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Static and Dynamic Investigations on Leaching/Retention of Nutrients from Raw Poultry Manure Biochars and Amended Agricultural Soil

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Abstract: In this study, nutrients release/adsorption from/by raw poultry manure-derived biochar produced at a pyrolysis temperature of 600 °C (RPM-B) was assessed under static and dynamic conditions. Batch sequential leaching experiments of RPM-B for a total contact time of 10 days showed that both phosphorus and potassium were slowly released but with higher amounts compared to various other animal- and lignocellulosic-derived biochars. The cumulated released P and K amounts were assessed to 93.6 and 17.1 mg g⁻¹, which represent about 95% and 43% of their original contents in the RPM-B, respectively. The column combined leaching/adsorption experiments showed that amending an alkaline sandy agricultural soil with two doses of RPM-B (at 5% and 8% w:w) resulted in an efficient retention of NO₃-N and NH₄-N, and on the contrary, important leached amounts of PO₄-P, K⁺, Mg²⁺, and Ca²⁺ but with relatively slow kinetic release rates for a long period. Even after 40 days of dynamic leaching, these latter nutrients continued to be released with kinetic rates lower than 10 mg kg⁻¹ d⁻¹. Thus, compared to synthetic fertilizers, RPM-B valorization as organic amendment for poor semiarid soils could be considered as an attractive, eco-friendly, and sustainable waste recycling option.

Keywords: poultry manure biochar; nutrients; sequential extraction; leaching; adsorption

1. Introduction

Animal biomasses including raw poultry manure (RPM) are organic wastes that are globally produced in large amounts from farming activities [1,2]. The absence of systematic mastered valorization pathways of these wastes could represent a real threat to the environment quality (bad odors and water resources quality deterioration) and could lead to social instability in the zones surrounding the corresponding facilities [2,3]. At the same time, RPM contains high concentrations of macro- and micronutrients, which could promote its application, instead of synthetic fertilizers, as nutrient sources for the cultivation of different crops [4–6]. However, RPM direct use has the drawbacks of nutrients availability scaling down and important greenhouse gas (GHG) emissions [7,8].

The thermochemical conversion of animal biomasses, in general, and RPM, in particular, via pyrolysis process has been suggested as an attractive and sustainable technology



Citation: Hadroug, S.; Jellali, S.; Jeguirim, M.; Kwapinska, M.; Hamdi, H.; Leahy, J.J.; Kwapinski, W. Static and Dynamic Investigations on Leaching/Retention of Nutrients from Raw Poultry Manure Biochars and Amended Agricultural Soil. *Sustainability* **2021**, *13*, 1212. https:// doi.org/10.3390/su13031212

Academic Editor: Elena Rada Received: 31 December 2020 Accepted: 21 January 2021 Published: 24 January 2021

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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). since it permits their turning into three valuable by-products: biogas and bio-oil (biofuels) for energy purposes and a solid carbonaceous residue named "biochar" [9]. This animal-biomasses-derived-biochars could be valorized in environmental applications as an effective adsorbent for pollutants contained in liquid and gaseous effluents [10] or in agriculture as an eco-friendly fertilizer [5]. In the latter purpose, these biochars are assumed to act as a soil conditioner and fertilizer by improving soil properties, nutrients availability, and crop yields [4,5,11]. Besides, the application of these biochars in agriculture could reduce emissions of carbon dioxide and methane gas for global warming mitigation [12]. However, the use of this type of biochars is mainly limited by [13]: i) some nutrients runoff and leaching loss that could negatively impact water resources (surface and underground) quality, ii) some other nutrients dissolution at lower concentrations as compared with synthetic inorganic fertilizers, which could significantly reduce plants' optimal growth and crops production. Therefore, investigating nutrients dynamic (both leaching and adsorption) by agricultural soils amended with animal-biomasses-derived-biochars is a crucial task in order to get a better appreciation of their possible impacts onto soils, water resources, and plants' growth [8]. Nutrients dynamic in biochars-amended-soils have been investigated under controlled laboratory conditions in batch, column, and pots devices and also in field trials [5,14–16]. Results indicated that nutrients dynamic is a very complex process that depends on various parameters such as the physicochemical properties of the nutrient, the biochar, and the agricultural soil as well as the used experimental conditions giving the impression that outcomes of different studies look like contradictory [6,12,14,16,17]. For instance, Zolfi-Bavariani et al. [6] and Hadroug et al. [17] showed that more alkaline biochars, that are produced at higher pyrolysis temperatures, released higher rates of potassium. However, P and micronutrients become less available due mainly to its trap into crystalline forms [18]. Moreover, Singh et al. [12] demonstrated that the adding of wood- and poultry litter-based biochars produced at 550 °C decreased NH₄-N leaching by about 55% to 65% in an Alfisol. In contrast, no significant impact was reported for the same biochars when produced at a temperature of 400 °C. However, all these four biochars have significantly reduced NH₄-N leaching in a Vertisol rich in smectite clay. On the other hand, Bohara et al. [8] studied in column mode nutrients and heavy metals leaching by 10 pore volumes of distilled water of an amended fined soil by mixtures of RPM and pinewood biochar (PWB). They reported that adding PWB at doses of 2.5% and 5% to the control column decreased the leached amounts of Al³⁺, Fe³⁺, and Zn²⁺, while it had no significant effect on Ca²⁺, Mg²⁺, PO₄-P, and K⁺. However, when the used dose was increased to 10%, the Ca²⁺ and Mg²⁺ leached amounts significantly increased due to the richness of the biochar in these two elements. Moreover, the addition of 10% of PWB to the soil initially amended with 10% of RPM significantly reduced the leached amounts of Mg²⁺, PO₄-P, and K⁺ by about 36%, 19%, and 32%, respectively. Finally, for PO₄-P, both leaching increase and decrease was reported when agricultural soils are amended with biochars despite the existence of high contents of Ca^{2+} and Mg^{2+} that could bind with this element [19–21].

It is important to underline that most of the studies on nutrients dynamic from animal-biomasses-derived-biochars were carried out in tropical and subtropical climates or acidic agricultural soils while there is a substantial lack of investigations in arid and semiarid regions with poor sandy soils [4,5,22,23]. Furthermore, there is an apparent lack of studies dealing with change over long time periods of simultaneous nutrients release and adsorption following the application of these biochars in sandy alkaline and poor soils. Accordingly, the ultimate goal of the current study is to get a better quantification of the major nutrients' loss/adsorption from/by a semiarid and alkaline sandy soil amended with various doses of a RPM-derived biochar (RPM-B). The specific objectives of this study are: (i) to assess RPM-B ability in releasing potassium and phosphorus in batch mode through five sequential extractions for a total duration of 10 days and (ii) to accurately evaluate and to better understand the effect of RPM-B doses on both major nutrients release and adsorption from/by an alkaline amended agricultural soil under dynamic conditions (column tests).

2. Materials and Methods

2.1. Biochar Preparation and Characterization

The used raw poultry manure in this study was gathered from a poultry farm in the city of Mornag (south of Tunis, Tunisia). This biomass was first dried in open air for 10 days then manually ground. Only the fraction with particles size comprised between 80 μ m and 1 mm was selected and used in this study. The thermal conversion of RPM into biochar was carried out through slow pyrolysis by using a laboratory furnace (Lenton, UK). The used heating rate and final temperature were fixed at 5 °C min⁻¹ and 600 °C, respectively. An in-depth physicochemical characterization of this biochar was carried out according with Hadroug et al. [17].

2.2. Soil Preparation and Characterization

The agricultural soil used in this study was sampled from the top layer (0–25 cm) of a local farmland located in the city of Menzel Bouzelfa (North East of Tunisia). The soil sample was air-dried for 10 days and then sieved with a mechanical sieve shaker (Retch, Haan, Germany). Only the fraction with particle size less than 2 mm was used in this study. The physicochemical characterization of this soil has concerned mainly the determination of its: (i) pH and electrical conductivity (EC) for a soil/water mass ratio of 1:10, (ii) particle size distribution, (iii) crystallinity through X-ray diffraction (XRD) analyses by Bruker D8 Advance powder diffractometer, and (iv) mineral composition by an X-ray fluorescence (XRF) (S8 Tiger Series 2 apparatus). For the XRF analysis, 150 mg of the soil were grinded into a fine powder then blended with 200 mg of boric acid. The sample was then pressed under a hydraulic pellet press then introduced into the analytical apparatus for analysis.

