

Article

Evaluation of Pig Manure for Environmental or Agricultural Applications through Gasification and Soil Leaching Experiments

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Abstract: The current study aimed at evaluating an untreated pig manure, firstly for its suitability for soil amendment in combination with an agricultural/bio-solid biochar, and secondly for its potential to be used for adsorption of hazardous species, replacing expensive activated carbons. Column soil leaching experiments were designed to simulate field conditions, and physical, chemical and mineralogical analyses were performed for raw materials and/or leachates. For activated carbon production, the manure was gasified by steam or carbon dioxide at high temperatures. Biochars were analyzed for organic and mineral matter, structural characteristics and organic functional groups. Activation by steam or carbon dioxide greatly enhanced specific surface area, reaching values of 231.4 and 233.3 m²/g, respectively. Application of manure to the soil promoted leaching of nitrates and phosphates and raised COD values of water extracts. Biochar addition retained these ions and reduced COD values up to 10 times at the end of the three-month period. The concentrations of heavy metals in the leachates were low and, in the presence of biochar in soil blends, they were significantly reduced by 50–70%. The manure presents a significant potential for adsorption of various pollutants or improvement of soil amendment if carefully managed.

Keywords: manure; leaching; soil; biochar; gasification; active carbon



Citation: Vamvuka, D.; Raftogianni, A. Evaluation of Pig Manure for Environmental or Agricultural Applications through Gasification and Soil Leaching Experiments. *Appl. Sci.* **2021**, *11*, 12011. <https://doi.org/10.3390/app112412011>

Academic Editor: Vincenza Ferraro

Received: 22 November 2021

Accepted: 14 December 2021

Published: 16 December 2021

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1. Introduction

Animal wastes such as manure, a low-value byproduct of livestock feedlots, are readily available in large quantities in most countries around the world, including those of South Europe. In Greece, where animal breeding activity is highly developed, about 41 Mm³ of animal wastes is produced annually [1] and stocked outside animal processing industries or in rural areas, causing environmental pollution. Thus, traditional land application is no longer a viable solution. EU directives 1991/31/EC and 1991/676/EC imposed a reduction in the quantity of biodegradable wastes going to landfill.

The use of animal manure as a fertilizer reduces the volume of wastes and ameliorates the physical, chemical and biological properties of soil, providing various nutrients for plant growth [2,3]. However, the process of composting can change the properties of manure and, if not carefully managed, can cause eutrophication or contamination of soil and water sources [3–5]. The limitations imposed by the composting process have turned scientific attention to investigate the blending of composts with other wastes, to potentially improving the availability of nutrients and leaching of toxic heavy metals in soils [6–10]. Such wastes may be agricultural residues, which are particularly abundant in Mediterranean countries, and contain significant concentrations of Ca, Mg and K [5], in addition to urban bio-solids, which are rich in N, Ca, P and Fe [11]. All of these elements are important for improving soil fertility. In Greece, about 3.8 M dry tons of agricultural residues are produced annually [12], whereas about 30 kg/capita/year of dry bio-solids [11] are produced from wastewater treatment plants.

As an alternative to soil application, animal manures can be converted to added-value products through thermal treatment. Pyrolysis destroys pathogens from these wastes [5], and generates bio-oil and gas, which provide useful energy [13,14], and a carbon rich and porous material, biochar, which is of high interest. In addition to its potential to be used as fuel, as a carbon sink in soils for thousands of years, or as soil fertilizer [15–18], biochar may exhibit similar properties as activated carbons, adsorbing various contaminants from soil and waste waters, such as heavy metals [19–21] and organic pollutants [17,22,23]. These properties, such as specific surface area, pore structure and organic functional groups, can be enhanced by physical or chemical activation [17,24], providing a bio-carbon of higher reactivity and lack of tar in the product gas [25]. Physical activation without using chemical reagents, such as alkali or acids, is more environmentally friendly and has a lower cost. When steam is used, the calorific value of the product gas is enhanced, whereas when carbon dioxide from residual flue gases is the activation agent, the process offers a potential solution to the greenhouse gas problem, avoiding its capture and sequestration [24,25]. Therefore, physical activation by steam or carbon dioxide is both environmentally and economically more advantageous. The final properties of biochar depend on the raw material and the conditions of the thermal process [5,13,14].

A large number of studies have been undertaken relevant to soil amendment using composts [3,4,26,27] or biochars [7,9,10,13,26–29] from various biomass materials (agricultural wastes, sewage sludge). Co-application of composts from animal manure and woody biochars has been less investigated (pig slurry/wood chips compost and rice husk biochar [2], chicken manure/straw compost and empty palm fruit biochar [6], pig manure/straw compost and maize straw biochar [23], horse and rabbit manure/grass, fruits, seaweed compost and oak wood biochar [30]). Reported results include reduction in heavy metals [2] and nutrients mobility [6] and bio-availability of organic pollutants [23] from contaminated soils, in addition to suppression of plant-parasitic nematodes [6]. However, combined utilization of untreated manure with mixtures of agricultural/bio-solid biochars is scarce (dairy cattle manure with hardwood biochar [31], swine manure with corn straw biochar [32]) and examines microbial respiration, fungi/bacteria abundance, and uptake of nitrogen and phosphorous upon bioleaching. Furthermore, generation of potential activated carbons has focused on agricultural wastes [33–35] and there is limited information in the literature on animal manure biochar activated by steam or carbon dioxide [24].

