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# Nutrient retention and release from raw exhausted grape marc biochars and an amended agricultural soil: Static and dynamic investigation

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ABSTRACT

Biochar is the solid by-product of biomass thermochemical conversion via pyrolysis technique. Biochar addition to croplands as an organic amendment can improve soil properties and increase agricultural productivity. However, these positive effects depend largely on biomass feedstock and pyrolysis conditions. In this study, nutrient release from biochars derived from the slow pyrolysis of exhausted grape marc (EGM) at 300, 400 and 500 °C (EGM300, EGM400 and EGM500) was investigated through five successive leaching assays in batch mode for a total duration of 10 days. Then, nutrient leaching/retention kinetics of an agricultural soil amended with EGM500 (1% and 5% w/w) was assessed under dynamic conditions in columns. The batch experiments showed that with the exception of P, the nutrient release efficiency from the three biochars significantly increased with the increase of the number of leaching trials. The highest released amounts were observed at the fifth leaching cycle for K, Ca, P and Mg, which were about 45.5%, 41.5%, 229.5% and 48.9% higher than those registered during the first leaching assay. Regarding the column release experiments, a biochar content of 5% in the agricultural soil resulted in an increase of water leached $NO_3^-$ and $K^+$ by about 181.4% and 521.3%, respectively, and a significant reduction in $Na^+$ and $Ca^{2+}$ transport as compared to unamended soil. In a second phase, outcomes of column feeding with a nutrient solution showed that $PO_4^{3-}$ and $NO_3^-$ retention by biochar-amended soils is low. Thus, the use of EGM biochar as a slow release biofertilizer could be considered as a promising agricultural practice and a sustainable solution for biowaste management.



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## 1. Introduction

On a global scale, agri-food industry generates huge amounts of by-products including wastewater and solid wastes (Joshi and Visvanathan, 2019; Tsangas et al., 2020). The produced solid residues are commonly composed of organic matter and chemical compounds that could induce serious human health and environmental concerns if mismanaged (Adams and Demmig-Adams, 2013; Pérez-Gimeno et al., 2019). Therefore, the recovery and recycling of these wastes for a subsequent reuse in the context of circular economy is considered as an important research focus that will certainly promote sustainability at a global level (Loizia et al., 2019; Pascual et al., 2018; Azzaz et al., 2018; Almendro-Candel et al., 2018).

Winery industry represents an important economic sector with an estimated annual amount of 70 million tons of wine grapes being produced worldwide (Cholette and Castaldi, 2005; OIV, 2019). Grape marc is the remaining solid residue after juice extraction for vinification. It contains the skin, pulp, seeds, and stems of the grape. Currently, these grape marc solid residues are exploited for ethanol production by distillation generating a second residue called exhausted grape marc (EGM). Up to 20% of these EGM finish as wastes that, if not adequately managed, may cause severe environmental issues (Xu et al., 2009; Zorpas et al., 2012).

Various methods have been proposed for the management and valorization of EGM wastes (Zorpas and Saranti, 2016). These include their reuse for the production of: (i) cosmetics and pharmaceuticals (Andjelkovic et al., 2015; Nunes et al., 2017), (ii) animal feed (Eleonora et al., 2014); (iii) composts (Carmona et al., 2012), and organic fertilizers (Moldes et al., 2007). However, some of these methods have various disadvantages including odor nuisance, social acceptance, technical feasibility and economic viability (Spigno et al., 2017; Zorpas, 2020).

The relatively high organic carbon content of exhausted grape marc (31%–54%) has motivated its thermochemical conversion through various processes (Muhlack et al., 2018) namely, combustion (Kraiem et al., 2016), gasification (Lapuerta et al., 2008), hydrothermal carbonization (Mäkelä et al., 2017), and pyrolysis (Ibn Ferjani et al., 2019). This latter process has the main advantage of zero-waste production through a total conversion of biomasses into biofuel (gas and bio-oil) that could be used inside the winery for heating or electricity production (Casazza et al., 2016; Demiral and Ayan, 2011; Xu et al., 2009), and a solid by-product named biochar. This residual solid fraction could be valorized in agriculture as a soil amendment/biofertilizer (Lone et al., 2015; Sashidhar et al., 2019; Jeguirim et al., 2019) as well as an effective adsorbent for contaminant removal from soils (Khan et al., 2020) and from gaseous and aqueous effluents (Abedi and Mojiri, 2019; Jellali et al., 2019; Li et al., 2019).