2.3. Static Nutrient Release Experiments

The main goal of static assays (batch mode) was to determine the efficiency and kinetic release of PO_4 -P and K⁺ from the RPM-B. A slow release process is an important agronomic property since it will allow crops to take maximum advantage of these nutrients and reduce groundwater pollution risks. For this reason, five successive leaching experiments using the same biochar were carried out for a total duration of 10 days. Each experiment consists in shaking this biochar with distilled water for 2 days at a dosage of 10 g L⁻¹ and 400 rpm using an IKA RT 15 Power IKAMAG multi-position magnetic stirrer. At the end of each experiment, the biochar sample was recovered using a vacuum pumping system with 0.45-µm paper filters, and then dried for 16 h at 40 °C. The dried sample was reused again for the subsequent leaching procedure. The concentrations of PO₄-P and K⁺ in the liquid leaching samples were analyzed by an inductively coupled plasma spectrometry (ICP) (Agilent Tech 5100 ICP OES).

For each leaching experiment "*i*", the released amount of PO₄-P per gram of biochar " $q_{P,i}$ (mg g⁻¹)" or K⁺ " $q_{K,i}$ (mg g⁻¹)" were determined as follows:

$$q_{P,i} = \frac{C_{P,i}}{D} \tag{1}$$

$$q_{K,i} = \frac{C_{K,i}}{D},\tag{2}$$

where $C_{P, i}$, and $C_{K,i}$ are PO₄-P or K⁺ concentration at the leaching step "i".

Besides, the kinetic release of PO₄-P ($S_{P,i}$) and K⁺ ($S_{K,i}$) (mg g⁻¹ d⁻¹) for a given leaching experiment "*i*", are given by:

$$S_{P,i} = \frac{q_{P,i}}{t} \tag{3}$$

$$S_{K,i} = \frac{q_{K,i}}{t},\tag{4}$$

where "t" is the contact time or the leaching experiment duration.

Finally, the cumulated leached percentages of P ($Y_{P,j}$) or K ($Y_{K,j}$) after "j" leaching experiments are calculated as follows:

$$Y_{P,j} = \frac{\sum_{i=1}^{l=j} q_{P,i}}{M_{P,b}}$$
(5)

$$Y_{K,j} = \frac{\sum_{i=1}^{t=j} q_{K,i}}{M_{K,h}},$$
(6)

where $M_{P,b}$ and $M_{k,b}$, (mg g⁻¹) are the P and K contents in the used biochar, respectively.

During this work, all batch nutrient release experiments were carried out in triplicate and data reported in this study are an average of these three independent parallel sample solutions.

2.4. Dynamic Nutrient Release Experiments

The nutrients leaching dynamics from RPM-B-amended soils was carried out using laboratory column experiments. It consists of plexiglass columns with a total height of 50 cm and internal diameter of 6.1 cm (Figure 1). Three leaching experiments were conducted by filling the columns with a total mass of 1400 g of hand mixed agricultural soil with RPM-derived-biochar at doses of 0% (blank test), 5%, and 8%, respectively. The soil, having a bulk density of 1.37 g cm⁻³, and the RPM-B-amended soil were packed into the column with small increments in order to ensure a homogenous compaction level. At both sides of the column, two glass particle layers were placed in order to guarantee a uniform flow in the column and an easy water drainage [24].

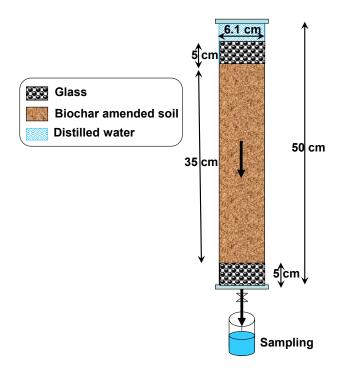


Figure 1. Schematic representation of the used laboratory column for leaching assays.

In this work, the dynamic behavior of the compounds (NO₃-N, PO₄-P, K⁺, Na⁺, NH₄-N, Ca²⁺, and Mg²⁺) was followed for a total duration of 40 days. It has concerned both their leaching potential from the soil/soil-amended biochars (phase 1) and their adsorption capacities by these same porous media (phase 2). Hence, phase 1 consists in the leaching of the RPM-amended-soil through a daily feeding with 400 mL (about one pore volume) of distilled water in gravity flow mode for 22 days. The second phase corresponds to nutrients adsorption assessment and begins on day 23 through the columns feeding

for twice (days 23 and 24) with 400 mL of synthetic solution containing 65.7 mg L⁻¹ of Na⁺, 50.4 mg L⁻¹ of K⁺, and 40 mg L⁻¹ of PO₄-P, NO₃-N, and NH₄-N. This solution was prepared from the following analytical-grade reagents KH₂PO₄, NaNO₃, and NH₄Cl. From the 25th to the 40th day, the columns were again daily fed with 400 mL of distilled water. The daily collected liquid samples at the columns' outlet were determined for pH, EC, and nutrients concentrations according to the protocols given in Section 3.3.2. The cumulated experimental collected amounts at the outlet of the column (MX) of a given nutrient "X" was determined using the trapeze method according to the following formula [25,26]:

$$M_X = \int_{V=0}^{V_{tot}} C_X \, dV = \sum_{i=1}^{i=n} \left(\frac{C_{X,i} + C_{X,i+1}}{2} \right) (V_{i+1} - V_i), \tag{7}$$

where V_{tot} is the total leached volume collected at the outlet of the column, $C_{X,i}$ and C X, i + 1 is the measured concentration of the nutrient "X" at the day "i" and "i + 1", respectively. V_i and V_{i+1} are the collected volumes at the outlet of the column at the same dates.

The collected samples at the outlet of the columns were filtered through 0.45 μ m paper filters before analysis by ion chromatography (Metrohm, Herisau, Switzerland) for the determination of their anions and cations' concentrations.

2.5. Statistical Analysis

Data from batch and laboratory column experiments were analyzed using STATISTICA 8.0 software (StatSoft, Tulsa, OK, USA). ANOVA with Duncan's multiple range test were applied for mean separation at $p \le 0.05$.

3. Results and Discussions

3.1. Biochar and Agricultural Soil Characterization

The RPM-B consists of a fine and homogenous porous media with an average diameter of 0.31 mm, a low BET surface area ($5.3 \text{ m}^2 \text{ g}^{-1}$), a high pH of zero-point-charge (pH_{ZPC}) (11.5), a moderate C (21.2%), and low N (0.6%) contents [17]. The K and P contents of the RPM-B were assessed to 6.6% and 4.3%, respectively. They are in the range of the values reported in the literature for RPM-derived biochars. However, compared to lignocellulosic materials, RPM-B appears to be exceptionally rich in nutrients (Table 1). For instance, K and "P" contents in the used RPM-B are, respectively, 3.2 and "5.3", 6.4 and "33.2", and 5.0 and "33.2" times higher than the ones reported for exhausted grape marc [27], wood chips residues [28], and pine sawdust [29]. This an important advantage for its valorization in agriculture as a biofertilizer since it can bring sufficient amounts of these two essential macronutrients for an optimal crop development.

