yet, conventional growing methods often rely on non-renewable resources; among these, peat has been long time considered a reference GM, but its use has been criticized both for economic reasons and for causing negative impacts on the environment at a global scale (Leifeld and Menichetti, 2018). In order to address this issue, there is a need for sustainable GMs that are made from renewable resources and can be recycled. The effectiveness of a GM is dependent on its ability to balance water and air, which are both crucial for plant growth (Carlile et al., 2015; Barrett et al., 2016). Many organic materials have been suggested for this purpose, and a special interest has been devoted to wastes and residuals, including woody residuals, animal manures, food industry wastes, and many others, mixed in various proportions and tested on several different crops (Raviv, 2005; Bilderback et al., 2013; Zhang et al., 2013). Indeed, the disposal of wastes is in many cases a serious issue, and recycling for horticultural purposes can be a satisfactory option (Gruda, 2019). Furthermore, as De Corato (2020) noted, the production of high-quality composts from agricultural waste and by-products can provide a valuable source of eco-friendly organic molecules and beneficial microorganisms.

Using recycled organic GMs from pruning wastes can be a sustainable and cost-effective option for growing plants in greenhouse conditions. This organic matter from pruning waste can provide a suitable environment for plant growth and improve soil structure, water-holding capacity, and fertility.



Basil (*Ocimum basilicum* L.), a fast-growing annual herb, is well-suited for greenhouse cultivation in pots packed with different GMs due to its quick germination and colonization abilities (Putievski and Galambosi, 2006). In some environments, the abundance of locally available plant waste, such as cactus pear pruning waste, makes it a promising and eco-sustainable option for GMs (Auteri et al., 2022). However, it is important to note that the addition of recycled materials can impact water and nutrient availability for crops. Research has shown that pH, iron, and calcium have the greatest influence on the growth of basil cultivation in GMs (Burducea et al., 2020; Farshchi et al., 2021). The goal of these experiments is to determine if pure or pre-treated cactus pear pruning biomass can be a sustainable and profitable option for basil cultivation.

5.2. Materials and methods

5.2.1 Location and experimental design

The experiment was conducted between May and July 2022 at the Department of Agricultural, Food and Forestry Sciences (SAAF), University of Palermo (PA) (38°06'27" N and 13°21'09" E, 42 m a.s.l.). The local climate is temperate subtropical (CS, Annual mean > 17°C; mean of coldest month > 10°C; 5 months with mean > 20°C; annual range 13°C to 17°C) according to Koppen classification (Chen and Chen, 2013).

Thirteen substrates (treatments) were prepared, each containing commercial potting soil (T) and increasing biomass content (, added at 2.5%, 5%, 10% w/w), differently endowed with Ca²⁺, Fe²⁺ or Fe³⁺ ions. Each prepared substrate was placed in an 80-mL pot, and 5 commercial basil seeds (*Ocimum basilicum* L. cv 'Blumen') were placed in each pot. All treatments were replicated 5 times.

5.2.2 Substrates preparation

Commercial potting soil (T) was used (Universal Potting Soil Radicom®, VigorPlant Italia SRL), which is sold for gardens, vegetable crops and terrace plants. A T₀ treatment was prepared using only T as a substrate

The biomass, characterized as indicated in Section 3.2.1., was mixed with T, according to the re-treatment received (T₁ – T₂ – T₃ – T₄ and the biomass amount added to the pot (2.5%, 5% and 10% w/w of total substrate). Table 16 shows the composition and the main characteristics (pH, bulk density, electrical conductivity, and initial Ca, Fe, and P contents) of the 13 individual growing substrates.

Table 16. Characterization of the substrates tested

ID	Treatments	B ⁽¹⁾ pre-treatment	% B	pH	EC ⁽²⁾ dS m ⁻¹	DBD ⁽³⁾ g cm ⁻³	Ca content mg g ⁻¹	Fe content mg g ⁻¹	⁽⁴⁾ Initial P content (P _i) µg pot ⁻¹	
1	T ₀	T	-	0	7.6	3.530	0.36	-	-	0.38±0.12
2	T _{1-2.5}	T + CP	-	2.5	7.0	2.946	0.37	40.2±17.9	3.0±2.6	0.39±0.06
3	T ₁₋₅	T + CP	-	5	7.6	2.795	0.39	80.5±17.9	6.0±2.6	0.88±0.15
4	T ₁₋₁₀	T + CP	-	10	7.8	2.361	0.40	161±17.9	12.0±2.6	1.19±0.07
5	T _{2-2.5}	T + Ca-CP-P	CaCl ₂	2.5	7.6	2.580	0.36	128.8±1.2	3.0±2.6	0.37±0.12
6	T ₂₋₅	T + Ca-CP-P	CaCl ₂	5	7.7	2.131	0.38	257.6±1.2	6.0±2.6	0.59±0.09
7	T ₂₋₁₀	T + Ca-CP-P	CaCl ₂	10	7.7	1.805	0.40	515±1.2	12.0±2.6	1.48±0.12
8	T _{3-2.5}	T + Fe ²⁺ -CP-P	FeSO ₄	2.5	7.0	1.964	0.35	40.2±17.9	42.5±8.2	0.37±0.17
9	T ₃₋₅	T + Fe ²⁺ -CP-P	FeSO ₄	5	7.6	1.870	0.36	80.5±17.9	85.1±8.2	0.92±0.16
10	T ₃₋₁₀	T + Fe ²⁺ -CP-P	FeSO ₄	10	7.4	1.774	0.38	161±17.9	170.2±8.2	1.72±0.21
11	T _{4-2.5}	T + Fe ³⁺ -CP-P	FeCl ₃	2.5	7.0	2.519	0.35	40.2±17.9	72.1±32.4	0.36±0.13
12	T ₄₋₅	T + Fe ³⁺ -CP-P	FeCl ₃	5	7.5	1.876	0.38	80.5±17.9	144.2±32.4	0.40±0.08
13	T ₄₋₁₀	T + Fe ³⁺ -CP-P	FeCl ₃	10	7.7	1.352	0.39	161±17.9	288.4±32.4	0.47±0.28

⁽¹⁾B: untreated biomass; ⁽²⁾EC: electrical conductivity; ⁽³⁾DBD: dry bulk density; ⁽⁴⁾ In each pot there were 28 g of biomass