Recently, biochars have been considered among the environmentally friendly fertilizers (EFFs) for sustainable and modern agriculture (Chen et al., 2018a). In this context, Ding et al. (2017) and Lone et al. (2015) reported that biochars can significantly contribute to the improvement of the physical (granulometry, density and porosity), chemical (pH, Electrical conductivity, cation exchange capacity), hydrodynamic (hydraulic conductivity, water storage capacity), and the biological properties of amended soils. Regarding nutrient release efficiency from biochars, it appears that this process is very dependent on the nature and characteristics of the used feedstock. Indeed, lignocellulosic biomasses and sewage sludge have relatively low capacity in releasing nutrients (Haddad et al., 2018; Laird et al., 2010; Wu et al., 2011; Yuan et al., 2016) when compared to animal biomasses (Hadroug et al., 2019; Wang et al., 2015).

When mixed with agricultural soils, some biochars especially those generated from animal wastes such as poultry manure, significantly increase the nutrient release rates as compared to unamended soils. For example, Chan et al. (2008) studied nutrient availability to radish at pot-scale by mixing a raw poultry manure (RPM) biochar generated at 550 °C with an agricultural soil at a dose of 50 t/ha. They showed that compared to unamended soil, nutrient uptake (g per pot) for N, P, Na, K and Ca increased by approximately 141%, 263%, 223%, 94%, and 124%, respectively. In the same time, other biochars are likely to have significant adsorption/retention capacity for some nutrients. When studying nutrient retention under dynamic conditions in a typical Plinthudult soil amended with sludge biochars (1%) produced between 300 °C and 700 °C , Yuan et al. (2016) demonstrated that biochar addition reduced ammonium, phosphorus and potassium release by 6.8–35.9%, 8.5–23.7% and 7.9–23.4%, respectively. Depending on biochar and soil nature, nutrients could present opposite dynamics and behavior (Pratiwi et al., 2016; Novak et al., 2009). For instance, Pratiwi et al. (2016) studied the impact of rice husk biochar added to a loamy soil at 4% (w/w) under dynamic conditions. They demonstrated that compared to control assays, biochar addition reduced the leaching of total ammonium and nitrates by about 11% and 23%, respectively. On the contrary, an increase of phosphates leaching by about 72% was observed. These outcome discrepancies have been mainly imputed to the properties of the used agricultural soils and biochars as well as the experimental conditions such as column dimensions, water leaching characteristics, volumes, and application rates (Chan et al., 2008; Pratiwi et al., 2016). However, as static assays, lignocellulosic biomass-derived biochars generally present lower nutrient release compared to those generated from animal residues (Hadroug et al., 2019; Pratiwi et al., 2016). This is mainly due to the low nutrient content of raw lignocellulosic by-products. Therefore, investigating agricultural by-products that are rich in nutrients for the production of biochars has been considered as a promising research option since they could bring a supplementary natural source of nutrients for agricultural soils and promotes sustainability (Ibn Ferjani et al., 2019; Sashidhar et al., 2019).

Exhausted grape marc (EGM) wastes have relatively high nutrients contents and could be valorized as low-cost feedstock for the production of biochars as eco-friendly biofertilizer. Our previous study has clearly shown that EGM could be converted to an interesting nutrient-concentrated-biochar when compared to traditional agricultural biomasses

(Ibn Ferjani et al., 2019; Khiari and Jeguirim, 2018). Moreover, the addition of EGM biochar to agricultural soils as amendment could present double benefits. Accordingly, they could initially act as a slow-release source of nutrients reducing therefore the use of chemical fertilizers, and then could behave as an adsorbent for the excess of synthetic nutrients added at later stages. To the best of our knowledge, the reuse of EGM-derived-biochars as amendment for agricultural purposes and specifically their effect on nutrient dynamics and behavior has not yet been investigated. Therefore, the main objectives of the present study were to: (i) determine in batch mode the successive nutrient leaching capacity for long term periods (10 d) of EGM biochars produced at different pyrolysis temperatures (300, 400 and 500 °C); (ii) assess in dynamic mode the effect of EGM biochar addition to an agricultural soil on the capacity of the amended soil to release and retain nutrients.