In the context of sustainable recycling of animal manures, meeting the policies of the EU on the environment and the circular economy [11] and based on the previous discussion, the current study aimed at evaluating an untreated pig manure, firstly for its suitability for soil amendment in combination with an agricultural/bio-solid biochar and secondly for its potential to be used for adsorption of hazardous species, replacing expensive activated carbons. The first objective was to conduct column soil leaching experiments, designed to simulate field conditions for a three-month period, and measure the concentrations of nutrients or toxic substances in water extracts. Physical, chemical and mineralogical analyses were performed for raw materials and/or leachates. The second objective was to produce a biochar material from manure for use as an adsorbent, through pyrolysis and subsequent activation by either steam or carbon dioxide at high temperatures. Each biochar was analyzed for organic and mineral matter, structural characteristics and organic functional groups.

2. Materials and Methods

2.1. Raw Materials Characterization

The manure (MAS) was provided from a swine breeding factory in the region of Rethymno-Crete. Before being used in the experiments, it was passed through a riffler in order to obtain representative samples and then sieved to particle sizes <500 µm. The soil used for the leaching tests was sampled from the top 20 cm of the area of Chania-Crete, following the rectangular grid method. After riffling and sieving to a particle size <2 mm, it was subjected to physical, mineralogical and chemical analyses. In these tests, two biomass

materials were also used: cotton stems (COS) provided by a ginning factory in Central Greece and a bio-solid (BIS) from the waste water treatment plant of the city of Chania. These were air-dried, ground to a particle size of $<500\ \mu\text{m}$ (cotton stems in a cutting mill, bio-solid in a ball mill) and riffled.

European standards CEN/TC335 were adopted for the characterization of raw materials in terms of proximate (moisture, volatile matter, fixed carbon, ash) and ultimate (C, H, N, S, O) analyses. An X-ray diffractometer (XRD), model A8 Advance of Bruker AXS, was employed for the detection and identification of mineral phases in ashes, by DIFFRAC plus Evaluation software in conjunction with the JCPDS database. Chemical analysis in major elements was conducted by an X-ray fluorescence spectrometer, model S2 Ranger/EDS of Bruker AXS.

2.2. Biochar Production and Activation

The equipment used for the production of biochars, through pyrolysis experiments in nitrogen, was a high temperature fixed bed unit, described in detail in a previous work [5]. In a typical test, about 15 g of sample was placed in a stainless steel grid basket supported by a rod and inserted into the reactor. The unit was assembled, introduced into the furnace and flushed with nitrogen for 30 min at room temperature. The furnace was set to the desired temperature at a heating rate of $10\ ^\circ\text{C}/\text{min}$. The temperature was measured by a Ni-Cr-Ni thermocouple, in contact with the sample bed. The flow rate of nitrogen during pyrolysis was 150 mL/min and the retention time at the final temperature 30 min. Volatile products were passed through iso-propanol cooled by ice-baths, to collect condensables. The system was cooled under nitrogen and the resultant biochar was weighed and stored for further tests.

In the case of adsorption experiments, the manure was pyrolyzed at 700 or 800 $^\circ\text{C}$. Following pyrolysis, manure was activated either by steam (flow rate 2500 mL/min), generated by distilled water flowing at 0.5 mL/min with a piston pump inside a spiral tube within the furnace, or by carbon dioxide (flow rate 150 mL/min), and was held at the activation temperature for 1 h, before being cooled under nitrogen.

In the case of leaching experiments, cotton stems and bio-solid were pyrolyzed as above, but the final temperature was 350 $^\circ\text{C}$, to maintain important properties for soil amendment [4,7,9,10,36].

Structural characteristics of both pyrolyzed and steam/carbon dioxide-activated manure were determined by an automatic volumetric apparatus, model Nova 2200 of Quantachrome, according to the BET method. Manure sample was out-gassed overnight at 150 $^\circ\text{C}$ under vacuum prior to each test. Furthermore, the chemical functional groups of this material were identified through a spectrophotometer, model Spectrum 100 of Perkin Elmer, recording FTIR spectra at a resolution of $4\ \text{cm}^{-1}$, in the range of 400–4000 cm^{-1} wavenumbers.

2.3. Leaching of Manure and Biochars through the Soil

Soil, manure and biochar (cotton stems/bio-solid 70:30) mixtures were prepared as follows: manure/soil 50 g/kg, manure/soil 100 g/kg, biochar/manure/soil 50 g/100 g/kg and biochar/manure/soil 100 g/50 g/kg, representing common application rates of 0–100 t/ha soil [37]. All mixtures were homogenized in glass pots and kept at 30 $^\circ\text{C}$ in the dark for a one-month period, during which they were wetted with de-ionized water and gently stirred, periodically. After this incubation procedure, simulating agronomic practices for soil amendment, admixed materials were packed into PVC (ID = 2.5 cm, H = 25 cm) columns, fitted with fiberglass and a valve at the base and saturated with de-ionized water. Leaching was discontinuous over a three-month period, simulating as much as possible local rainfall conditions and percolating through each column an amount of de-ionized water corresponding to the average annual quantity of rainfall in the area between the years 2015–2020 (about 600 mm). Keeping the hydraulic head constant on the basis of communicating vessels and after collecting enough liquid for the chemical

analyses, each effluent was filtered through micropore membrane filters several times and kept in acid washed bottles in the refrigerator.

The apparent density of solid materials before and after incubation was measured following the ASTM D-285 method [38], and the water holding capacity was measured following the method proposed by Ye et al. [39]. pH and electrical conductivity were measured with a pH-meter type Toledo LE438 of Mettler and an EC215 of Hanna, respectively. For solid samples, the solid-to-deionized water ratio was 1:5. A spectrophotometer UV-VIS, model Smart 3 of LaMotte, was used for analyzing leachates in chemical oxygen demand (COD; by the mercury digestion method 0077-SC, measuring range 0–15,000 mg/L), N-NO₃ (by the zinc reduction method 3689-SC, measuring range 0–60 mg/L), P-PO₄ (by the vanadomolybdophosphoric acid method 3655-SC, measuring range 0–90 mg/L) and phenols (by the aminoantipyrine method 3652-SC, measuring range 0–6 mg/L). Analysis of trace elements in leachates was performed by an inductively coupled plasma mass spectrometer, model ICP-MS 7500cx of Agilent Technologies, assisted by an Anton Paar Multiwave 3000 oven, for samples' digestion.