5.2.3 Growth parameters measured on basil plants

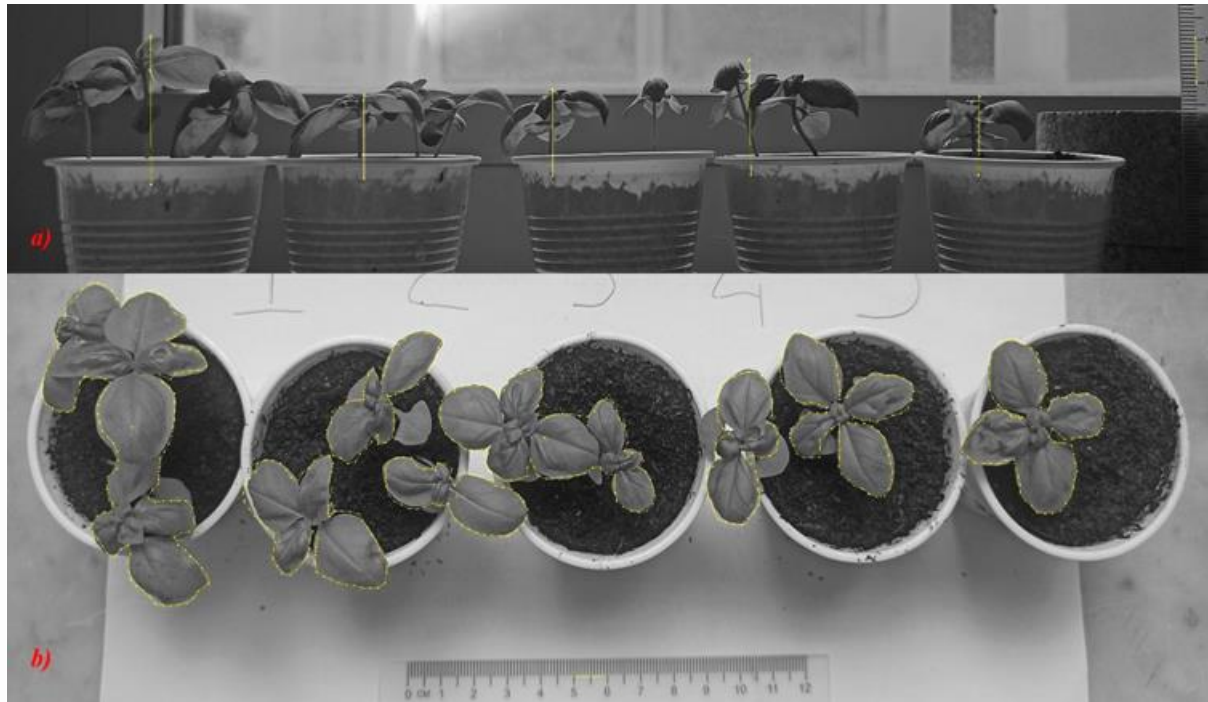
Basil seeds were sown on May 20, 2022 (5 seeds pot⁻¹) in plastic truncated cone pots having an upper diameter of 5.7 cm, a lower diameter of 3.6 cm, a height of 5.3 cm and a total volume of 80 cm³.

Seed germination was observed in the first 14 days after sowing (DAS), and regardless of the used substrate, seed germinated between 9 and 11 DAS. At 20 DAS, all pots containing fully established plantlets were positioned outdoors, sheltered from wind and rain.

The experiment was considered over at 64 DAS. Hence, plants' growth was monitored from 24 to 64 DAS, taking note of the following parameters: plantlets' height, leaf area pot⁻¹, SPAD values, and the number of leaves plant⁻¹. In total, five measurements of the above parameters were taken, at 31, 41, 51, and 64 DAS.

The data about seedlings' height, leaf area development in each pot, and the number of leaves per plant were acquired by taking photographs including the 5 replications of each treatment and a metric reference, further analyzed with the image analysis software Digimizer v. 4.6.1 (MedCalc Software, 2005-2016) (Figure 14). When more than 1 plant was present in each pot, the average value of all individuals was considered.

Figure 14. Acquisition of leaf height (a) and leaf area per pot (b)



On 51 and 64 DAS, due to the increased size of basil leaves, SPAD measurements were taken in all treatments employing the SPAD-502 meter (Minolta corporation, Ltd., Osaka, Japan). Being quick and noninvasive determinations, SPAD values are widely used in horticultural research as a key indicator of plant health and represent a reliable measurement of chlorophyll content in leaves (Markwell et al., 1995; Uddling et al., 2007).

5.2.4 Determination of available phosphorus

In all substrates, available P content was determined before seeding (P_i) and at the end of the experiment (P_f), to assess any eventual variation of P available to plants throughout their development. Available P content was first assessed through the Olsen method (Olsen et al., 1954) followed by spectrophotometric determination at 720 nm. For this determination, 2 grams of samples were weighed, to which 40mL of an extractive solution (0.5 mol L^{-1}) of sodium bicarbonate (pH 8.5) and 0.5 g of activated carbon were added. After shaking for 30 minutes, the samples were filtered with Whatman No. 42 paper, collecting the filtrate in 50mL Falcon tubes. These measurements were conducted in triplicate. No fertilization was conducted during the experiment. Watering was carried out every other day, supplying each pot with about 15 mL of water.



5.2.5 Statistical analysis

All treatments were submitted to analysis of variance (ANOVA), according to a randomized design with 5 replications. First, a General Linear Model (GLM; $Y=f(x)$) was adopted, in which all determinations on plants and substrates were the dependent variable (Y), whereas the experimental factors (DAS, different P-enrichments and mixing ratios) were the independent variables (X). Later on, separate analyses were conducted for each survey date, and the Dunnett's HSD test was run when significant differences ($P \leq 0.05$) were observed among the treatments. All statistical analyses were performed using the statistical package Minitab® 17.1.0 (Minitab Inc., State College, PA, USA, 2013).

5.3. Results

5.3.1 Growth parameters measured on plants

A first descriptive analysis conducted on the trend of plantlets' height over time, by grouping the collected information by biomass treatment type, showed that the different biomass content in the tested substrates influenced plant growth. From the analysis of variance conducted on the parameter "plant height" (Table 17), both factors "DAS" and "treatment" caused significant differences ($p=0.000$) in plant height values. Starting from this information, we studied the trend over time of this variable for every individual treatment, each including different biomass rates (Figure 15).

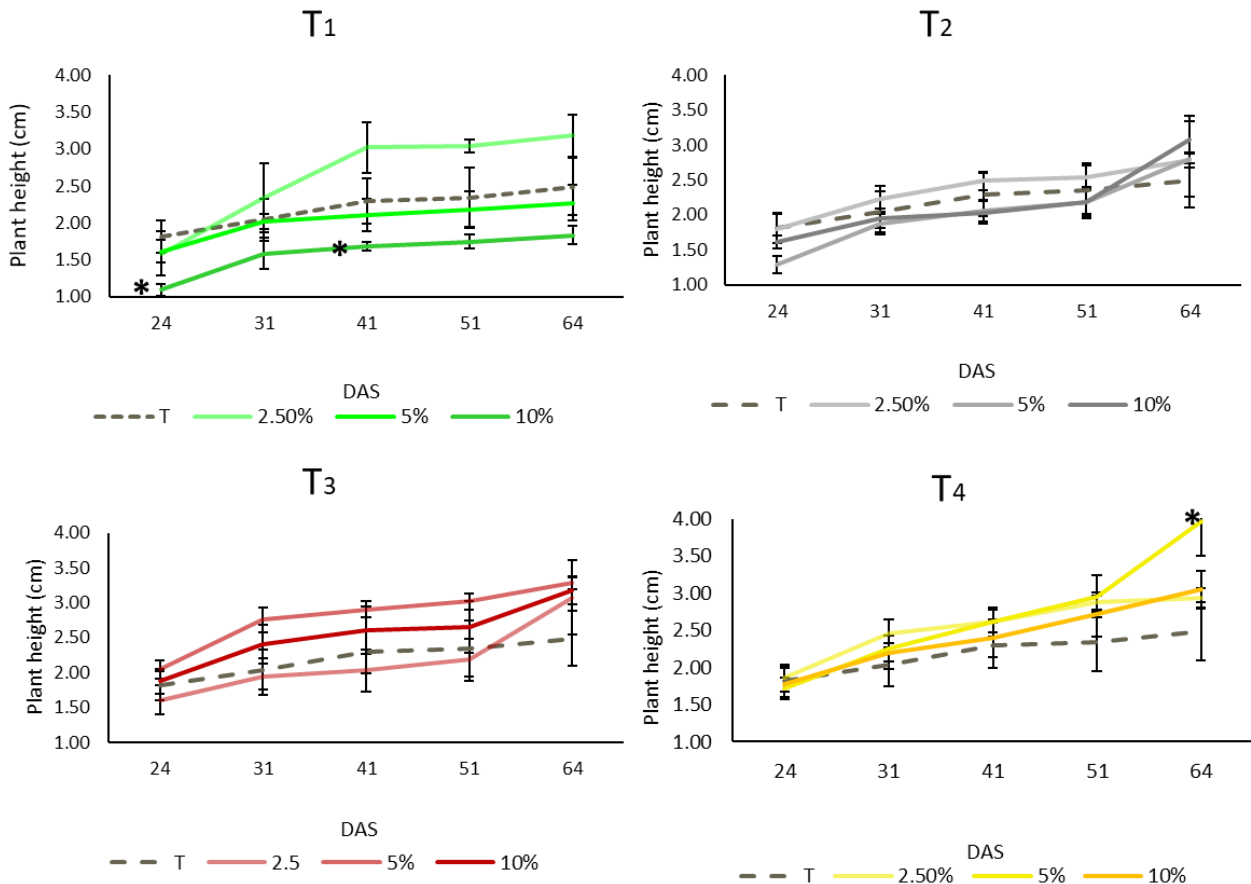
In all survey dates (DAS 24) and all four groups of treatments, the biomass did not influence plant height, and the measured values were not statistically different from the control (T_0). The only exception was T_{1-10} (T containing 10% biomass), which instead showed a lower growth than all the other treatments, with significant differences from the control at 24 and 41 DAS. Likewise, plants grown in the T_3 and T_4 substrates ($T+Fe^{2+}$ -B and $T+Fe^{3+}$ -B) did not exhibit any significant difference from the control, except for T_{4-5} (5% biomass), which at 64 DAS were significantly higher than the control.