## 2. Materials and methods

### 2.1. Biochar preparation and characterization

The EGM was collected from the Sigolsheim distillery (France) after ethanol extraction by distillation process. In a first step, the feedstock was dried for 24 h at 60 °C and the stems were removed manually. The dried EGM was ground to a particle size of 0.25–0.4 mm then stored in a desiccator. EGM pyrolysis was performed in a vertical tubular furnace according to the experimental conditions described by Ibn Ferjani et al. (2019). Accordingly, three EGM biochars were produced at pyrolysis temperatures of 300, 400 and 500 °C (named EGM300, EGM400 and EGM500, respectively). An in-depth characterization of these biochars has already been performed (Ibn Ferjani et al., 2019). This includes particle size distribution, pH, elemental and proximate analysis, scanning electron microscopy (SEM), Energy Dispersive X-ray (EDX), specific area, porosity, X-ray Photoelectron Spectroscopy (XPS), and Raman spectroscopy. The surface area, microporous volume, ash and fixed carbon contents of EGM500 were 205 $m^2$ $g^{-1}$, 0.06 $cm^3$ $g^{-1}$, 9.5% and 58.2%, respectively. Furthermore, EGM500 has the highest nutrient concentrations, especially in terms of K, Ca and P with respective contents of 2.17%, 1.34 and 0.62%. For that reason, Ibn Ferjani et al. (2019) have recommended its valorization as an efficient biofertilizer or effective nutrient adsorbent for agricultural purposes.

### 2.2. Soil properties

The agricultural topsoil used for nutrient leaching experiments in laboratory columns was sampled from a citrus orchard located in northeastern Tunisia. It was first air dried then sieved through 1-mm mesh. Soil particle size distribution was determined by a laser diffraction analyzer (Malvern Mastersizer STD06). Soil pH was measured in 1:10 soil–water slurry. Na, Mg, Al, Si, P, K, Ca, Fe, Zn, and Mn were analyzed by X-ray Fluorescence (XRF) that was carried out using S8 TIGER Series 2 apparatus.

### 2.3. Batch leaching experiments

The assessment of the release kinetics of P, K, Ca and Mg from the three derived EGM biochars was performed through successive batch experiments for an overall duration of 10 days. During this investigation, five successive separated assays were carried out with consecutive contact times of 1, 1, 3, 3 and 2 days, respectively. These durations were chosen on the basis of the nutrients release from biochars is a time dependent process and the maximum of this release occurs during the first days of contact times (Hadroug et al., 2019). For each leaching assay, the same biochar samples were shaken at 400 rpm in 50 mL of distilled water at a fixed dosage of 10 g $L^{-1}$, a natural (non-adjusted) initial pH of 6.8 and an average room temperature of 20 ± 2 °C. At the end of each batch nutrient-release experiment, the biochar samples were recovered by vacuum filtration through 0.45–μm paper filters, and then dried for 16 h at 40 °C. These dried samples were re-extracted with water during the following assay under the same experimental conditions described above.

The concentrations of K, Ca, Mg and P in the filtrates were analyzed by ion chromatography (Metrohm, Herisau, Switzerland). For a given leaching experiment, the released amount of K "$q_K$ (mg $g^{-1}$)", Ca "$q_{Ca}$ (mg $g^{-1}$)", Mg "$q_{Mg}$ (mg $g^{-1}$)" and P "$q_P$ (mg $g^{-1}$)" per g of tested biochar were determined as follows:

$$q_K = \frac{C_K}{D} \tag{1}$$

$$q_{Ca} = \frac{C_{Ca}}{D} \tag{2}$$

$$q_{Mg} = \frac{C_{Mg}}{D} \tag{3}$$

$$q_P = \frac{C_P}{D} \tag{4}$$

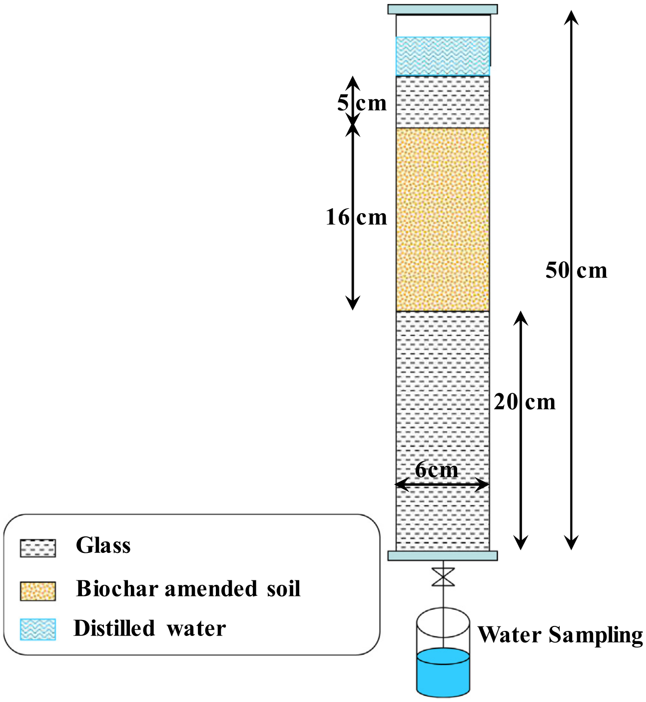



**Fig. 1.** Schematic representation of the column used for nutrient release and adsorption studies from/by EGM500 biochar.

where $C_K$, $C_{Ca}$, $C_{Mg}$, $C_P$ are the released concentrations of K, Ca, Mg and P respectively (mg $L^{-1}$) and $D$ is the used biochar dose (g/L).

All the batch experiments addressing nutrient release were carried out in triplicate and each data given in this work is an average of at least three parallel independent analysis of liquid samples.

### 2.4. Column leaching experiments

Column leaching experiments were performed in order to investigate the effect of EGM500 addition to the selected agricultural soil at three doses of 0% (blank test), 1% and 5% on the release and the possible adsorption of nutrients. The choice of EGM500 is justified by its interesting physicochemical characteristics compared to the two other produced biochars (Ibn Ferjani et al., 2019). The columns were made of Plexiglas with a total length and inner diameter of 50 and 6 cm respectively (Fig. 1). The soil was first hand-mixed with the biochar at the chosen rate. Then, this mixture (a total constant mass of ∼701 g for all experiments) was packed into the column with small increments in order to guarantee a homogenous compaction. At both sides of the column, a 5 cm layer of glass particles was placed in order to ensure a uniform flow through the column and a free water drainage (Jellali et al., 2016). The nutrient release experiments consisted of feeding the column for the first 8 days with a distilled water volume of 146 mL $d^{-1}$ (gravity flow), which corresponds to about a pore volume of the packed soil (Phase 1). In order to quantify the ability of the amended soil in retaining nutrients, at the ninth and tenth day, columns were fed with the same water volume but containing 50 mg $L^{-1}$ of N-$NO_3$ and P-$PO_4$, and 63.06 mg $L^{-1}$ of K. From the 11th to 17th day, the columns were again daily flushed with 146 mL of distilled water. Leachates at the outlet of the columns were collected every day and their pH, EC and nutrient concentrations were determined.

### 2.5. Statistical analysis

Data from the batch and column leaching experiments were analyzed using STATISTICA 8.0 (Statsoft, Tulsa, OK, USA). ANOVA with Duncan's multiple range test was applied for mean separation at $P \leq 0.05$.

## 3. Results and discussion

### 3.1. Biochar and soil characterization

A detailed characterization of the three used EGM biochars (EGM300; EGM400 and EGM500) has already been reported in Ibn Ferjani et al. (2019). It is worth mentioning that the pH of these biochars increase with raising pyrolysis temperature

**Table 1**
PH and mineral composition of the exhausted grape marc biochars (mg/g) in comparison with biochars from other biomasses (–: not given).