3. Results and Discussion

3.1. Chemical and Mineralogical Properties of Raw Materials

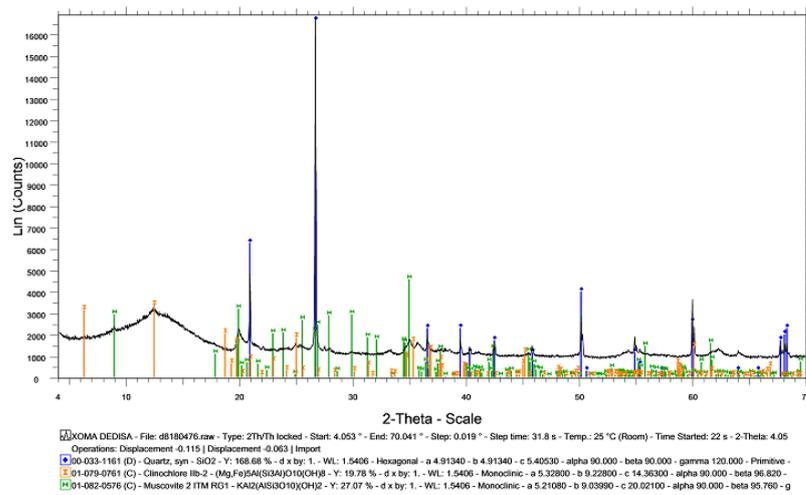
A comparison of proximate and ultimate analyses of the raw materials studied is represented in Table 1. All samples were rich in volatiles. Cotton stems had the highest volatile matter content, fixed carbon and oxygen contents, and the lowest ash, nitrogen and sulfur concentrations. By comparison, the ash content of manure was high, whereas its carbon, hydrogen and oxygen contents were lower among the other materials. However, the amounts of sulfur and particularly nitrogen of manure and bio-solid samples were significant, revealing gaseous emissions during thermal treatment, but also increased capacity for plant nutrition when applied to soils for amelioration.

Table 1. Proximate and ultimate analysis of raw materials (% dry).

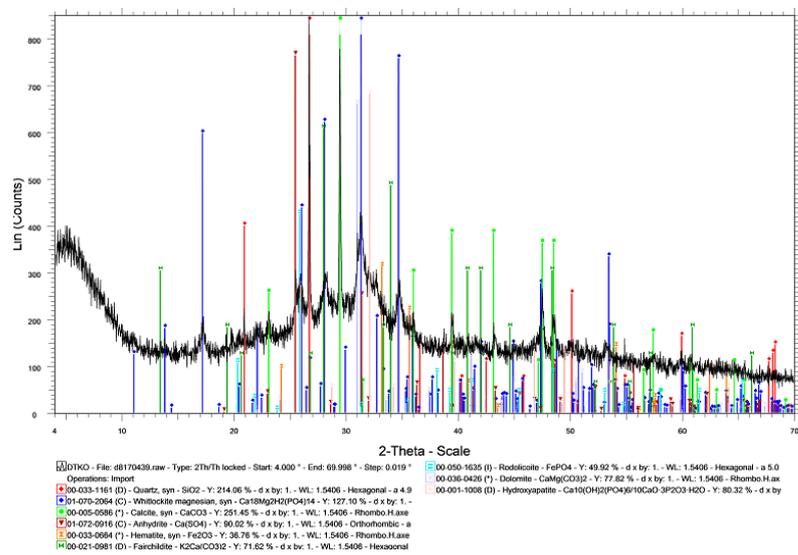
Sample	Volatiles	Fixed Carbon	Ash	C	H	N	O	S
Manure (MAS)	51.9	16.5	31.6	35.8	5.3	3.6	22.2	1.5
Cotton stems (COS)	73.4	18.3	8.3	46.8	6.5	1.6	36.7	0.2
Bio-solid (BIS)	65.6	16.6	17.8	43.0	6.6	7.9	22.9	1.8

Figure 1 illustrates the XRD spectra of the samples. The soil was of quartzitic nature, with small amounts of muscovite and chlorite minerals. The manure was rich in Ca, Mg, P and Fe phases, such as calcite, dolomite, whitlockite magnesian, hematite and rodolicoite. P was also incorporated in hydroxyapatite, whereas K was found in fairchildite. The bio-solid consisted mainly of whitlockite magnesian and considerable amounts of Ca and Fe bound in calcite, hematite and kennedyite. The cotton stems sample was dominated by K and Mg, in the forms of sylvite, arcanite and dolomite, respectively, and to a smaller extent by Ca identified in carbonates, phosphates and aluminosilicates.