On the other hand, the used soil is a sandy alkaline with a pH of 8.1. It has relatively low electric conductivity and moderate rich organic matter with values of 146 μ S cm⁻¹ and 3.0%. Relatively similar values were reported for a Sassafras loam soil [33]. Its mineral composition indicates that it is mainly composed by silicone dioxide, calcite, and alumina with percentage values of 96.2%, 1.4%, and 1.3%, respectively. This result was confirmed with the XRD analyses (Figure 2) showing the presence of several peaks related to SiO₂ at $2\theta = 21^{\circ}$, 26.6°, 36.6°, 39.4°, 42.6°, 50.2°, 54.8°, 60°, and 81.5°. Microcline (KAlSi₃O₈) was identified with a single peak at $2\theta = 64^{\circ}$. Besides, the carbonates represented by dolomite was observed by a diffraction peak at $2\theta = 68.6^{\circ}$. Finally, sulfates represented by the gypsum was observed at $2\theta = 75.9^{\circ}$. It is important to underline that the macronutrient contents in the experimental soil are relatively low. Indeed, K₂O, P₂O₅, MgO, and CaCO₃ were assessed to be only about 0.03%, 0.15%, 0.06%, and 1.42%, respectively, which indicates the need of a supplementary external source of nutrients to sustain crops growth (Table 2). Therefore, the RPM-B with its high contents of nutrients (especially K and P) could contribute to the soil enrichment with these elements.

| Raw Feedstock | Pyrolysis Conditions | Ν | Р | К | Ca | Mg | Na | Al | Reference |
|------------------------|--|------|------|------|-------|------|------|------|---------------|
| Poultry manure | T = 600 °C; G = 5 °C min ⁻¹ ; t = 3 h | 0.6 | 43.2 | 66.2 | 100.4 | 7.1 | 28.7 | 23.2 | Current study |
| Poultry litter | T = 600 °C; G = 20 °C min ⁻¹ ; t = 2.2 h | 1.2 | 30.5 | 91.5 | 94.0 | 24.2 | - | _ | [30] |
| Poultry litter | $T = 600 \degree C;$ $G = -\degree C \min^{-1};$ t = - | 4.0 | 15.4 | 58.8 | 35.9 | 15.7 | - | _ | [31] |
| Poultry manure | T = 500 °C; G = 20 °C min ⁻¹ ; t = 6 h | 3.8 | 29.5 | 54.8 | 43.7 | 13.6 | - | - | [32] |
| Poultry manure | T = 400 °C; G= -; t = 8 h | 26.3 | 27.0 | 72.0 | 49.1 | 13.5 | 15.2 | 4.8 | [33] |
| Exhausted grape marc | T = 600 °C; G = 5 °C min ⁻¹ ; t = 1 h | 1.7 | 8.2 | 20.1 | 18.0 | 2.9 | 0.4 | 0.3 | [27] |
| Residues of wood chips | $T = 620 \circ C;$ $G = -\circ C \min^{-1};$ t = - | _ | 1.3 | 10.4 | 42.2 | 2.9 | 0.7 | _ | [28] |
| Pine sawdust | T = 550 °C; G = 7 °C min ⁻¹ ; t = 2 h | - | 1.3 | 13.3 | 2.1 | 5.2 | - | 58.2 | [29] |

Table 1. Mineral composition of RPM-B (mg g^{-1}) in comparison with other biochars derived from poultry manure/litter and lignocellulosic biomasses.

(T: pyrolysis temperature; G: heating gradient; t: residence time).

3.2. Static Biochar Leaching Experiments

The leaching experiments of K and P from RPM-B were carried out with the same biochar for five cycles with a total duration of 10 days under the experimental conditions given in Section 2.3. Results (Figure 3a,b) showed that the release kinetic of potassium significantly decreases when increasing the number of successive leaching assays. As such, K release kinetic during the first assay was evaluated to 19.2 mg $g^{-1} day^{-1}$. It decreases by 78.0%, 79.2%, and 87.8% for the second, third, and fourth leaching assay, respectively, and reaches about 0.6 mg $g^{-1} d^{-1}$ in the last leaching experiment. For phosphorus, the variation was less obvious and there was an apparent lower mobility than K in terms of release in the aqueous solution (Figure 3b). Indeed, the PO₄-P release kinetic observed during the first leaching test was measured at only 0.7 mg $g^{-1} d^{-1}$. This rate increased during the second assay, then attained a plateau with an average kinetic value of 0.8 mg $g^{-1} d^{-1}$. Afterwards, this kinetic decrease to 0.6 mg $g^{-1} d^{-1}$ at the last leaching assay. The low release rates of PO₄-P, compared to K⁺, is mainly imputed to the fact that the pyrolysis process most probably converted a non-negligible portion of the RPM-contained P into crystalline metal phosphates such as tricalcium phosphate, hydroxyapatite, calcium or iron-phosphate-precipitates, and whitlockite [14,18,33–35]. Based on solid-state ³¹P nuclear magnetic resonance (NMR) techniques, Li et al. [36] demonstrated that the P species in RPM-derived biochars at pyrolysis temperatures higher than 450 °C include mainly hydroxyapatite and oxyapatite, which are much less available than the forms existing in the raw animal biomasses [11]. On the contrary, the pyrolysis process has converted potassium into a more water-soluble form through dissociation mechanisms [37]. For this reason, the biochar-borne potassium RPM-B was more easily leached by distilled water. Accordingly, the leached K percentage (calculated by Equation (6)) increased significantly with the increase in the number of leaching assays. Indeed, it increased from about 58% at the first assay to more than 82% at the third cycle and reached 94% at the fifth one. However, the maximal leached percentage of P (see Equation (5)) observed at the fifth cycle was only 17.1% of its total content in the biochar. Liang et al. [35] showed that after 10 leaching days, P release from their RPM-derived biochar at a temperature of 450 $^{\circ}$ C reaches about 10.3% of the total P. This lower percentage could be attributed to their used protocol, which is based on a nonsequential extraction mode. It is important to underline that the actual K and P water-leachable amounts and rates are much important compared to those reported for biochars derived from lignocellulosic biomasses or sludge. For instance, Ibn Ferjani et al. [38] reported that for exhausted grape marc produced at a temperature of 500 °C, the K and P leached percentages at the fifth (last) sequential extraction assay were assessed to 83% and 18%, respectively. Furthermore, they showed that the P leached percentage appear to significantly decrease with the increase in the pyrolysis temperature due to its encapsulation in crystalline forms. Regarding sludge-derived biochars generated at a temperature of 600 °C, K and P were likely to be more chemically retained than in RPM-B since for a continuous contact time of 3 days, the corresponding release percentages were only about 2.6% and 1.2%, respectively [39]. These outcomes could be mainly imputed to the relatively lower nutrient content in these biomass-derived biochars compared to RPM-B, which might significantly limit the nutrient diffusive flux from these solid matrices to the water phase.

On the other hand, it is worth mentioning that even after 5 consecutive leaching tests (10 days), K⁺ and PO₄-P continue to be released with non-negligible rates (Figure 3a,b). Gwenzi et al. [40] observed similar trend when studying the sequential release of NO_3^- , PO_4^{3-} , and K⁺ from an artificially nutrients-doped-sawdust biochar for a duration of 68 days. They suggest the existence of three possible nutrients pools: i) a readily available and water-soluble fraction, ii) a sparingly water-soluble fraction, and iii) an insoluble fraction that is strongly adsorbed to the solid phase and its release occurs only through microbial degradation. This slow release is an attractive property of the RPM-B since it will permit, in real cases, a long-term supply of required nutrients for an optimal plant development. Simultaneously, it will reduce pollution risks of surface and underground water resources by these compounds.

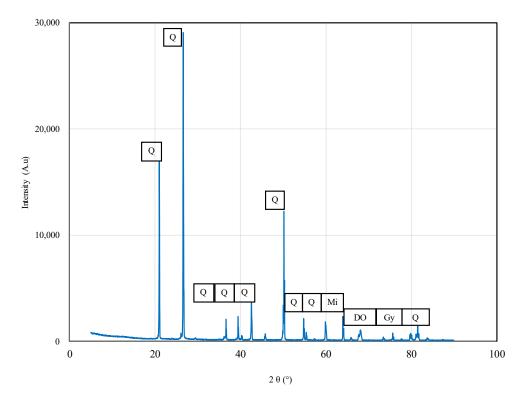


Figure 2. XRD analysis of the agricultural soil (Q: quartz; Mi: microcline; Do: dolomite; Gy: gypsum).

| Physicochemical Properties | Value |
|--|--------|
| Sand (%) | 93.9 |
| Silt (%) | 6.1 |
| pH | 8.1 |
| Electrical conductivity (μ S cm ⁻¹) | 146.2 |
| Organic matter (%) | 3.0 |
| Sodium oxide (Na ₂ O) | 0.101 |
| Magnesium oxide (MgO) | 0.056 |
| Alumina (Al_2O_3) | 1.297 |
| Silicon dioxide (SiO ₂) | 96.209 |
| Phosphorus pentoxide (P_2O_5) | 0.145 |
| Sulfur trioxide (SO_3) | 0.034 |
| Potassium oxide (K_2O) | 0.034 |
| Calcite (CaCO ₃) | 1.420 |
| Titanium dioxide (TiO_2) | 0.134 |
| Chromium oxide (Cr_2O_3) | 0.001 |
| Iron oxide (Fe_2O_3) | 0.570 |
| Zinc oxide (ZnO) | 0.006 |
| Strontium oxide (SrO) | 0.012 |
| Manganese oxide (Mn_2O_3) | 0.012 |

Table 2. Physicochemical properties of the used agricultural soil.