Table 17. Results of the ANOVA on plantlets' height values

Source	DF	F-Value	P-Value
DAS	4	24.41	0.000
Treatments	4	12.10	0.000
DAS* Treatments	16	0.62	0.871
Error	273		
Total	297		

Note: Factor Information: DAS (24; 31; 41; 51; 64); Treatments (T_0 ; T_1 ; T_2 ; T_3 ; T_4)

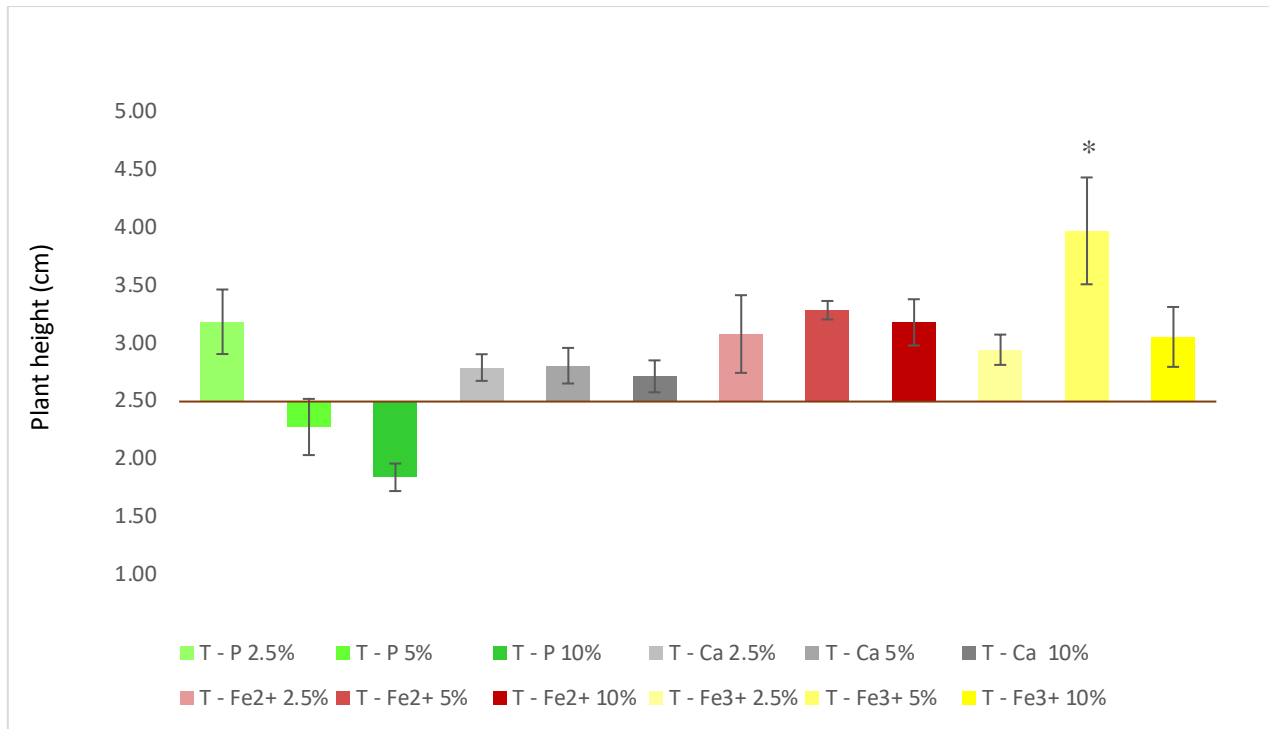
Figure 15. Average trend of plant height (cm) in the four groups of treatments (T₁, T₂, T₃, and T₄) with increasing addition of biomass (0, 2.5%, 5%, 10%), measured throughout the whole observation period (24 to 64 DAS). Each value is the average of 5 replications. Vertical bars represent the standard deviation of each mean.



For each survey date, mean values marked with * are significantly different from the control according to the Dunnett's test and 95% confidence.

At the end of the measurements, the observation of the differences in plant height between all the treatments and the T₀ (2.49 cm) (Figure 16), showed that only the individual treatment T₄₋₅ (T+ Fe³⁺-B with 5% biomass) had a significant ($p \leq 0.05$) higher height value than the control (3.97 cm). The lowest value (1.84 cm) was noticed in the T₁₋₁₀ treatment (T containing 10% biomass), but Dunnett's test did confirm this difference.

Figure 16. Differences in height values (cm) between basil plantlets grown in the 12 tested substrates and plantlets from the control (T_0) at 64 DAS. Each value is the average of 5 replications. Vertical bars represent the standard deviation of each mean.



The position of the x-axis corresponds to the average height value in the control plants (T_0). For each treatment, mean values marked with * are significantly different from the control level according to Dunnett's test and 95% confidence.

The ANOVA conducted on the variable "leaf area" (Table 18) enlightened that both factors DAS and treatment caused significant differences ($p=0.000$), but no effect of their interaction was assessed. Based on this information, also in this case we studied the trend of the variable over time for individual treatments, including different biomass rates for each treatment (Figure 17).

As shown, in all treatments T_1 , T_2 and T_3 the addition of biomass induced a lower leaf area compared with the control (T_0) throughout all measurements (24, 31, 41, 51, 64 DAS). Dunnett's test confirmed this outcome in rather all surveys in the T_1 and T_2 treatments containing 10% biomass, and in the T_2-5 in the first two observations (24 and 31 DAS). Plants grown in the T_4 substrates ($T+Fe^{3+}$) with 10% and 5% biomass seemingly showed a wider leaf area than the others, although Dunnett's test did not overpass the significance threshold.