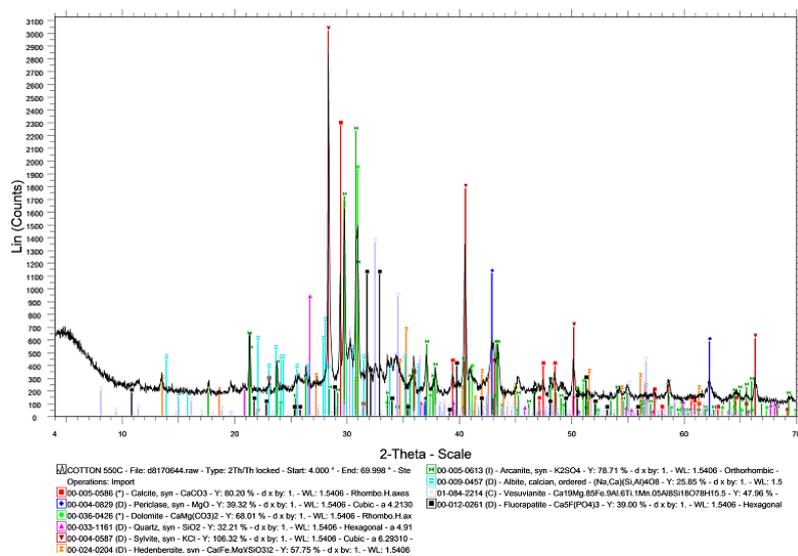
The concentrations of the major elements in manure and biochars, represented in Figure 2, are in accordance with the XRD analysis discussed above. Regarding nutrients, the higher quantities of Ca and Mg were measured in manure, the higher amounts of P and Fe were measured in the bio-solid, and those of K were measured in cotton stems biochar. These concentrations are comparable to those of similar materials reported by previous investigations [13,18,28]. However, it must be noted that the solubility of the minerals incorporating these nutrients governs their bio-availability in soils [18,28].



(a)



(b)



(c)

Figure 1. Cont.

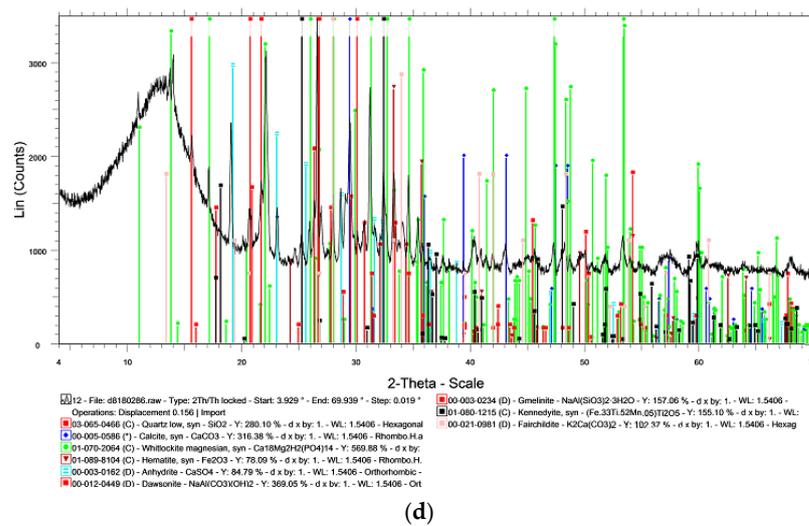


Figure 1. XRD spectra of (a) soil, (b) pig manure, (c) cotton stems, (d) bio-solid ashes.

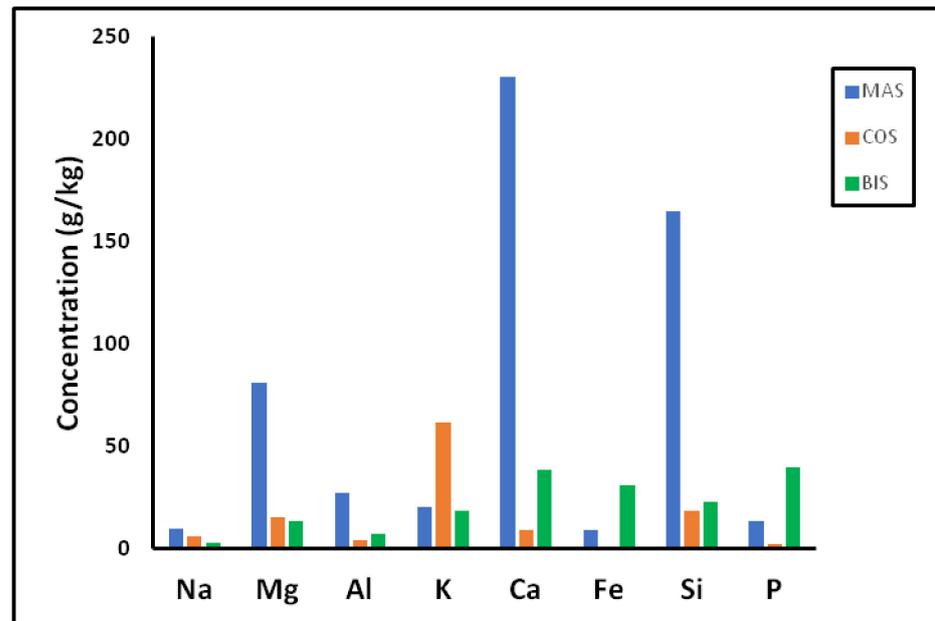


Figure 2. Concentration of major elements in pig manure, cotton stems and bio-solid biochars.

3.2. Physical Activation of Manure

3.2.1. Yield of Products under Different Atmosphere

The yield of solid products of pyrolysis under nitrogen and of those activated by gasification under steam or carbon dioxide, as a function of temperature, is compared in Figure 3. As can be seen, when the pyrolyzed material was activated with either steam or carbon dioxide, the yield of biochar was lower with respect to pyrolysis only and the drop was higher in the presence of steam. In a previous work by the authors, it was found that the higher reactivity of steam was due to favored reactions of the oxygen organic functional groups of biochar, whereas carbon dioxide disrupted the hydrogen char structure [35]. Moreover, a higher activation temperature led to the production of less biochar, due to enhanced thermal decomposition of manure and secondary cracking of vapors. The proportions of bio-oil and gas (not shown in Figure 3) varied between 37.5% and 9.5–12.5%, respectively, at 700 °C, and between 24.6% and 27.5–41.6%, respectively at 800 °C, with higher heating values 20–40 MJ/kg for bio-oil and 11–15 MJ/m³ for

gas [40]. These values were considered highly satisfactory for the energy requirements of the pyrolysis/gasification unit.