3.3. Dynamic Leaching Experiments

3.3.1. Effect of Biochar Addition on Soil pH and EC

The effect of the soil amendment with 5% and 8% of RPM-B on its pH and EC was measured in batch mode under the experimental conditions described in Section 2.2. Experimental results (Figure 4) showed that the addition of the alkaline RPM-derived biochar significantly impacted soil pH. As such, the increase in the applied biochar dose has resulted in a significant increase in pH values of amended soils. These values were determined to 8.1, 9.1, and 9.7 for the control soil and 5% and 8% of RPM-B doses, respectively. However, this increase should be a short-term effect, and the native soil properties, in particular, the cation exchange capacity should be quite low and did not protect from rapid pH fluctuations. This behavior is nevertheless due to the presence of elevated contents of bases in RPM-B and highlight its liming effect when applied to acidic agricultural soils [5,14]. Indeed, Masud et al. [5] showed, similarly, that the liming effect of RPM-B adding to an agricultural soil depend on the biochar used dose. For an incubation period of 2 months, the soil's pH increase was assessed to 0.3, 0.7, and 1.2 pH units for RPM-doses of 0.5%, 1%, and 1.5%, respectively. A smaller increase was reported by Laird et al. [41] for a lignocellulosic biochar adding to a Midwestern agricultural soil at a dose of 2% (almost 1 unit after an incubation period of 500 days). It is worth mentioning that significant elevation of soil pH could limit some nutrients bioavailability such as P and other micronutrients [6,42]. At the same time, pH values increase could significantly reduce the toxic aluminum element availability [4] and positively affect fungal and bacterial distribution as well as organic carbon fate for a better assimilation by plants [43]. On the other hand, RMP-B addition also sensibly affected EC (1:10 w:v) of the mixed soils (Figure 4). Indeed, the original EC of the agricultural soil (without amendment) increased significantly from 146 μ S cm⁻¹ to more than 642 and 1029 μ S cm⁻¹ when amended with RPM-B doses of 5% and 8%, respectively. This elevation could be mainly attributed to the dissolution of biochar-contained ashes, which are dominated by exchangeable bases, phosphates precipitates, alkali and alkaline metals carbonates, and organic and inorganic nitrogen compounds [44].

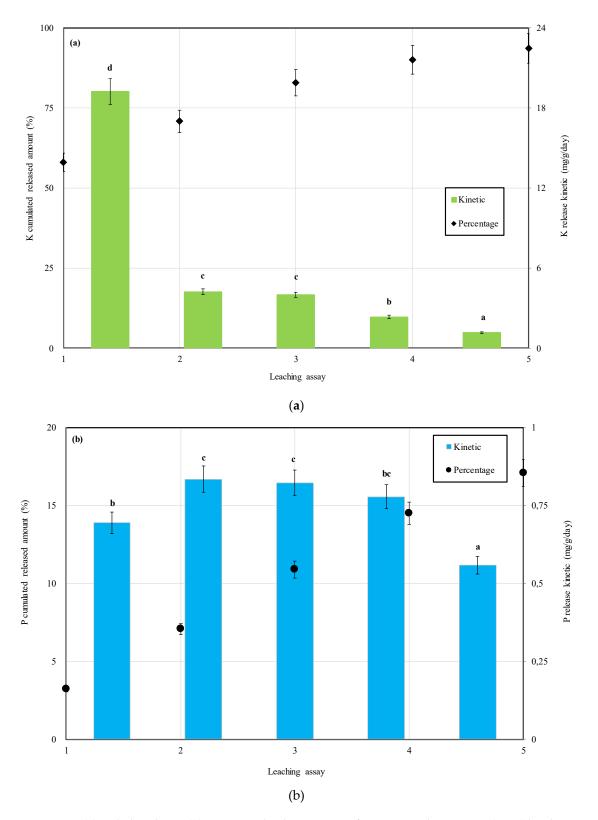


Figure 3. Potassium (**a**) and phosphorus (**b**) successive leaching capacity from raw poultry manure (RPM) biochar. For each element, mean release kinetics with the same lowercase letters are not significantly different at $p \le 0.05$.

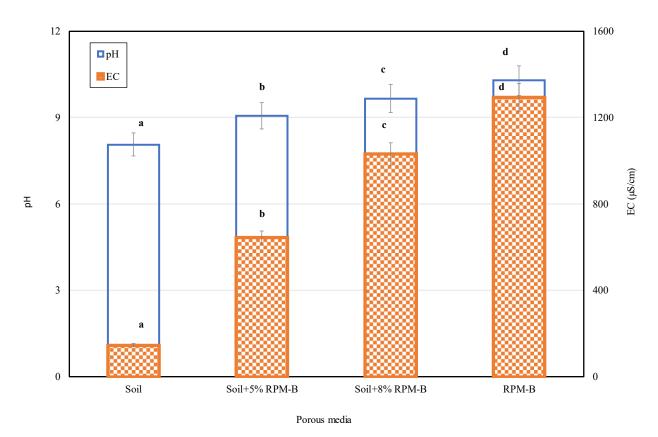


Figure 4. Mean pH and electrical conductivity (EC) values of agricultural soil, RPM-B, and RPM-B-amended-soil at 5% and 8% in batch mode. For each parameter, values with the same lowercase letters are not significantly different at $p \le 0.05$.

3.3.2. Column-Leaching Results Variation of pH and EC

Figure 5a,b illustrates the pH and EC measurements at the outlet of the columns for the three soil treatments. For all the assays, pH and EC values were the highest at the beginning of the leaching process due to the existence, at this stage, of important diffusion fluxes of leachable salts from the solid to the liquid phase. A quasi plateau was then reached after about 20 days (Figure 5a,b). The second phase of the leaching experiment (following the addition of the synthetic solution containing NO₃-N, PO₄-P, K⁺, Na⁺, and NH₄-N instead of distilled water at the 23rd and 24th days) was accompanied by a slight increase in these two physical parameters right after the application (Figure 5a,b). Higher the used biochar doses, more important the measured pH and EC values at the exit of the column. For instance, increases of pH and EC values of more than 2.4 units and 170%, respectively, was observed at the beginning of the experiments for an RPM-B dose of 8%. Such a behavior is frequently observed for amended soils with biochars produced at relatively elevated pyrolysis temperatures (>400 $^{\circ}$ C), which generally dispose of high contents of salts of alkali and alkaline elements (Na, K, Ca, and Mg) and calcite [6,22]. Therefore, the presence of these elements in RPM-B can be considered as a useful attribute for soil pH buffering, however, it can contribute to the decrease in the availability of P and some micronutrients such as Cu and Mn [6]. The impact onto the EC is very limited since after only 5 leaching days, it decreased to less than 2.5 mS/cm. Therefore, its impact on plants' growth should be negligible.

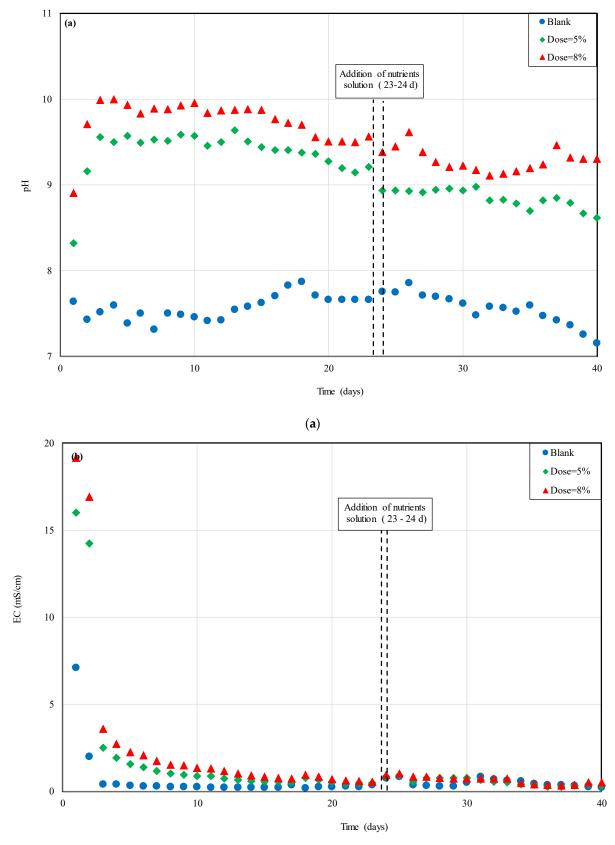
Anions Dynamic Behavior

Released NO₃-N amounts during the phase 1 (until day 22) significantly increased with the rising of the biochar dose in amended soils (Figure 6a and Table 3). The cumulated leached NO₃-N amounts at the 22nd day were assessed to 93.1, 127.4, and 206.0 mg for the

control soil and biochars doses of 5% and 8%, respectively. These observations prove that RPM-B could be considered as a supplementary source of NO_3 -N ions, which is a bioavailable N form essential for plant growth. However, its initial release kinetic is exceptionally high since the released NO_3 -N amounts after only 2 days represent about 94%, 78%, and 88% of the total leached mass during the entire phase 1 for soil treatments with 0%, 5%, and 8% biochar, respectively. A similar finding was reported by Teutsherova et al. [45] when investigating in column mode NO_3 -N leaching from two amended soils by a lignocellulosic biochar at doses of 1% and 2%.