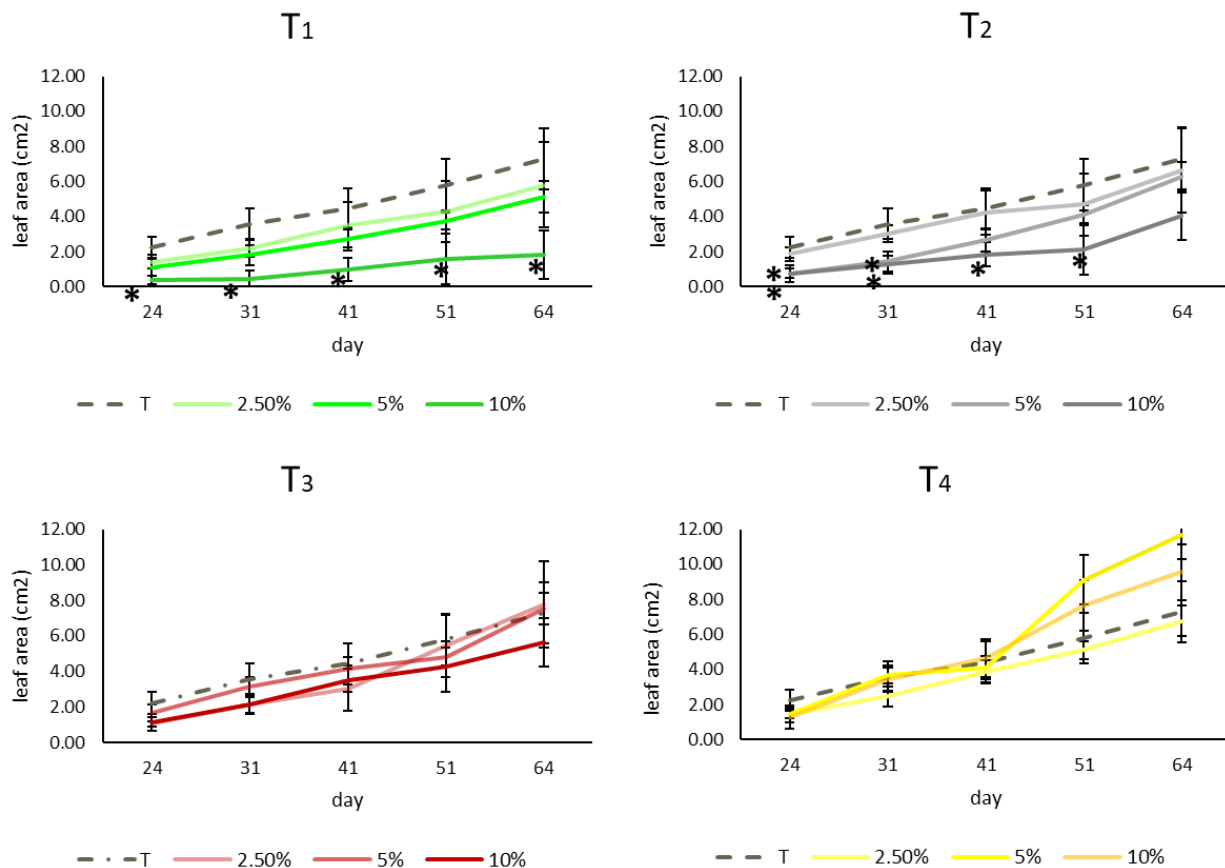
In the final survey (64 DAS) (Figure 18), although leaf area measured in T_0 (7.3 cm^2) resulted wider than in T_1-10 (1.82 cm^2) and smaller than in T_4-5 (11.36 cm^2), only the first difference was statistically confirmed at the Dunnett's test.

Table 18. Results of the ANOVA on plantlets' leaf area

Source	DF	F-Value	P-Value
DAS	4	48.61	0.000
Treatments	4	18.37	0.000
DAS* Treatments	16	1.65	0.056
Error	273		
Total	297		

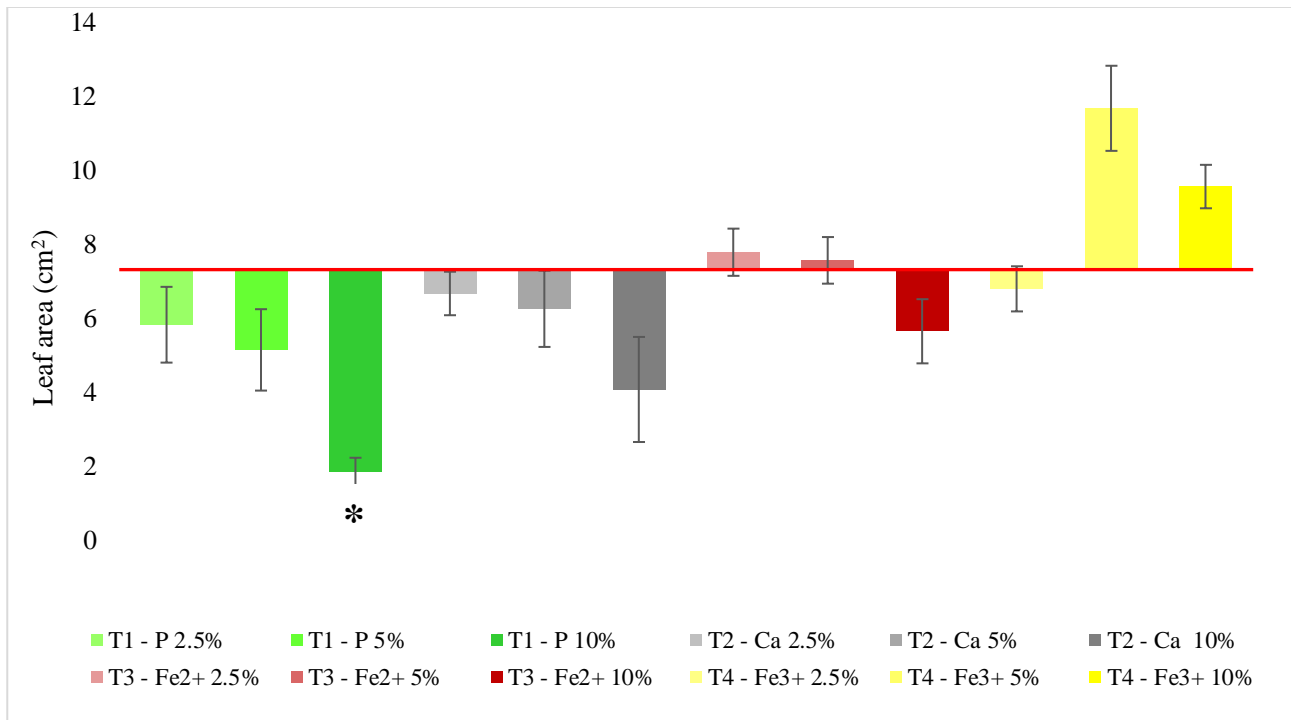
Note: Factor Information: DAS (24; 31; 41; 51; 64), Treatments (T₀; T₁; T₂; T₃; T₄)

Figure 17. Average trend of plantlets' leaf area (cm²) in the four groups of treatments (T₁, T₂, T₃, and T₄) with increasing addition of biomass (0, 2.5%, 5%, 10%), measured throughout the whole observation period (24 to 64 DAS). Each value is the average of 5 replications. Vertical bars represent the standard deviation of each mean.



For each survey date, mean values marked with * are significantly different from the control according to the Dunnett's test and 95% confidence.

Figure 18. Differences in leaf area (cm^2) between basil plantlets grown in the 12 tested substrates and plantlets from the control (T_0) at 64 DAS. Each value is the average of 5 replications. Vertical bars represent the standard deviation of each mean.



The position of the x-axis corresponds to the average leaf area in the control plants (T_0). For each treatment, mean values marked with * are significantly different from the control level according to Dunnett's test and 95% confidence.