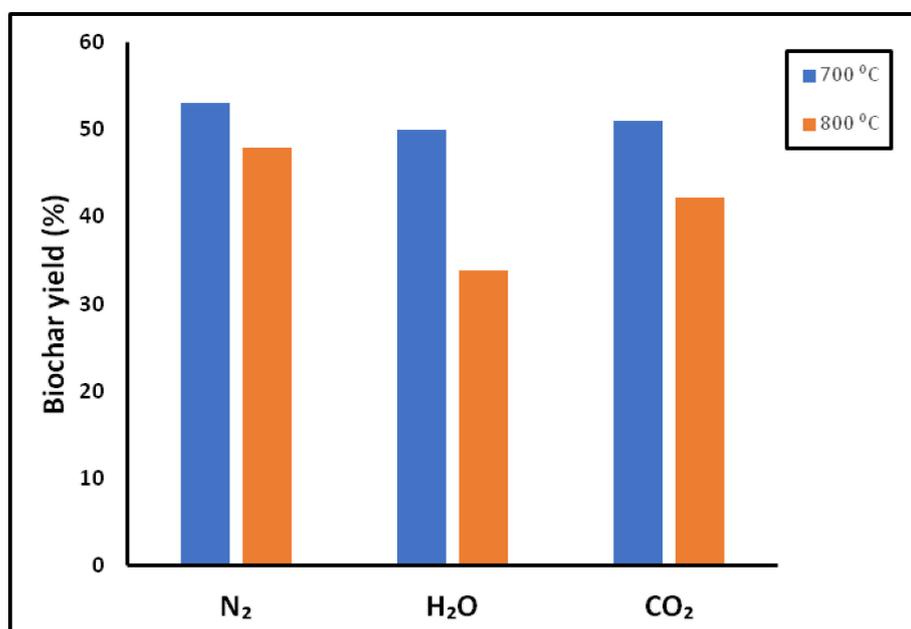


Figure 3. Yield of biochar under N₂, H₂O_v or CO₂ atmosphere as a function of temperature.

3.2.2. Structural Characteristics and Chemical Functional Groups under Different Atmosphere

The structural characteristics of manure biochar produced after pyrolysis with nitrogen or combined pyrolysis-gasification with steam or carbon dioxide are summarized in Table 2. As can be seen, a rise in pyrolysis temperature from 700 to 800 °C, associated with a greater decomposition and release of volatile products, elevated pore volume and size and increased the surface area by 45%. Nevertheless, the value of 69 m²/g was quite low, most probably due to the high ash content of manure biochar, which can hinder the access of nitrogen to the pores. Previous investigations have reported [19,22,24,41,42] even lower surface areas of 2.4–17 m²/g at 500 °C and 8.3 m²/g at 700 °C.

Table 2. Structural characteristics of manure biochar produced after pyrolysis/gasification.

Temperature (°C)	Activation Gas	Specific Surface Area (m ² /g)	Micropore Volume × 10 ² (cm ³ /g)	Average Pore Size (Å)
700	N ₂	47.6	4.4	37.0
	H ₂ O _v	231.4	15.9	33.0
800	N ₂	68.9	5.9	49.3
	H ₂ O _v	228.7	21.5	45.1
	CO ₂	233.3	16.2	33.3

When manure biochar was further activated with steam at 700 °C, it is clearly shown that micropore volume and surface area were greatly enhanced 4.9-fold, reaching a value of 231.4 m²/g. At the higher temperature of 800 °C, microporosity increased, in addition to the size of the pores, which are characterized as mesopores. By comparison, upon activation of manure biochar with carbon dioxide at 800 °C, microporosity was developed, the average pore size was smaller and specific surface area was elevated 3.4-fold, reaching a value of 233.3 m²/g. Some authors reported [24] a further increase in microporosity and specific surface area at a higher temperature, 900 °C, enabling a value of 700 m²/g to be attained.

From the above results, taking into consideration the yield and surface area of manure biochar activated by either steam or carbon dioxide at 700 and 800 °C, it can be inferred that this material presents a significant potential for adsorption of various inorganic or organic contaminants and it is promising for further investigation.

Table 3 compares the chemical functional groups identified [43] from the FTIR spectra of the manure sample produced under nitrogen, steam and carbon dioxide activation at 800 °C. The Pyrolyzed material represented C=C alkene groups at 666 cm^{-1} , whereas C-O sharp peaks in the range 1000–1400 cm^{-1} are associated with alcohols and ethers. Peaks at 1454, 1650 and 1714 cm^{-1} are characteristic of C-H, C=C and C=O stretching vibration bands from alkanes, alkenes and carboxylic acids, respectively, and were also identified in a previous study [24]. Smaller bands in the range 2000–2400 cm^{-1} correspond to O=C=O stretching, whereas those in the range 2500–3000 cm^{-1} are assigned to C-H deforming vibration from aldehydes or alkanes. Finally, the broad band between 3000 and 4000 cm^{-1} indicates the presence of –OH stretching groups from alcohols or carboxylic acids. FTIR spectra are generally in agreement with those obtained for different manure biochar samples [22,41].

Table 3. FTIR analysis of manure biochar produced under nitrogen, steam, or carbon dioxide.