Just after the addition of the synthetic solution rich in NO₃-N during the second phase (141.7 mg on the 23rd and 24th days), low to moderate peaks of NO_3 -N concentrations were observed for all soil treatments at the outlet of the columns (data not shown). At the end of this second phase (Figure 6b), the recovered NO_3 -N amounts were about 47.1%, 25.1%, and 29.0% lower than the artificially added NO₃-N mass in the synthetic solutions for the control soil and those amended with RPM-B at 5% and 8%, respectively. These observations indicate that NO₃-N ions were efficiently adsorbed by the added RPM-derived biochar. NO₃-N adsorption by the biochar-amended soils involves several mechanisms including ligand exchange and complexation [46]. The importance of each one of these mechanisms depends mainly on the physicochemical characteristics of the porous media such as the specific surface area, the microporosity volume and the contained surface functional groups [47–49]. This finding is in agreement with several other studies [21,50,51]. For instance, [21] studied the impact of a lignocellulosic biochar on leaching of nutrients after the application of swine manure to a typical Midwestern agricultural soil in column mode. The soil columns containing 0%, 0.5%, 1%, and 2% of biochar with and without 0.5% of dried swine manure were leached weekly with 200 mL of 0.001 M CaCl₂ for 45 weeks. They reported that compared to the blank test (without manure), the NO_3 -N leached amount decreased by about 11% for a biochar dose of 2%. Likewise, Yao et al. [50] observed a net decrease in NO₃-N leaching capacity by about 34% when an agricultural soil was amended with 2% of a biochar generated from the pyrolysis of a mixture of peanut hull and Brazilian pepperwood. In contrast, some other studies have oppositely showed an increase in NO_3 -N leaching when biochars was applied as amendment [23,38]. For instance, Ibn Ferjani et al. [38] found that amending an agricultural soil with 5% biochar generated from exhausted grape marcs (EGM) increased NO_3 -N leaching by 43.5%. This discrepancy might be partly attributed to the porous media physicochemical characteristics. Indeed, nitrates adsorption was generally reported for biochars produced at pyrolysis temperatures higher than 600 °C [50–52]. However, no significant NO₃-N retention was observed for biochars produced at lower temperatures [38,53,54].

As for NO₃-N variation during the first experimental phase, the measured concentrations of PO₄-P at the outlet of the column were proportional to biochar dose in the soil (data not shown), and consequently, the released amounts from the used porous media (Figure 7a and Table 3). Indeed, the total released PO₄-P at the end of this first phase were assessed to 2082.8 and 1563.9 mg in soils treated with biochar at 8% and 5%, respectively, which are about 24- and 18-fold higher than the leached amount from the un-amended soil (Table 3).



(**b**)

Figure 5. Variation of pH (a) and EC (b) in control soil (blank) and soil treated with 5% and 8% RPM biochar.

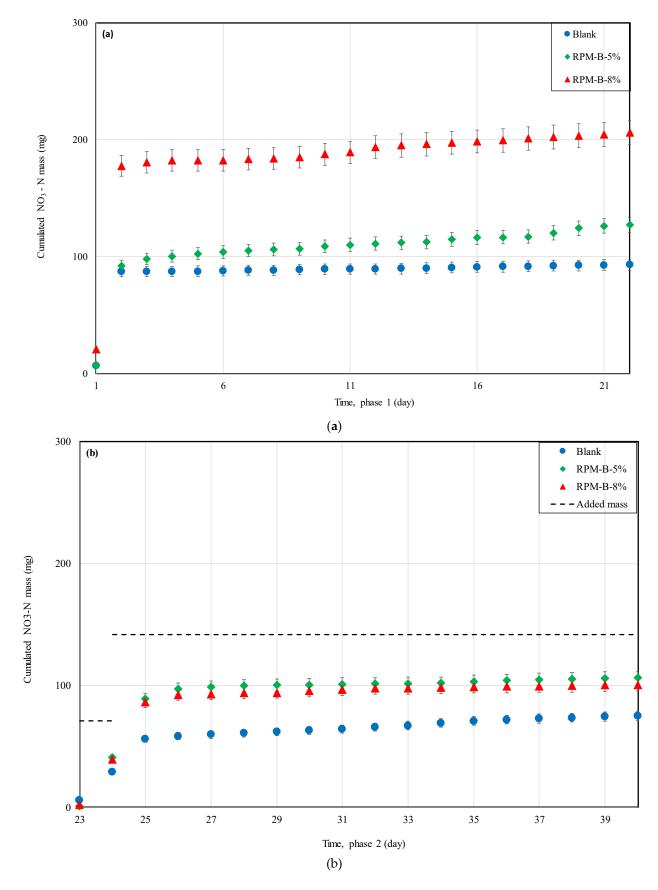


Figure 6. Cumulated NO₃-N collected at the outlet of the columns containing nonamended and RPM biochar-amended agricultural soil during phase 1 (**a**) and phase 2 (**b**).

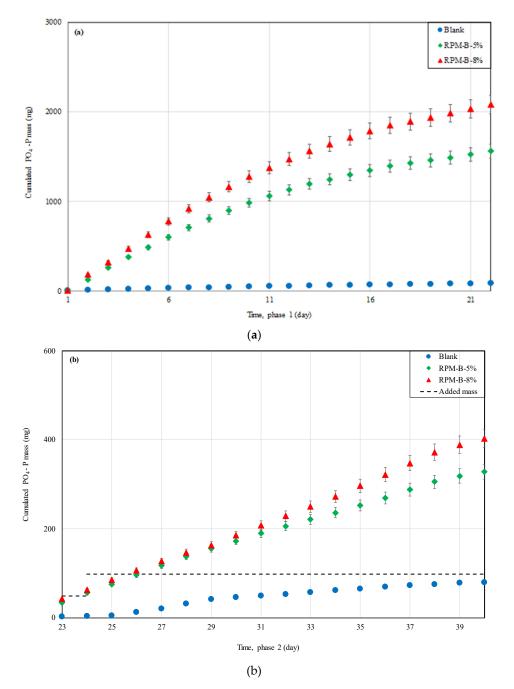
| | Assay | Parameter | PO ₄ -P | NO ₃ -N |
|---------|----------|---------------------------|--------------------|--------------------|
| | D1 1 | RM-b (mg) | 87.8 a | 93.1 a |
| Phase 1 | Blank | ARR (mg $g^{-1} d^{-1}$) | 0.0028 | 0.0029 |
| | | RM (mg) | 1563.9 b | 127.4 ab |
| | RPM-B-5% | RM/RM-b ratio | 17.8 | 1.4 |
| | | ARR (mg $g^{-1} d^{-1}$) | 0.0494 | 0.0040 |
| | | RM (mg) | 2082.9 b | 206.0 b |
| | | RM/RM-b ratio | 23.7 | 2.2 |
| | RPM-B-8% | ARR (mg $g^{-1} d^{-1}$) | 0.0657 | 0.0065 |
| | | AM (mg) | 98.1 | 141.7 |
| | | RM (mg) | 79.9 a | 75.0 a |
| | Blank | RM/AM ratio | 0.8 | 0.5 |
| | | FRR (mg $g^{-1} d^{-1}$) | 0.0015 | 0.0005 |
| | | RM (mg) | 327.6 b | 106.2 b |
| Phase 2 | RPM-B-5% | RM/AM ratio | 3.3 | 0.7 |
| | | FRR (mg $g^{-1} d^{-1}$) | 0.0063 | 0.0003 |
| | | RM (mg) | 402.7 с | 100.6 b |
| | RPM-B-8% | RM/AM ratio | 4.1 | 0.7 |
| | | FRR (mg $g^{-1} d^{-1}$) | 0.0097 | 0.0003 |

Table 3. Release kinetics of anionic nutrients from nonamended and amended agricultural soil with RPM biochars at 5% and 8%.