| Biomass | pH | K | Ca | P | Mg | Fe | Al | Na | Reference |
|---|---|---|---|---|---|---|---|---|---|
| EGM (300 °C) | 8.7 | 11.00 | 7.01 | 3.37 | 1.15 | 0.51 | 0.55 | 0.20 | Current study |
| EGM (400 °C) | 9.9 | 16.40 | 10.3 | 4.94 | 1.43 | 0.77 | 0.43 | 0.30 | Current study |
| EGM (500 °C) | 10.1 | 21.70 | 13.4 | 6.23 | 1.90 | 0.93 | 0.47 | 0.41 | Current study |
| Mallee wood biochar (500 °C) | – | 3.79 | 5.83 | 0.88 | 1.69 | – | – | 1.06 | Wu et al. (2011) |
| Mallee leaf biochar (500 °C) | – | 13.06 | 25.56 | 3.57 | 4.45 | – | – | 19.02 | Wu et al. (2011) |
| Wheat straw biochar (400 °C) | 9.2 | – | 78.8 | 1.2 | 0.14 | 36.0 | 0.14 | – | Zhang et al. (2020) |
| Wheat straw biochar (500 °C) | 9.5 | 20.9 | – | 4.4 | – | – | – | – | Sun et al. (2019) |
| Residues of wood chip biochar (620 °C) | 10.1 | 10.4 | 42.2 | 1.3 | 2.9 | 2.42 | – | 0.74 | Prodana et al. (2019) |
| Mixture of 70% wood chip and 30% of deciduous European beech trees (550–600 °C) | 9.0 | 6.07 | 19.07 | 1.63 | 2.09 | 2.59 | – | 3.3 | Haider et al. (2017) |
| Sugarcane straw biochar (700 °C) | 10.2 | 11.7 | 7.7 | 0.9 | 2.0 | – | – | – | Puga et al. (2016) |
| Biochar for a mixture of 80% hardwood and 20% coniferous wood (750 °C) | 9.5 | 9.03 | 20.5 | 0.81 | 2.58 | – | – | – | Zainul et al. (2017) |

**Table 2**
Main physico-chemical characteristics of the agricultural soil (1) dx: mesh diameter that allows x% of the soil to pass through; (2) UC: uniformity coefficient ($d_{60}/d_{10}$).

| Parameter | Value |
|---|---|
| $d_{10}$ (mm) | 0.064 |
| $d_{50}$ (mm) | 0.161 |
| $d_{60}$ (mm) | 0.183 |
| UC (–) | 2.8 |
| pH (–) | 7.66 |
| Organic matter (%) | 3.05 |
| Ca (mg/g) | 9.162 |
| Al (mg/g) | 6.478 |
| Fe (mg/g) | 3.791 |
| K (mg/g) | 2.847 |
| P (mg/g) | 0.567 |
| Na (mg/g) | 0.336 |
| Mg (mg/g) | 0.320 |
| Mn (mg/g) | 0.076 |
| Zn (mg/g) | 0.024 |

(Table 1). Besides, their mineral composition indicates that they are relatively rich in nutrients especially potassium, calcium and phosphorus compared to other biochars generated from lignocellulosic materials (Table 1). These contents increase with the increase of pyrolysis temperature to reach values of 2.17%, 1.34% and 0.62% for K, Ca and P, respectively for EGM500 biochar. These findings point out the importance of using pyrolysis as a thermochemical conversion process instead of combustion and the advantage of using these biochars as potential biofertilizers in agriculture.

The physico-chemical characterization of the agricultural soil (Table 2) indicates that it is a relatively fine and heterogeneous sandy soil since its mean diameter ($d_{50}$) is assessed to only 0.161 mm and its uniformity coefficient is higher than 2 (Das, 2004). This light texture explains its vocation for citrus tree cultivation. Furthermore, in comparison with typical Mediterranean soils, it is relatively rich in organic matter with a content of 3.05% (Allison, 1973). It has also relative high Ca, Al, Fe and K contents compared to other soils (Chen et al., 2018b; Iqbal et al., 2015).

### *3.2. Biochar batch lixiviation tests*

The cumulated amounts and release kinetics of K, Ca, Mg and P from EGM300, EGM400, and EGM500 biochars are illustrated in Fig. 2-A–D, respectively. It can be clearly noticed that for all of the three solid matrices, the cumulative amount of released nutrients significantly increased with the number of leaching experiments. The highest cumulative amounts of released K, Ca, P and Mg were therefore observed at the fifth leaching cycle (17.9, 10.4, 2.1 and 1.6 mg/g, respectively) as shown in Table 3. These contents are respectively 45.5%, 41.5%, 229.5% and 48.9% higher than the ones determined at the first cycle. However, the release kinetics of nutrients from the three biochars decreased rapidly versus time. For instance, for EGM500, the calculated rates for K and Ca decrease by respectively 95.9% and 96.2% between the first and the third cycle (Fig. 2A–B). The released rates of nutrients remain relatively important even after five leaching cycles with values of 0.14 and 0.24, 0.03 and 0.03 mg/g/d for K, Ca, P and Mg respectively (Figures A–D). Similar trends were reported by Mukherjee and Zimmerman (2013) when studying dissolved organic carbon, N and P release from five successive leaching assays of various biochars generated from lignocellulosic biomasses, and by Hadroug et al. (2019) during their investigation related to P and K release from raw poultry manure (RPM) and RPM-derived-biochars at temperatures of 400 and 600 °C. However, the nutrients release kinetics of EGM derived-biochars are so much lower than