Wavenumber (cm^{-1})/Functional Groups	N ₂	H ₂ O	CO ₂
500–600/C-X halo compounds		556 592	564 592
650–1000/C=C alkenes	666		
1000–1400/C-O alcohols, ethers	1046 1114 1146 1156 1234	1030 1090	1036
1300–1600/C-H alkanes, C=C aromatic compounds	1454	1550	1440
1600–1670/C = C alkenes	1650		1602
1650–1750/C = O carboxylic acids	1714		
2000–2400/O = C = O carbon dioxide	2318 2350		
2500–3000/C-H aldehydes, alkanes	2848 2918		
3000–4000/-OH alcohols, carboxylic acids	3292		3436

When the material was activated by steam, Table 3 shows that, in addition to the small peaks at 500–600 cm^{-1} corresponding to C-X stretching from halo compounds, a new broad peak appeared at 1550 cm^{-1} , indicating the presence of C=C stretching from aromatic compounds. No peaks were detected at higher wave numbers (Figure 4). By comparison, in the case of carbon dioxide activation, an additional broad band was identified at 3436 cm^{-1} , characteristic of –OH stretching from alcohols, implying that the aromaticity of char was higher in the presence of steam.

3.3. Leachability of Manure Blends through the Soil

3.3.1. Physicochemical Properties before and after Incubation

The physicochemical properties of manure and cotton stems/bio-solid biochar, with different combinations before and after the incubation period, are represented in Table 4. The most important properties that affect the leachability of nutrients and heavy metals from soil, in addition to the retention of moisture by soil and, consequently, plant growth, are the pH and the water holding capacity of the solid materials, respectively. As can be noted, before incubation all solid mixtures were slightly alkaline (pH = 7.6–7.8) with small electrical conductivity values (1.05–1.1 mS/cm), properties which positively influence soil amelioration [4,32]. After incubation, there was a small drop in pH and a marked

decrease in electrical conductivity, revealing that some alkaline salts were released, leaving a solid material with a higher potential for uptake of nutrients or water by plants upon soil application [4]. This is strengthened by the fact that after incubation the volume (density decrease) and the water holding capacity of all blends, especially those containing the biochar, were increased (d was decreased up to 42% and WHC was increased up to 30%), improving absorption of water by soil.

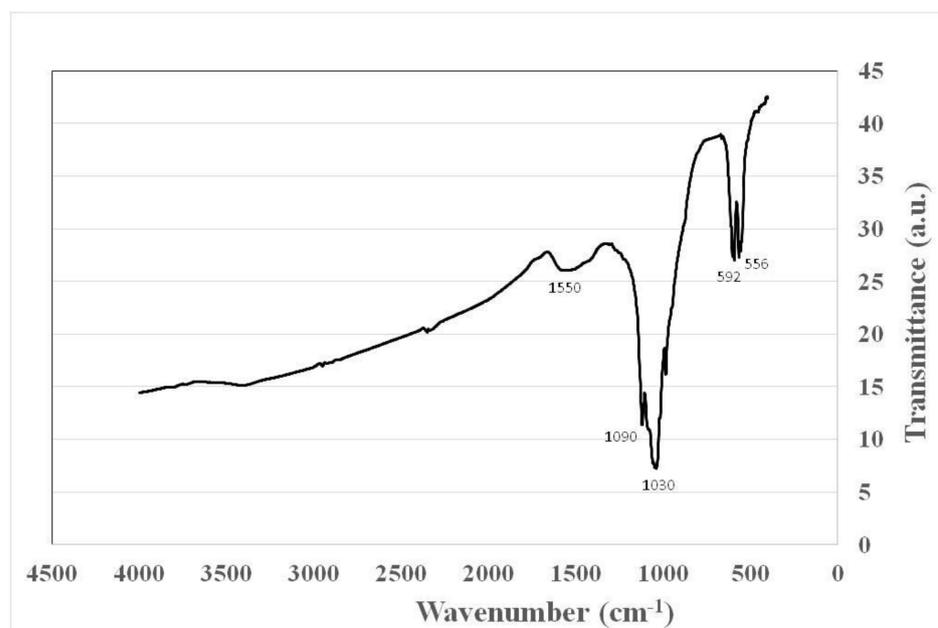


Figure 4. FTIR spectra of pig manure biochar activated by steam at 800 °C.

Table 4. Physicochemical properties of solid blends.

Sample	Before Incubation				After Incubation			
	d (g/cm ³)	pH	EC (mS/cm)	WHC (g/g)	d (g/cm ³)	pH	EC (mS/cm)	WHC (g/g)
Soil	1.06	7.80	1.05	0.92				
MAS/soil 50 g/kg	1.02	7.70	1.10	0.94	1.0	6.35	0.20	1.0
MAS/soil 100 g/kg	1.01	7.60	1.10	0.94	0.63	6.30	0.40	1.0
COS-BIS/MAS/soil 50 g/100 g/kg	1.01	7.68	1.06	0.94	0.64	6.38	0.45	1.18
COS-BIS/MAS/soil 100 g/50 g/kg	1.0	7.79	1.05	0.94	0.61	6.41	0.20	1.20

3.3.2. Leaching of Nitrogen, Phosphorous Anions and Phenols

The leaching behavior of nitrogen and phosphorous anions and phenols with time from the soil/manure/biochar mixtures, together with the variation of pH and electrical conductivity in the leachates, is illustrated in Table 5. Addition of a higher amount of manure to the soil (100 g/kg instead of 50 g/kg) reduced the pH of the first water extract from 8.1 to 6.2. In both cases, the pH became neutral after a three-month period (7.1 in the case of MAS/soil 50 g/kg and 7.2 in the case of MAS/soil 100 g/kg). However, the more biochar was added (100 g/kg of COS-BIS, instead of 50 g/kg), the higher was the pH of the leachates (up to 8.5), due to the dissolution of some alkaline substances from biochar, such as carbonates of Ca, Mg and K (calcite, dolomite and fairchildite seen in Figure 1). Moreover, Table 5 shows that some readily soluble salts were released from the soil/manure blend in the first leachate, increasing the electrical conductivity values (2.8 mS/cm in the case of MAS/soil 50 g/kg and 4.9 mS/cm in the case of MAS/soil

100 g/kg). In the presence of COS-BIS biochar, these values dropped significantly and were very low after 22 days leaching time (0.4–1 mS/cm). As previously mentioned, a higher pH and a lower electrical conductivity favor availability of nutrients for plants.