(RM: released mass; b: blank assay; AM: added mass from synthetic solutions; ARR: average release rate; FRR: final release rate). For each anion at each phase, RM values followed by the same lowercase letters are not significantly different at $p \le 0.05$).

Outcomes of the second experimental phase (PO₄-P retention assessment) showed that the agricultural soil exhibited a relatively low retention of PO_4 -P since 81.5% of the added PO₄-P was recovered (leached) at the outlet of the column at the end of the assay (40 days). However, no PO_4 -P retention was ever recorded following biochar addition at 5% and 8% because the released amounts at the end of the second phase were about 3.3 and 4.1 times higher than the artificially added PO₄-P amount (Figure 7b). Similar observations have been reported by several authors [38,50,51,55]. For instance, Troy et al. [55] found that compared to control, the leaching for 30 weeks of an amended tillage soil with a pig manure biochar at a dose of 18 t ha⁻¹ resulted in an increase in the dissolved phosphorus amounts by a factor higher than 3. They attributed this effect to the higher P contents of the used biochar. Similarly, El-Bassi et al. [56] showed that compared to a blank test, amending an agricultural soil with EGM biochars at doses of 1% and 5% increased the PO₄-P release by about 4% and 27%, respectively. At contrary, Laird et al. [21] reported that adding a lignocellulosic biochar at a dose of 2% to an agricultural soil containing 0.5% of swine manure reduced the total dissolved phosphorus leached amount by about 69%. This results inconsistency might be due to the physicochemical characteristics of the soil and especially the biochars. Indeed, PO₄-P adsorption is generally favored for biochars that dispose of low PO₄-P water extractable fraction [51,55] and are rich in hydroxyl functional groups [57,58] and mineral salts such as Mg and Ca [59,60], which is not the case of our used RPM-B [17]. Finally, the increase in pH of the mixture soil/biochar (see Section Anions Dynamic Behavior) could promote alkaline metals oxides formation, which, in turn, might reduce the development of insoluble phosphates precipitates [61].

It is important to underline that, compared to batch tests (Section 3.2), PO₄-P ions were released during the phase 1 at very slow rates with average kinetics of 0.0028, 0.0494, and 0.0657 mg g⁻¹ d⁻¹ for the blank and the biochar-amended soil treatments with 5% and 8%, respectively. Even after 22 days of daily leaching, the agricultural soil amended with biochar at doses of 5% and 8% continued in releasing PO₄-P ions at non-negligible rates of 0.0249 and 0.0338 mg g⁻¹ d⁻¹, respectively. These kinetic release rates were calculated to be 0.0063 and 0.0097 mg g⁻¹ d⁻¹ at the end of phase 2 (Table 3). This long-term PO₄-P



release at slow rates is a very attractive property in agriculture since it ensures an adequate supply to crops and reduces the pollution risks of water resources.

Figure 7. Cumulated PO₄-P collected at the outlet of the columns containing nonamended and RPM biochar-amended agricultural soil during phase 1 (**a**) and phase 2 (**b**).

Cations Dynamic Behavior

Cations dynamic during the leaching of the three soil columns seems to depend mainly on the targeted element and its content in the followed porous media as well. Indeed, at the end of the phase 1, except for NH_4 -N, all the released cations amounts increased with the increase in the RPM-B dose in the soil (Figures 8a–12a and Table 4). The utmost released amounts were observed for potassium, which is the most contained element in the RPM-B (Table 1). This finding confirms the batch results (Section 3.2) assuming that compared to PO₄-P, the K⁺ ions exist in more easily leachable forms. At the end of this first phase, the released amounts of K⁺, Na⁺, Mg²⁺, and Ca²⁺ for soils amended with RPM-B doses of 5% and "8%" were 17.1, 7.7, 4.2, and 2.1, and "24.3", "9.6", "5.3", and "2.4" times higher than those measured for the unamended control, respectively (Table 4). This outcome suggests that RPM-B could be considered as an important source of bioavailable cationic nutrients (especially K⁺, Mg²⁺, and Ca²⁺) that are essential for plants' growth. Depending on the crop requirements, this biochar could partly or totally replace chemical fertilizers, especially those rich in K, Mg, and Ca [62,63]. Similarly, based on laboratory column assays, [8] reported that the leaching with 10 pore volumes of distilled water of an amended very fined sandy soil by a mixture of RPM (5%) and a pinewood biochar (5%) significantly increases the K⁺, Mg²⁺, and Ca²⁺ release from 26.1, 19.0, and 9.9 mg kg⁻¹ (blank test) by factors of about 87, 8, and 13, respectively. These factors become equal to 166, 7, and 27 when the RPM and the biochar dosages were doubled.

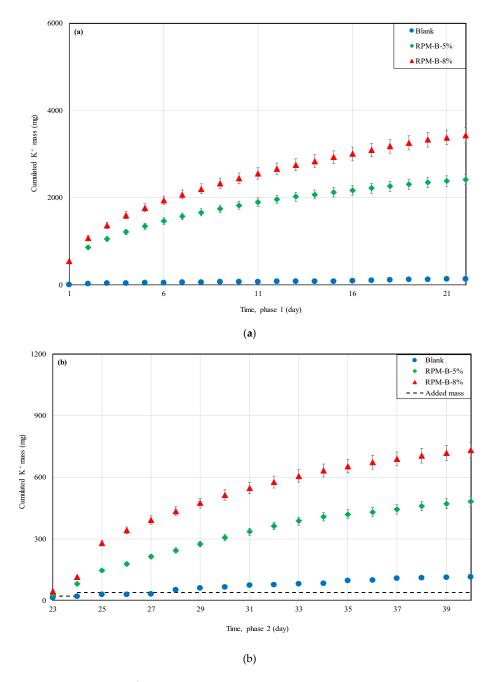


Figure 8. Cumulated K⁺ collected at the outlet of the columns containing nonamended and RPM biochar-amended agricultural soil during phase 1 (**a**) and phase 2 (**b**).

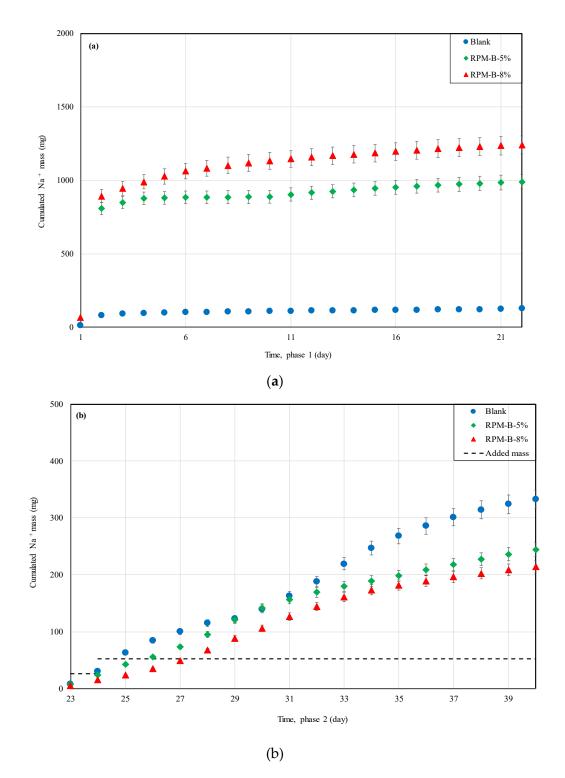


Figure 9. Cumulated Na⁺ collected at the outlet of the columns containing nonamended and RPM biochar-amended agricultural soil during phase 1 (**a**) and phase 2 (**b**).