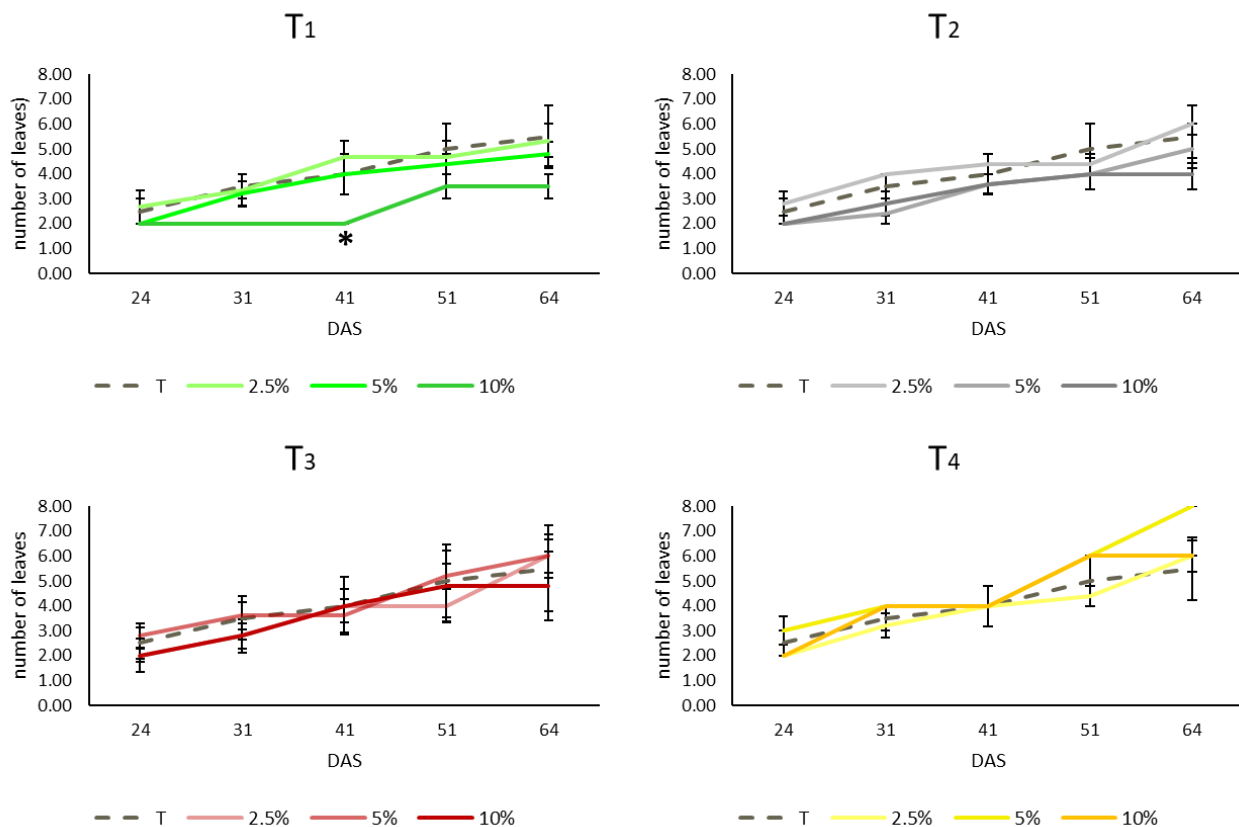
The ANOVA carried out on the number of leaves per plant (Table 19) showed the occurrence of highly significant differences ($p=0.000$) due to both experimental factors "DAS" and "treatments", whereas their interaction resulted not being significant. Based on this information, we studied the trend of the parameter over time for individual treatments, including different biomass rates for each treatment (Figure 19). Compared with the control (T_0), the different treatments did not affect the number of leaves of plants, which, irrespective of the treatment and the biomass content, in all cases showed an increasing trend over time. A slightly reduced number of leaves per plant compared with the control could be detected in the T_{1-10} treatment (Figure 19), although Dunnett's test confirmed this behavior only in the third survey (41 DAS).

Table 19. Results of the ANOVA on the number of leaves per plant

Source	DF	F-Value	P-Value
DAS	4	62.03	0.000
Treatments	4	8.71	0.000
DAS* Treatments	16	1.20	0.270
Error	273		
Total	297		

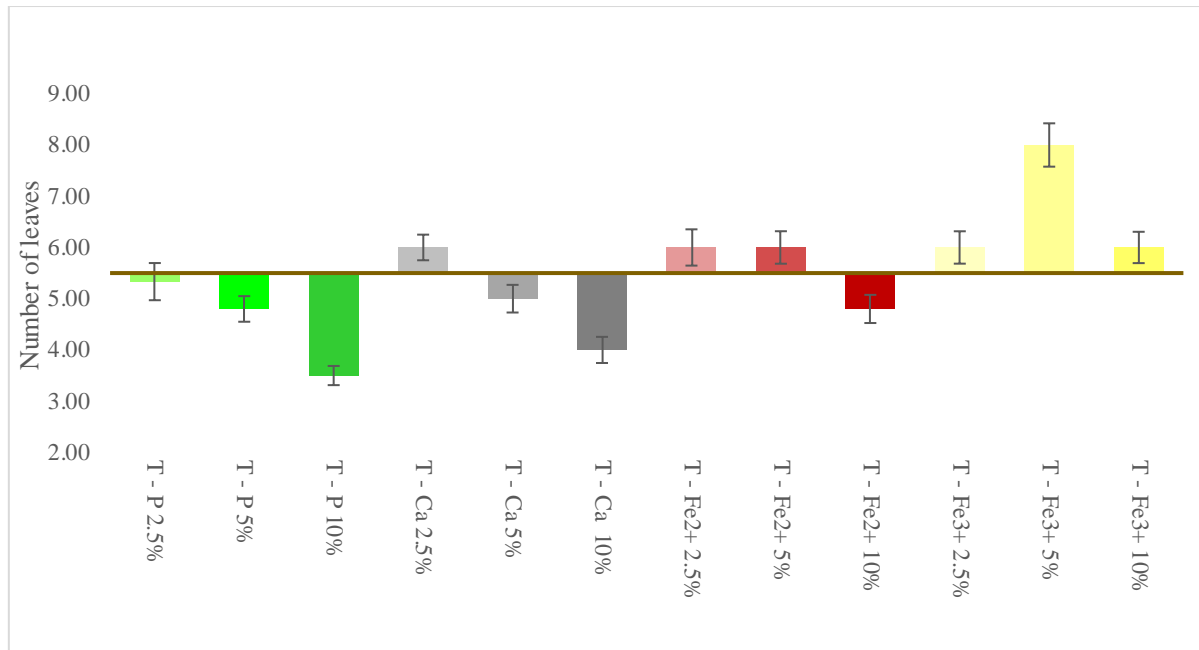
Note: Factor Information: DAS (24; 31; 41; 51; 64), Treatments (T₀; T₁; T₂; T₃; T₄)

Figure 19. Average trend of the number of leaves per plant in the four groups of treatments (T₁, T₂, T₃, and T₄) with increasing addition of biomass (0, 2.5%, 5%, 10%), measured throughout the whole observation period (24 to 64 DAS). Each value is the average of 5 replications. Vertical bars represent the standard deviation of each mean.



At the end of the measurements, the observation of the differences in leaf area between all the treatments and the T₀ (Figure 20), did not show any significant difference among treatments. However, although not confirmed in Dunnett's test, the visual observation of mean values shows a certain superiority of T₄-5 (8 leaves/plant) and, conversely, a reduced number of leaves in T₁-10 (3.5 leaves/plant).