Table 5. Leaching of ions and phenols from solid mixtures.

Sample	Leaching Time (days)	pH	EC (mS/cm)	NO ₃ [−] (mg/L)	PO ₄ ^{3−} (mg/L)	Phenols (mg/L)
MAS/soil 50 g/kg	1	8.1	2.8	26	6	1.7
	8	8.1	0.8	45	31	
	22	7.5	0.9	38	33	
	36	7.4	1.0	32	34	
	60	7.2	0.6	25	36	
	90	7.1	0.4	20	40	
MAS/soil 100 g/kg	1	6.2	4.9	43	62	2.4
	8	6.4	3.6	42	69	
	22	6.5	2.3	41	75	
	36	6.7	1.1	40	82	
	60	7.0	0.7	30	85	
	90	7.2	0.4	21	89	
COS- BIS/MAS/soil 50 g/100 g/kg	1	6.8	2.6	27	21	2.9
	8	7.1	2.1	26	-	
	22	7.4	1.5	25	-	
	36	7.7	1.0	24	-	
	60	7.8	1.0	20	-	
	90	7.8	1.0	17	-	
COS- BIS/MAS/soil 100 g/50 g/kg	1	8.5	3.8	22	5	1.7
	8	7.9	1.4	20	-	
	22	7.8	0.7	17	-	
	36	7.6	0.6	13	-	
	60	7.5	0.5	10	-	
	90	7.5	0.4	7	-	

Regarding the concentration of NO₃[−] in effluents, from Table 5 it can be seen that this was higher in the case of soil/manure mixtures (21–45 mg/L) and decreased with leaching time. However, upon addition of COS-BIS biochar to the mixture some retention of nitrate ions occurred (concentration in leachates 7–27 mg/L), revealing either their adsorption on biochar surface, or nitrogen binding in heterocyclic compounds that were not easily solubilized [18]. According to previous research [44], this retention can improve the uptake of manure nitrogen by plants. Furthermore, Table 5 clearly indicates that no phosphates were released in the presence of biochar in the solid blends, in accordance with the insoluble whitlockite magnesian in biochar (Figure 1). Phosphate ions measured in the soil/manure leachates (6–89 mg/L) were most probably associated with the hydroxyapatite mineral identified in the manure sample (Figure 1). Therefore, the extractability of phosphate ions was mainly correlated with the mineral phases, in which phosphorous was incorporated. Field experiments, however, may provide more relevant information. Finally, the quantity of extracted phenols in all cases was low (1.7–2.9 mg/L).

The decrease in COD with leaching time for all solid mixtures is represented in Figure 5. As can be observed, COD values of soil/manure mixtures were higher than soil/manure/biochar mixtures, but also exceeded literature data reported for other manure samples [45]. Once biochar was admixed to the above mixture, COD was reduced up to 10 times at the end of the three-month period. It has been reported [45] that oxygen-rich biochars, such as that in the study (Table 1), can adsorb organic and inorganic species on their surface from the soil/water system, leading to lower COD values in water extracts.

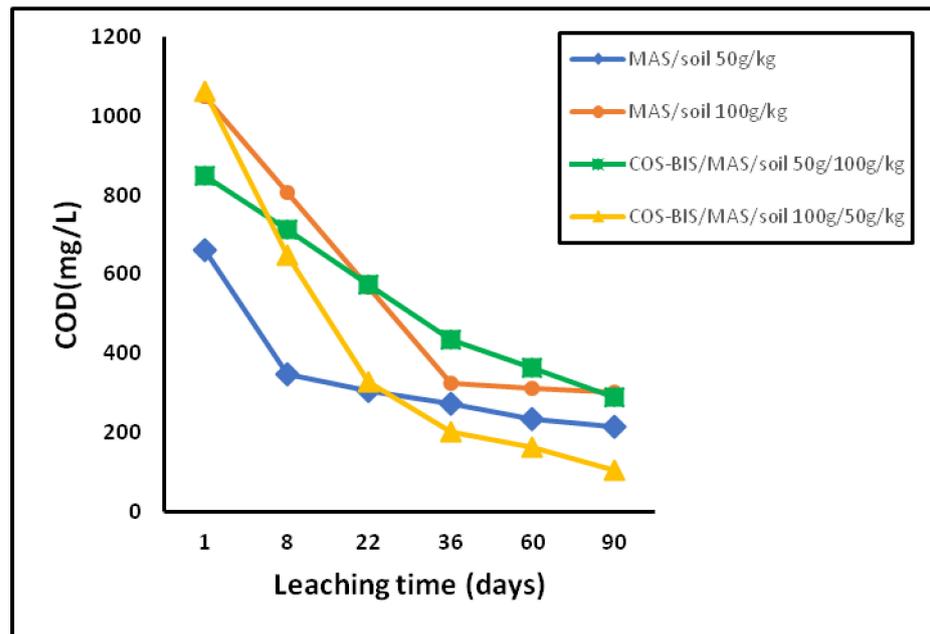


Figure 5. Variation of COD with time in biochar/manure/soil leachates.