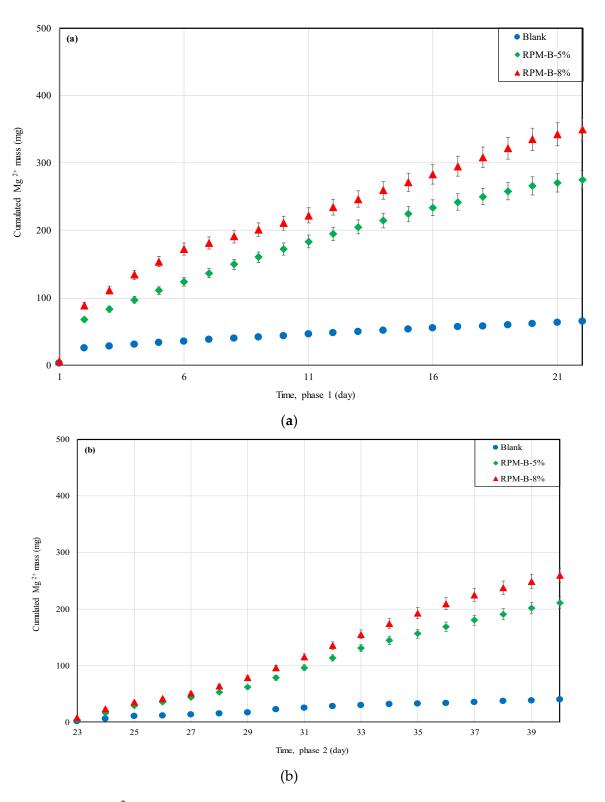


Figure 10. Cumulated Mg²⁺ collected at the outlet of the columns containing nonamended and RPM biochar-amended agricultural soil during phase 1 (**a**) and phase 2 (**b**).

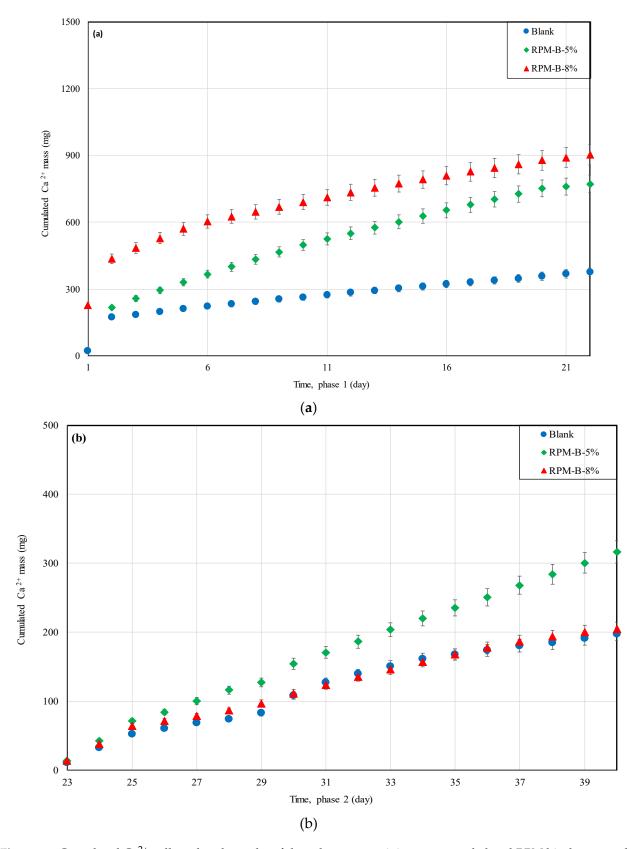


Figure 11. Cumulated Ca²⁺ collected at the outlet of the columns containing nonamended and RPM biochar-amended agricultural soil during phase 1 (**a**) and phase 2 (**b**).

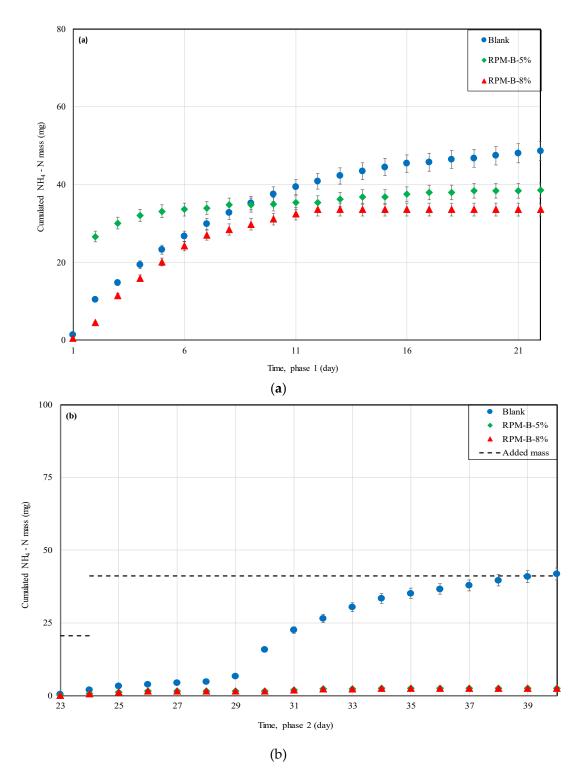


Figure 12. Cumulated NH₄-N mass collected at the outlet of the columns containing nonamended and RPM biocharamended agricultural soil during phase 1 (**a**) and phase 2 (**b**).

| | Assay | Parameter | K+ | Na ⁺ | Mg ²⁺ | Ca ²⁺ | NH ₄ -N |
|---------|----------|---------------------------|----------|-----------------|------------------|------------------|--------------------|
| Phase 1 | Blank | RM-b (mg) | 141.4 a | 129.1 a | 65.8 a | 378.2 a | 48.6 c |
| | | ARR (mg $g^{-1} d^{-1}$) | 0.0045 | 0.0041 | 0.0021 | 0.0119 | 0.0015 |
| | RPM-B-5% | RM (mg) | 2418.5 b | 990 b | 275.2 b | 772.4 b | 37.1 b |
| | | RM/RM-b ratio | 17.089 | 7.671 | 4.182 | 2.042 | 0.792 |
| | | ARR (mg $g^{-1} d^{-1}$) | 0.076 | 0.0313 | 0.0087 | 0.0244 | 0.0012 |
| | RPM-B-8% | RM (mg) | 3431.6 c | 1240.8 с | 349.9 c | 904.2 c | 33.6 a |
| | | RM/RM-b ratio | 24.262 | 9.613 | 5.317 | 2.391 | 0.692 |
| | | ARR (mg $g^{-1} d^{-1}$) | 0.108 | 0.0392 | 0.0110 | 0.0285 | 0.0011 |
| Phase 2 | A | M (mg) | 50.45 | 65.68 | * | * | 51.43 |
| | Blank | RM (mg) | 114 a | 332.7 с | 39.9 a | 198 a | 41.8 c |
| | | RM/AM ratio | 2.259 | 5.065 | * | * | 0.813 |
| | | FRR (mg $g^{-1} d^{-1}$) | 0.0011 | 0.0059 | 0.0008 | 0.0046 | 0.0007 |
| | RPM-B-5% | RM (mg) | 482.9 b | 244.6 b | 211.4 b | 316.5 c | 2.4 a |
| | | RM/AM ratio | 9.572 | 3.723 | * | * | 0.047 |
| | | FRR (mg $g^{-1} d^{-1}$) | 0.0081 | 0.0058 | 0.0069 | 0.0109 | ** |
| | | RM (mg) | 731.5 c | 214.4 a | 259.5 с | 204.9 b | 6.2 b |
| | RPM-B-8% | RM/AM ratio | 14.498 | 3.264 | * | * | 0.121 |
| | | FRR (mg $g^{-1} d^{-1}$) | 0.0087 | 0.0040 | 0.0075 | 0.0033 | ** |

Table 4. Release kinetics of cationic nutrients from nonamended and amended agricultural soil with RPM biochar at 5% and 8%.

(RM: released mass; b: blank assay; AM: added mass from synthetic solutions; ARR: average release rate; FRR: final release rate; *: nutrient not added in the synthetic solution; **: no release at the end of the assay). For each cation at each phase, RM values followed by the same lowercase letters are not significantly different at $p \leq 0.05$).