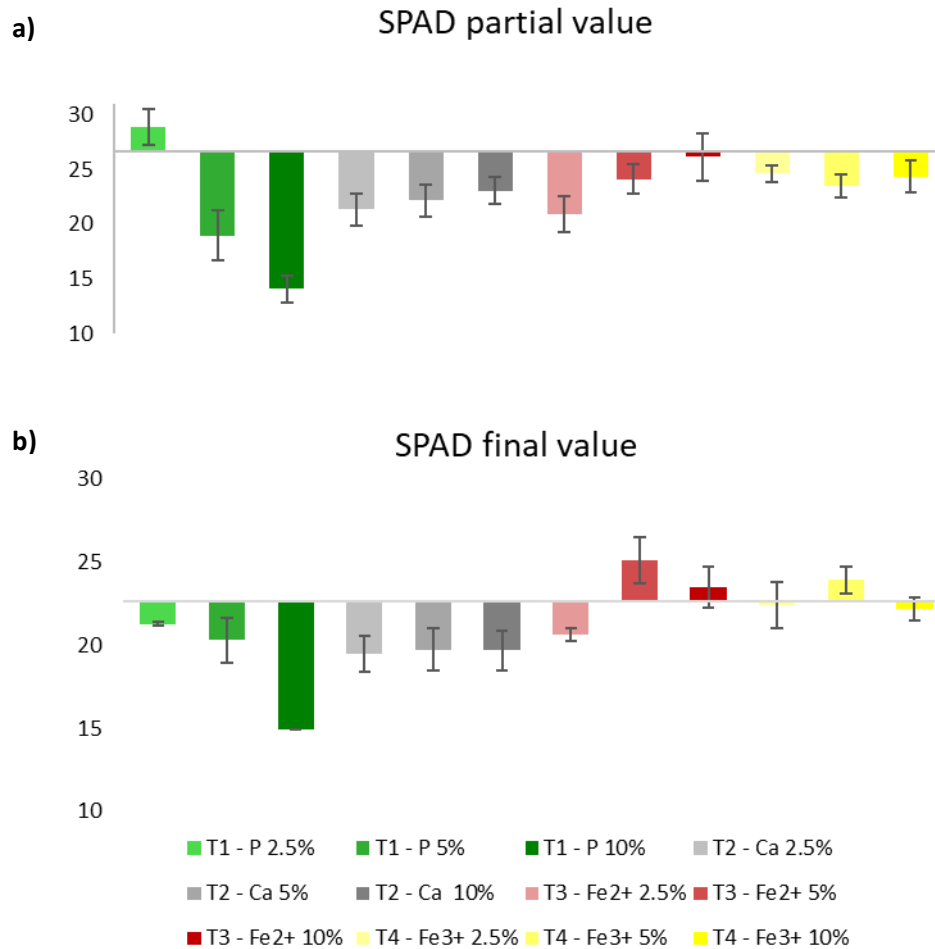
Figure 20. Differences in the number of leaves per plant between basil plantlets grown in the 12 tested substrates and plantlets from the control (T) at 64 DAS. Each value is the average of 5 replications. Vertical bars represent the standard deviation of each mean.



The position of the x-axis corresponds to the average number of leaves in the control plants (T_0). For each treatment, mean values marked with * are significantly different from the control level according to the Dunnett's test and 95% confidence.

Finally, some differences were noted between SPAD measurements at 51 and 64 DAS. The higher average partial SPAD values (26.17 and 28.92) were recorded in the control pots (T_0) and in the treatment $T_{1-2.5}$ and were like those reported by other researchers (Paparozzi et al., 2022) on Italian basil leaves. As shown in Figure 21a, in all treatments the recorded SPAD values were initially lower than those of the control, with remarkable differences in the T_1 treatments at 5% and 10% biomass. In the second measurement (Figure 21b), the SPAD values were lower than the partial values in all treatments, including the control (T_0). T_{1-10} was confirmed to have the lowest SPAD value; however, the differences between each treatment and the control decreased, and the groups of treatments T_3 and T_4 started showing slightly higher values than the control (T_0).

Figure 21. Differences in partial (a) and final (b) SPAD measurements between basil plantlets grown in the 12 tested substrates and plantlets from the control (T_0). Each value is the average of 5 replications.



The position of the x-axis corresponds to the average SPAD values measured in the control plants (T_0).

5.3.2 Measurements of available P in the substrates.

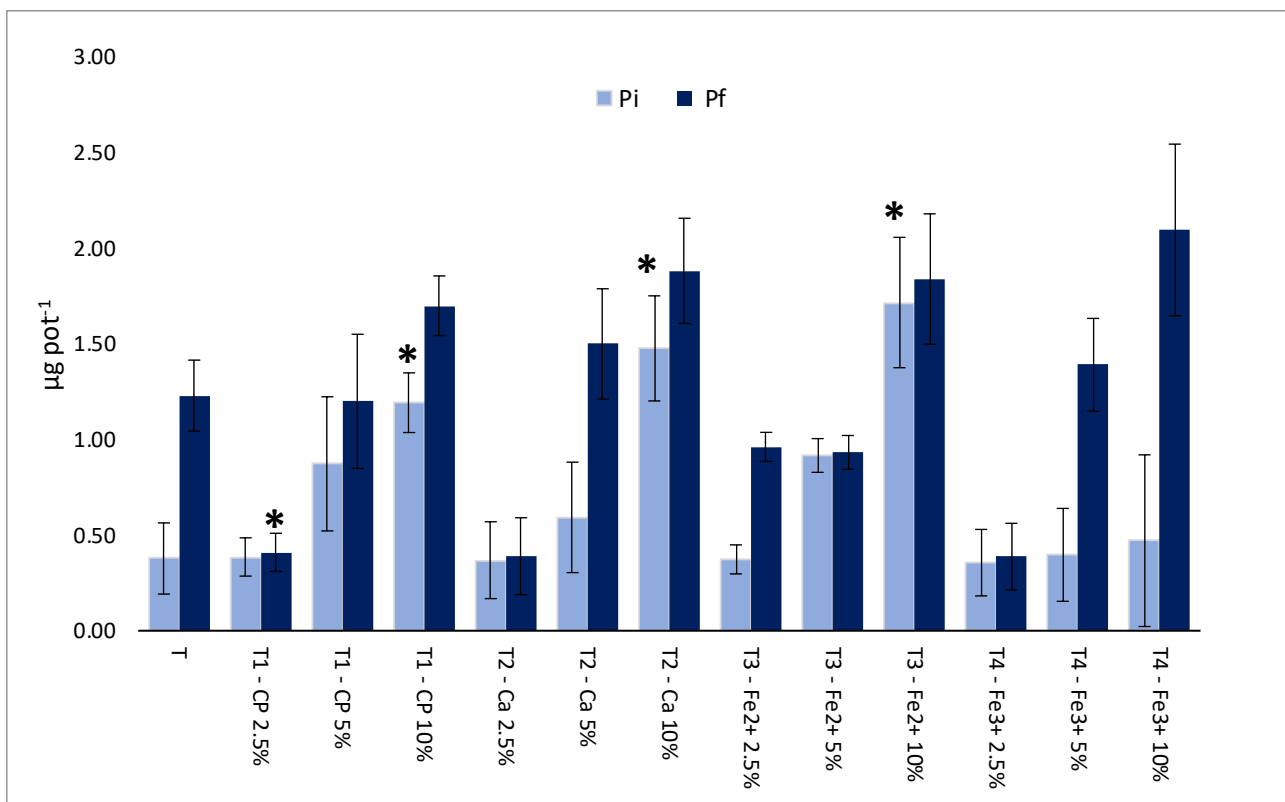
Statistical analysis conducted on the initial and final values of available P content in the tested substrates (Table 20) showed significant differences ($p=0.000$) due to both experimental factors (DAS and treatments), as well as their interaction. Hence, significant variations could be found between the two survey dates and among the different treatments, but the treatments' behavior resulted differently over time. The graph in Figure 22 brings evidence of a significant increase in time of available P in all treatments including the control. Furthermore, the comparison between the different biomass rates for each treatment clearly evidences a higher level of available P with increasing the biomass content within the substrate. However, Dunnett's test confirmed a significant difference between treatments

and control (T_0) only in the initial P content (P_i) of T_{1-10} , T_{2-10} and T_{3-10} substrates, where significantly higher P levels were detected. Oppositely, the final available P in the substrates (P_f) was not affected by the type of treatment but by the variations of biomass amounts, except for $T_{1-2.5}$ where a significantly lower P_f value was measured.