3.3.3. Leaching of Metals

Figure 6 compares the release of major elements from all soil combinations in the leachates. The application of manure to the soil increased significantly the amounts of Ca and Mg dissolved in water, principally attributed to the high contents of soluble calcite and dolomite minerals in manure (Figure 1). Upon addition of biochar, it can be seen that the extractability of Ca was reduced, suggesting that the surface or porosity of biochar provided retention sites for this element. By comparison, the leachability of K was greatly intensified with a higher amount of biochar, due to the high concentrations of the soluble forms of sylvite and arcanite in this (Figure 1).

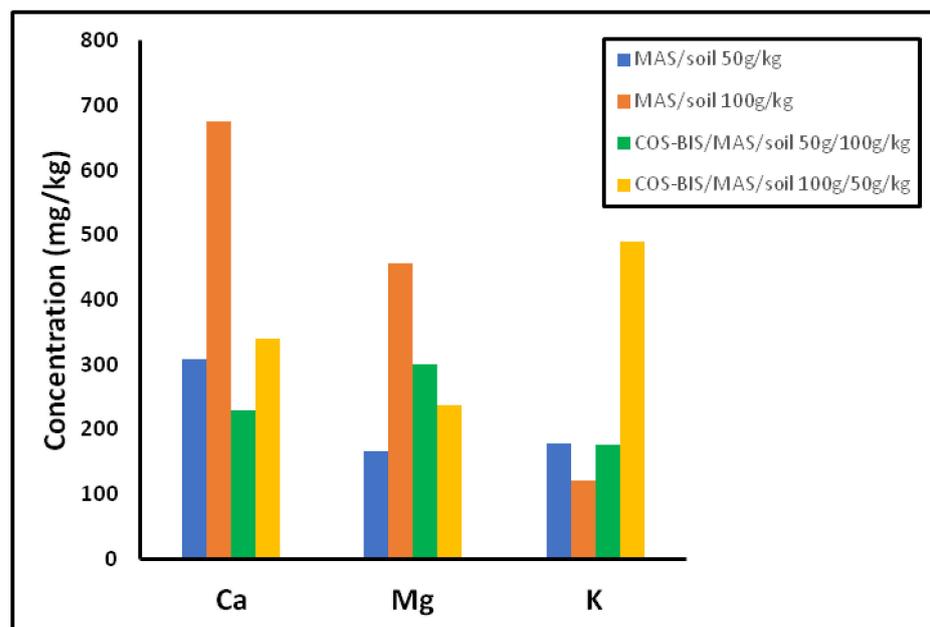


Figure 6. Cumulative concentration of major elements in biochar/manure/soil leachates.

Regarding the leaching behavior of heavy metals from the materials studied, Table 6, presenting the cumulative concentrations in liquid effluents, indicates that only Sr, Zn and

Mn were extracted in considerable amounts, of 413–1145, 145–487 and 215–462 $\mu\text{g}/\text{kg}$, respectively. The higher extractability of Sr suggests that this element was associated with organic matter, or salts dissolved in the water effluents [5]. In the presence of biochar in the mixtures, heavy metal levels in the leachates were significantly reduced by about 50–70% (Cu by 50%, Mn by 54%, Sr by 64%, Zn by 70%). Toxic metals Cr, Co, Hg and As were not quantified at all in the extracts, being below detection limits, and Pb, which is known to have calcium or organic affinity [11], was very low, implying no risk to the environment. All measured values were below the legislation limits of EC [46]. Possible reasons for the low leachability of metals from the biochar may be their bounding in stable oxides, phosphates or aluminosilicates, such as quartz, hematite, whitlockite magnesian, albite and vezouvia (Figure 1), or other mechanisms, including electrostatic attraction, competition between elements or complexation [47].

Table 6. Cumulative concentrations of trace elements in the leachates ($\mu\text{g}/\text{kg}$).

Sample	MAS/Soil 50 g/kg	MAS/Soil 100 g/kg	COS- BIS/MAS/Soil 50 g/100 g/kg	COS- BIS/MAS/Soil 100 g/50 g/kg
Mn	-	461.8	214.6	-
Ni	-	89.3	136.0	-
Cu	92.0	111.1	119.8	137.8
Zn	-	487.0	144.8	-
Sr	504.5	1144.9	413.3	703.4
Pb	7.3	-	-	4.0

4. Conclusions

When manure biochar was activated with either steam or carbon dioxide at high temperatures, the yield was lower with respect to pyrolysis only and the drop was greater in the presence of steam. Activation by steam at 700 °C greatly enhanced the specific surface area by 4.9-fold, reaching a value of 231.4 m^2/g , whereas at 800 °C favored enlargement of pores and increased the aromaticity of char. Activation by carbon dioxide at 800 °C favored microporosity and elevated the specific surface area by 3.4-fold, reaching a value of 233.3 m^2/g .

Incubation of manure/biochar blends improved soil properties, by lowering significantly the electrical conductivity and increasing the water holding capacity. Application of manure to the soil promoted leaching of nitrates and phosphates, and raised COD values of water extracts. Biochar addition retained these ions and reduced COD values by up to 10 times at the end of the three-month period. The extractability of Ca and Mg nutrients was higher from the manure/soil mixture, whereas that of K was higher upon co-application of biochar. The concentrations of heavy metals in the leachates were low and below legislation limits. In the presence of biochar in soil blends they were significantly reduced, by 50–70%.

Overall, the manure material studied presented a significant potential for adsorption of various pollutants and, if carefully managed and admixed with biochar produced from different wastes, may improve soil amendment for agricultural applications.

Author Contributions: Conceptualization, D.V.; software, A.R.; investigation, D.V. and A.R.; writing-review, D.V. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: This study did not report any data.

Acknowledgments: Permission obtained. The authors kindly thank the laboratories of Hydrocarbons Chemistry and Technology, Ore Processing and Beneficiation and Hydrogeochemical Engineering and Soil Remediation for specific chemical analyses.

Conflicts of Interest: The authors declare no conflict of interest.

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