**Table 3**
Nutrient release efficiency after 1 and 5 leaching cycles from EGM biochars produced at different temperatures.

| Biochar | Element | Released amount at the first leaching assay (mg/g) | Percentage from the contained fraction in the biochar[a] (%) | Cumulative released amount at the fifth leaching assay (mg/g) | Percentage from the contained fraction in the biochar[a] (%) |
|---|---|---|---|---|---|
| EGM300 | K | 3.1 | 28.3 | 8.8 | 79.8 |
| | Ca | 3.6 | 51.0 | 6.2 | 88.4 |
| | Mg | 0.6 | 53.0 | 1.0 | 86.2 |
| | P | 0.6 | 19.0 | 2.1 | 62.5 |
| EGM400 | K | 4.8 | 29.3 | 11.2 | 68.2 |
| | Ca | 4.2 | 40.6 | 7.0 | 68.1 |
| | Mg | 0.8 | 57.5 | 1.3 | 87.5 |
| | P | 0.3 | 6.5 | 1.5 | 30.2 |
| EGM500 | K | 12.3 | 56.8 | 17.9 | 82.6 |
| | Ca | 7.4 | 55.0 | 10.4 | 77.9 |
| | Mg | 1.1 | 57.1 | 1.6 | 85.0 |
| | P | 0.3 | 4.8 | 1.1 | 17.6 |

[a]See Table 1.

those observed for RPM biochars. This finding represents an important asset in agricultural application since EGM biochars will permit to slowly provide nutrients to cultivated crops, and to prevent groundwater contamination by leaching as well.

It is important to underline that except for P (Fig. 2D), the release efficiency of all other nutrients significantly increased with pyrolysis temperature. For instance, the maximum released amounts of K, Ca and Mg from EGM500 biochar were respectively 104.2%, 68.5% and 63.0% higher than those observed for EGM300. It is likely that the increase of pyrolysis temperature converts the EGM-contained K, Ca and Mg into more leachable and water-soluble forms through thermal dissociation mechanism (Chen et al., 2017). Accordingly, increasing pyrolysis temperature might transform the existing $CaCO_3$ into $Ca(HCO_3)_2$ which has much higher solubility in the percolating water (Wu et al., 2011). Similar trends were reported by Hadroug et al. (2019) and by Song and Guo (2012) for K release from poultry manure-derived biochars. However, the total released amount for P by EGM500 biochar was 48.1% lower than the one registered for the biochar generated at 300 °C (Table 3). This is due mainly to the fact that the increase of pyrolysis temperature converts a fraction of EGM-contained phosphorus into non-available forms. The prevailing forms are apatite, hydroxyapatite, tricalcium phosphate, and calcium–iron phosphate precipitates such as whitlockite and phosphate adsorbed onto the calcium carbonate surface (Hadroug et al., 2019; Sun et al., 2017; Wang et al., 2015) . These stable forms are less water-soluble and consequently less available (Peak et al., 2002). Similar behavior was noticed by Hadroug et al. (2019) and Manolikaki et al. (2016) when studying P release kinetics under batch mode after several successive leaching tests of biochars derived from poultry manure and olive pomace, respectively.

The highest percentages of released nutrients in comparison with the available ones in the EGM-derived biochars were estimated at 82.6% (EGM500), 88.4% (EGM300), 87.5% (EGM400) and 62.5% (EGM300) for K, Ca, Mg and P, respectively (Table 3). These nutrient release capacities are much important compared to biochars generated from other raw (Wu et al., 2011) and modified (Lateef et al., 2019) lignocellulosic biomasses as well as sewage sludge (Yuan et al., 2016). For instance, Wu et al. (2011) studied, in batch mode, nutrient release from biochars derived from a lignocellulosic biomass (mallee leaves) at temperatures varying between 300 and 750 °C. They reported that only 1.3%, 0.8–24.2%, 40.8–69.3%, 1.2% and 16.9% of N, P, K, Mg and Ca were respectively released for a contact time of 24 h. Besides, for sludge-derived biochars produced at pyrolysis temperatures varying between 300 and 700 °C, the maximum released percentages of N, $PO_4$ and K after a contact time of 72 h were 16.9%, 1.4% and 16.6%, respectively (Yuan et al., 2016). This finding confirms the potential of using EGM-derived biochars as an eco-friendly soil amendment and a precious additional source of needed nutrients for crops development and growth.