Table 20. Results of the ANOVA for the values of available P in the tested substrates.

Source	DF	F-Value	P-Value
DAS	1	58.35	0.000
Treatments	12	17.71	0.000
DAS* Treatments	12	2.45	0.013
Error	52		
Total	77		

Figure 22. Initial (P_i) and final (P_f) available P content in the 12 tested substrates and in the control (T_0). Each value is the average of 5 replications. Vertical bars represent the standard deviation of each mean.



For each treatment, mean values marked with * are significantly different from control according to the Dunnett's test and 95% confidence.



5.4. Discussion

In pot cultivation of basil, the proper choice of growing substrates has a paramount importance to achieve a high-quality product (Moncada et al., 2021). Hence, the possibility to add cactus pear pruning residuals -a cheap and largely available biomass in Mediterranean environments- to the growing substrates could represent a suitable choice for partial or total replacement of peat. The descriptive analysis conducted on the leaf area of plantlets over time, grouping the information collected by biomass treatment type, shows that the different biomass content in the tested substrates influenced plant growth.

Basil plants grown on the T₄₋₅ substrate had an overall better response than the control (T₀) in terms of height, leaf area and number of leaves per plant, and a moderate SPAD value, lower only than plants grown on the T₃₋₅ substrate. A similar response was found on the substrate T₄₋₁₀. With the difference that the increase in the biomass content within the substrate slightly reduced all the variables considered, but recorded a significant increase in available P_f.

Plants on the T₃₋₅ treatment also reached a similar height value to the plants grown in the T₄₋₅ substrate. However, the same trend was not manifested by leaf area, which was lower than the control and the T₄₋₅. This behavior was not evident in the other substrates, which differed by type of treatment received (Ca, Fe²⁺ and/or Fe³⁺) or by biomass content (2.5, 5, and/or 10%). The positive effects on basil growth on T₄₋₅, T₄₋₁₀, or T₃₋₅ might be due the presence of Fe in the added biomass, which promoted nutrient assimilation (Borlotti et al., 2012).

Iron (Fe), a critical element, is involved in various cellular processes in plants, such as chlorophyll synthesis, photosynthesis, and respiration (Guerinot and Yi, 1994). Despite its abundance in soil, Fe³⁺ in its oxidized, insoluble form prevails under aerobic conditions, making it inaccessible to plants (Guerinot and Yi, 1994). To overcome the limited availability of Fe, higher plants have developed strategies to acquire Fe from the rhizosphere, with non-graminaceous plants reducing soil pH and converting Fe³⁺ to soluble Fe²⁺ via Fe³⁺-chelate reductase and Fe²⁺ transport (Marschner et al., 1986). However, Fe³⁺ is a more stable and effective form of iron for plant growth than Fe²⁺. Fe²⁺ is readily oxidized to Fe³⁺, but is not as easily absorbed by plant roots, while Fe³⁺ is more easily absorbed and less likely to form insoluble compounds in the soil, making it more available to plants over a longer period (Schwertmann, 1991). In our experiment, the addition of Fe³⁺-loaded biomass to the growing media helps ensure the plants have access to the soluble iron they need for growth.

Unlike N availability, which was found to affect SPAD values due to an increase in the plant's chlorophyll content (Matsumoto et al., 2013), P availability did not affect SPAD measurements.



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5.5. Influence of cactus pear pruning waste on the potted growth of basil plants: Concluding remarks and synopsis

The use of recycled organic substrates from pruning waste, such as those from cactus pear pruning waste, can represent a sustainable and economical option for growing pot plants, such as basil (Figure 23). This organic matter can provide a suitable environment for plant growth and also improve soil structure, water retention capacity, and fertility as shown in chapter 4. The addition of recycled materials can affect water and nutrient availability for crops, and iron and calcium have been shown to have the greatest influence on basil growth in substrates.

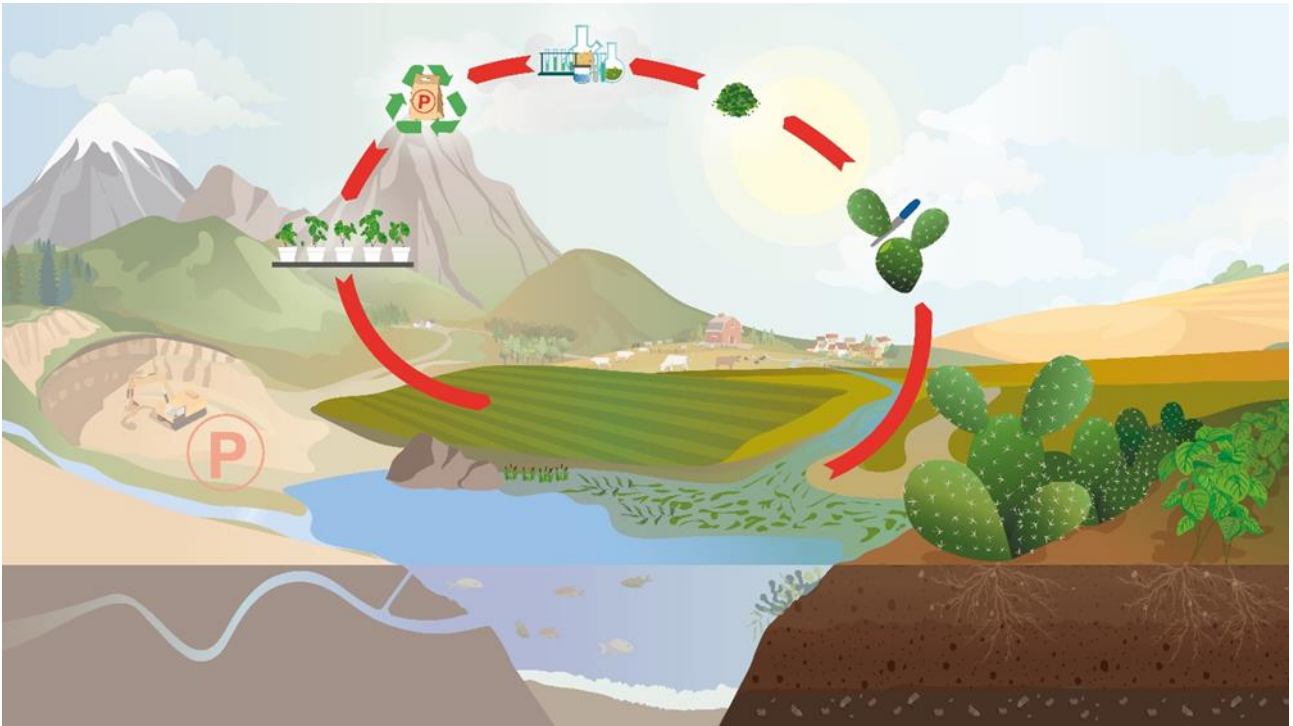
The research results show that basil plants grown in substrates with 5% content biomass had better growth responses in terms of height, leaf area, and number of leaves per plant. The addition of biomass loaded with Fe^{3+} to growth substrates helped improve nutrient assimilation in plants, suggesting that the positive effects of biomass on basil growth may be attributed to the presence of Fe in the biomass.