Concerning the second phase of the leaching assays, it could be clearly noticed that the dynamics of the studied cations after synthetic solution addition depended mainly on the targeted nutrient (Figures 8b-12b). Indeed, outcomes showed that the released amounts of K⁺ and Mg²⁺ has significantly increased with biochar amendment rate and time indicating that these two elements were not adsorbed for the three soil treatments (Figures 8b and 10b). For instance, K⁺ was likely to be continuously released from the RPM-B. At the end of this second phase, the released amounts of K^+ by the amended agricultural soil at doses of 5% and 8% were 9.6 and 14.5 times greater than the added K mass in the synthetic solution (Table 4). A similar trend was observed by Laird et al. [21] when investigating nutrients behavior in column mode of an agricultural soil amended with various lignocellulosic biochar doses (between 0% and 2.5%) in presence and in absence of a fixed swine manure dose of 0.5%. They showed that K⁺ and Ca²⁺ released amounts increased with the increase in the biochar dose. The greatest increases were evaluated to be about 33% and 12% for K⁺ and Ca²⁺, respectively, for a biochar dose of 2.5%. Moreover, in a field study with a total monitoring duration of more than 1.6 years, Major et al. [23] showed that adding a local lignocellulosic biochar to a tropical acid soil at a dose of 20 t ha^{-1} has increased Ca^{2+} , Mg^{2+} , and K^+ leaching at a depth of 0.6 m by about 164%, 110%, and 9%, respectively compared to the unamended soil. However, leaching capacities at 1.2 m was reduced for these elements by about 14%, 22%, and 31%, respectively. This behavior was imputed to a possible combination of nutrients retention and plants' uptake.

Regarding Na⁺, the released amounts from all soil treatments were higher than the added mass in the synthetic solutions (Figure 9b). However, compared to the release trend in phase 1 (Figure 9a), the blank test in phase 2 released more Na⁺ compared to biochar-amended soils. This outcome suggests that the Na⁺ liberated by the agricultural soil might be partially fixed by the RPM-B. Sodium adsorption by the RPM-B could occur through cation exchange process with other leached cations such as K⁺ and Mg²⁺ whose released masses significantly increased compared to the blank assay (Figures 8b and 10b).

Concerning NH₄-N, for both leaching phases, the released amounts by biocharamended agricultural soils were lower than control (Figure 12a,b). This result suggests that the released NH_4 -N ions by the soil were efficiently retained by the RPM-B. This trend is obvious on Figure 12b where the released amount of ammonium by the RPM-B-amended soil at 8% was about eightfold lower than its added mass in the synthetic solutions (Table 4). Various previous studies have indicated that NH₄-N adsorption is significantly promoted for biochars having developed porous structure, negative surface charges, and high specific surface areas and C/N ratios [32,51,64,65], which is the case of our RPM-derived biochar [17]. Similar observations were reported for biochars derived from various feedstock such as RPM [32], sewage sludge [39], and lignocellulosic biomasses [51]. For instance, Tian et al. [32] indicated that NH₄-N adsorption efficiency from a storm water increases from 1.7% to 91.7% when an RPM biochar at a dose of 10% was added to a sandy filter. However, based on column tests, Bohara et al. [8] showed that amending a very fine sandy loam soil with pinewood biochar at doses varying between 2.5% and 10% did not significantly affect the release of NH_4 -N. An increased leaching of N was even reported for some other biochars [21,66]. This behavior could be imputed to the biochars properties and especially their original high N contents, which depend mainly on the feedstock type and pyrolysis production temperature. In our case, due to the relatively high used pyrolysis temperature, the N content (0.06%) is low compared to various biochars including those derived from RPM (Table 1), which has probably limited its dissolution and leaching. As a consequence, due to the low released N components amounts from the RPM-B-amended soil, cosupplying this essential macroelement by synthetic fertilizers to similar sandy agricultural soils is highly recommended in order to ensure soil chemical properties and enzymatic activity potential improvement for higher cultivated plants' yields [1,65]. Opportunely, RPM-B exhibits important adsorption capacities of nitrogen bioavailable forms, namely, NH₄-N and NO₃-N, which will limit their loss by lixiviation or volatilization [67]. It would be very beneficial if these adsorbed elements will be slowly released from biochar-amended soils into the rhizosphere for optimal plant growth and yield.

It is worth mentioning that as for PO₄-P, cationic nutrients were also slowly released from the leached porous media. For instance, for the assay with the agricultural soil amended with 5% of RPM-B, the average release rates during phase 1 (from the 1st to the 22nd day) were assessed to only 0.0763, 0.0087, and 0.0244 mg $g^{-1} d^{-1}$ for K⁺, Mg²⁺, and Ca^{2+} , respectively (Table 4). At the end of this phase, these rates were evaluated to be 0.0232, 0.0031, and 0.0084 mg $g^{-1} d^{-1}$, respectively. These rates should be significantly decreased in cultivated real sites with important unsaturated zones depths due to nutrients' assimilation by plants and adsorption onto soil particles [23]. Therefore, compared to fast-release synthetic fertilizers, the current slow-release RPM-B amended soil should present lower nutrients loss, and hence lower negative impacts on groundwater quality [40]. Similar trends were reported for raw biochars derived from animal wastes [21], lignocellulosic biomasses [15,38], a sawdust-derived biochar artificially doped with N, P, and K elements [40], and a 10% straw-wheat-shells-derived biochar/struvite composite [68]. For instance, Gwenzi et al. [40] showed that nutrients-doped sawdust-biochars released NO₃⁻, PO₄³⁻, and K⁺ at lower rates and amounts compared to synthetic fertilizers. Indeed, after 15 sequential extractions, their cumulated released amounts of these three nutrients from the doped biochars were at most approximately the half of those of the synthetic fertilizer.

Finally, it is important to underline also that the majority of anions and cations nutrients (PO₄-P, K⁺, Mg²⁺, and Ca²⁺) were released from RPM-B at amounts and rates higher than those derived from lignocellulosic biomasses [38,55]. Therefore, mixing lignocellulosic biomasses with animal wastes before the pyrolysis process could promote biochars production with higher nutrient contents. These biochars will offer non-negligible supplementary PO₄-P and other essential macroelements such as K⁺, Ca²⁺, and Mg²⁺. However, the transport of these elements in the underground compartments and the related environmental risks should be accurately assessed.

4. Conclusions

The main objective of this research study was to assess the capacity of a biochar generated from poultry manure to release/adsorb nutrients under both static and dynamic conditions. Outcomes suggest that this biochar could be considered as a promising and attractive soil conditioner. Indeed, besides its high capability to supply agricultural soils with essential nutrients (especially, K⁺, Mg²⁺, Ca²⁺, and PO₄-P), their release occurs over extended periods with very slow rates. This is particularly important for both optimal crop development and reduced environmental pollution risks by these elements. On the other hand, RPM-B exhibited, respectively, important and moderate adsorption capacities for NH₄-N and NO₃-N, which could be very interesting if synthetic nitrogen fertilizers have to be applied. Biochar valorization in agriculture is a pathway for a sustainable management of abundant RPM wastes and the reduction in synthetic fertilizer use, which is more profitable for farmers. However, further investigations regarding the long-term impacts of RPM-B and also biochars generated from mixture of RPM and lignocellulosic biomasses on soil properties, crop yields, and underground water resources possible contamination would be of great interest.

Author Contributions: This paper was written with the contribution of all authors as follows: Conceptualization, S.H., S.J., and W.K.; methodology, S.H., S.J., M.J., and W.K.; software, S.H. and H.H.; validation, S.J., M.J., M.K., J.J.L., and W.K.; formal analysis, S.H., S.J., M.K., J.J.L., and W.K.; investigation, S.H., S.J, and W.K.; resources, S.J. and W.K.; data curation, S.J., M.J., H.H., and W.K.; writing—original draft preparation, S.H., and S.J.; writing—review and editing, M.J., H.H., and W.K.; visualization, S.J., M.J., and W.K.; supervision, S.J. and W.K.; project administration, S.J. and W.K.; funding acquisition, S.J., M.K., J.J.L., and W.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the TUNISIAN MINISTRY OF HIGHER EDUCATION AND SCIENTIFIC RESEARCH and ERASMUS+ International Credit Mobility Program.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data available on request.

Acknowledgments: This research work was carried out within the framework of an ERASMUS+ International Credit Mobility Program between CERTE (Tunisia) and UL (Ireland). The authors gratefully thank this program and also the Tunisian Ministry of Higher Education and Scientific Research for financing this work.

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

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