These released nutrient amounts are however lower than those corresponding to biochars generated from animal biomasses. For example, biochars produced at a temperature of 400 °C from RPM released about 18.5% and 60% of the initially contained P and K for a contact time of 48 h (Hadroug et al., 2019). These percentages reached 51% and more than 99%, respectively after six successive leaching assays with a total duration of 12 days.

On the basis of these batch leaching experimental results, it could be concluded that in contrast to high soluble chemical fertilizers, the slow release of nutrients from EGM-derived biochars represents a real advantage for plant growth as well as for the preservation of freshwater resources against contamination.

### *3.3. Column experiments*

The column experiments were carried out based on the outcomes of the batch leaching experiments. Accordingly, the impact of EGM500 biochar addition at three rates of 0% (control), 1% and 5% in the agricultural soil was studied as detailed in Section 2.4. Firstly, it is important to precise that, as expected, the measured pH and electrical conductivity (EC) at the outlet of the columns (data not shown) increased with the increase of the used EGM500 dose. The highest values of pH and "EC" were obtained at the beginning of the leaching experiments and were assessed to 7.87, 8.30 and

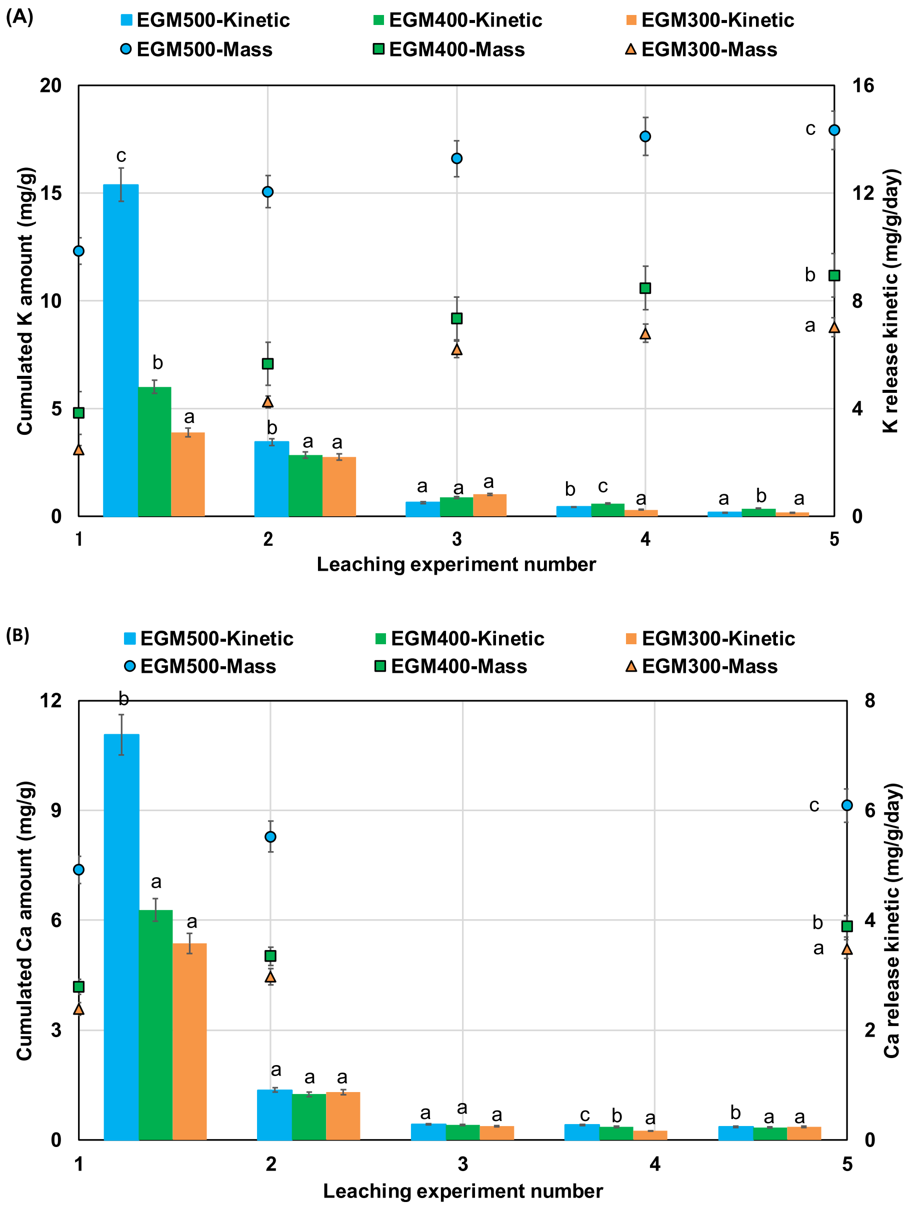
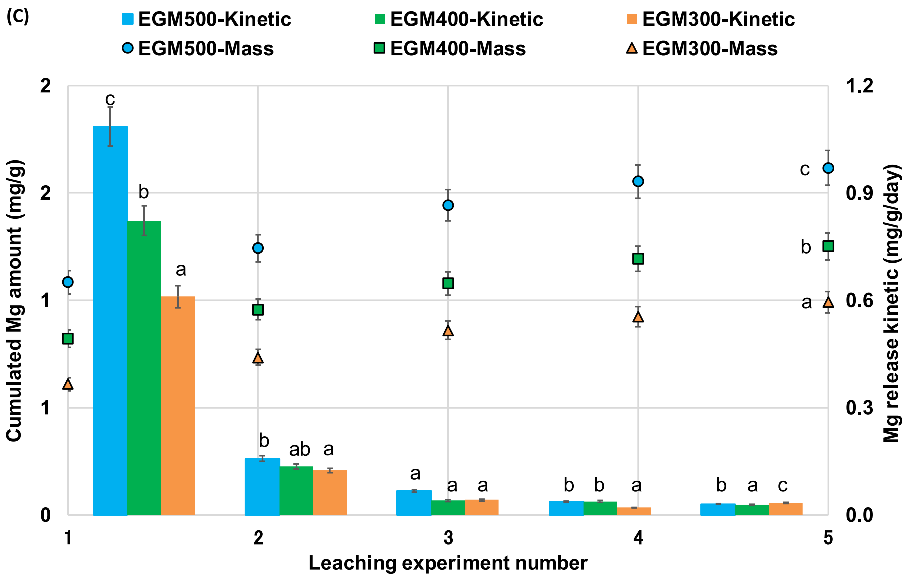