This approach can be particularly useful in areas where cactus pear pruning waste are an economical and widely available biomass, such as in Mediterranean environments.

Overall, this study highlights the potential of using recycled cactus pear pruning waste, as a sustainable and economical option for pot plant cultivation.. Further research is needed to optimize the use of these materials and determine their potential for widespread adoption in horticultural production.



Figure 23. The addition of cactus pear pruning waste showed positive effects on the water retention characteristics of two different soils.





6. Comprehensive conclusions

Given all the P-related issues, and to the need to find alternative P supplies, which will meet the ever-increasing global demand, becoming, thus, less dependent on phosphate rock, a limited resource, this thesis aimed to provide an overview, from both general and specific perspectives, on the P issue, which has become a sensitive issue at the international level today.

The conclusion from Chapter 2 focuses on the P flows from nonpoint sources. Annually, from European watersheds, about 0.084 Mt of P, due to runoff and erosion, escape from the system. The challenge is to reinsert P, relatively easily, into crop cycles before it becomes detrimental to the total environment. The most effective solutions come through the economic enhancement of its recovery from water bodies and reuse in soils. Current adsorbents, which recover P are mainly waste materials from the steel industry, which provide a high removal rate but do not allow direct reuse as a fertilizer. On the other hand, relatively few studies have been conducted on the desirability of recovering P with green and sustainable technology, taking, for example, agricultural waste into consideration.

Chapter 3 studied the use of cactus pear pruning waste (biomass), dried, ground and enriched in calcium (Ca) or iron (Fe), as a low-cost and eco-friendly adsorbent for removing P from artificially contaminated water solutions. The results showed that chemical enrichment led to a significant increase in calcium and iron content in the biomass, improving its ability to adsorb P. In particular, the experimental removal values obtained were 2.16 ± 0.02 , 1.3 ± 0.16 and 2.0 ± 0.3 mg P per g of biomass., respectively for the Ca-enriched, Fe²⁺-enriched, and Fe³⁺-enriched biomass. The Langmuir model was determined to be the most suitable for describing the equilibrium conditions of adsorption behavior in the sorbate-sorbent system, where low values of K_1 , suggest high sorbent affinity for sorbate, while the Freundlich model was not effective in describing the collected data. Desorption tests confirmed that the P adsorbed on the enriched biomass is stably retained, making it difficult to recover and regenerate the adsorbent for a new recovery cycle. However, this result suggests that the enriched biomass could be used directly in a real system as a soil amendment or plant substrate, providing the soil with nutrients that will be slowly released through microbial degradation. In this way, the use of biomass as an adsorbent can offer a sustainable and low-cost solution for removing P from contaminated water solutions.

This conclusion opened the way for other questions. Specifically, does the applicability of this new material in a real system in the form of a soil conditioner affect the physical structure and water content of the soil? So, in Chapter 4, we highlight that the biomass amendment showed positive



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effects on the water retention characteristics of two contrasting soils widely spread in the Mediterranean basin, a Terra Rossa soil (red soil, RS), and a Vertisol (black soil, BS). In both soil types, the addition of biomass resulted in a decrease in soil bulk density (BD) under dry conditions, which could be advantageous in fine textured compacted or degraded soils, having BD values $> 1.3 \text{ Mg m}^{-3}$, in which root elongation may be prevented and soil aeration reduced. At the same time, biomass showed a relatively high swelling potential. It resulted in a further decrease in wet BD, in addition to that caused by swelling of soil clay particles, which, when the soil is not free to swell, can lead to a reduction in soil porosity, which negatively affects air and water circulation. But also, a limited dose of biomass (a few percentage units) increased the drainable water capacity (DWC) of RS and had no effect on BS. Higher doses of biomass, caused a decrease in DWC both soils, thus confirming that biomass can hinder the soil's ability to drain water and limit air circulation. Plant available water capacity (PAWC) was also found to be affected by the addition of biomass, however observable benefits require very high biomass proportions, more than 20% by volume. Overall, the results showed that the addition of biomass, in both soil types, could trigger benefits on hydrological processes and agronomic services by promoting the increase of PAWC, while maintaining the biomass content below 20%, and the infiltration of plant roots due to the observed swelling phenomena. Therefore, biomass application, as a soil improver, can contribute to efficient water management in arid and semi-arid regions, which are characterized by limited water availability and low soil fertility. The type of soil is very important in the management choice, the use in soils with high clay content may not obtain the desired results.

Horticulture relies on growing media, GM, or plant support and nutrients, but traditional methods can be unsustainable. Sustainability requires using renewable GMs that can be reused or recycled, reducing synthetic fertilizers and pesticides. Peat is a reference GM, but its usage is controversial. Recycling pruning waste into organic GMs is sustainable but must be free of contaminants. Mixing pruning waste with other organic matter provides a balanced nutrient source. Basil is a perfect species for intensive horticulture due to its short growing period and fast germination and colonization of GMs. Locally available vegetable waste is a promising alternative GM. The goal of experiments, described in ch. 5, is to determine if biomass -mixed commercial substrate- is a sustainable and profitable option for basil cultivation. GMs' pH, iron and calcium have the greatest influence on basil growth (Chapter 5). In conclusion, the use of recycled pruning wastes from cactus pear as an amendment for basil plants in pots did not lead to improved growth on its own. However, when treated with a Fe^{3+} solution, these wastes had the potential to significantly enhance growth conditions for



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basil. These findings provide insights into the potential of recycled cactus pear waste as a valuable resource for improving soil health and plant growth in horticultural settings. Further research is needed to fully understand the interactions between cactus pear waste and other soil amendments to optimize its benefits for agriculture.

The results obtained, during these years, are encouraging and suggest that investing time, money and experience is crucial to deepen some aspects of research in the future, covering what I have not examined, such as extending the feasibility of recovering P directly from runoff channels or waterways, or testing new agricultural waste materials, making a comprehensive assessment of their potential as P adsorbents and the effects their interaction with the soil-plant system would cause. Addressing the problems associated with the reckless use of P in agriculture, which inevitably leads to excessive losses of P, and turning attention to alternative sources of P to avoid the collapse of fertilizer supplies, is the easiest way forward to ensure access to a limited and nonrenewable resource for future generations.

The results of this doctoral thesis demonstrate the potential of using biomass as a low-cost, environmentally friendly alternative for P removal from water and reintegration into the soil-plant system, providing positive effects on soil water retention and promoting efficient water management in arid and semi-arid regions. However, the impact of this new material on the soil-plant system requires further research to optimize its application and explore new agricultural waste materials as P adsorbents. Based on this, future research needs could try to study the stability of biomass in the soil to *i*) test how long biomass remains as such in the soil before it is decomposed by microorganisms; *ii*) assess whether Fe-bound P will be available to plants or is too strongly adsorbed that none of the decomposers can detach it; *iii*) compare a P fertilizer and P-enriched biomass by assessing its solubility, stability, and availability to plants.



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