**Fig. 2.** Effect of successive leaching trials on the release of potassium (A), calcium (B), magnesium (C) and phosphorus (D) from EGM derived biochars at 300, 400 and 500 °C (dosage = 10 g $L^{-1}$; pH = 6.8; T = 20 ± 2 °C). For each element, release kinetic means and total cumulated amounts with the same lowercase letters are not statistically different at $P \leq 0.05$.

8.43, and "2740", "4280" and "5960" µS $cm^{-1}$ for the blank test, EGM doses of 1% and 5%, respectively. Furthermore, these values gradually decrease with time. The average pH and "EC" values during the overall experiments were 7.44, 7.64 and 8.00, and "658", "816" and "1021" µS $cm^{-1}$ for the blank test, used EGM doses of 1% and 5%, respectively.

The Figs. 3 to 7 illustrate the daily leached concentrations and the calculated cumulated masses at the outlet of the columns for $NO_3^-$; $PO_4^{3-}$; $Ca^{2+}$; $Na^+$ and $K^+$. For all the assessed ions, it is important to distinguish two phases during the experimental procedure. The first phase (or phase 1) is related to the intrinsic capacity of the unamended or biochar-amended soils in releasing nutrients. The second phase (or phase 2) begins after the addition of synthetic nutrient solutions and highlights the aptitude of the control or amended soils/ in retaining these elements.

During the first phase, the released concentrations of $NO_3^-$ and therefore the corresponding cumulated leached amounts significantly increased with the increase of the biochar dose in soil (Fig. 3). Indeed, the cumulated released amounts at the 8th day (just prior to the addition of the nutrient synthetic solution) were 21.3, 43.7 and 56.2 mg for control, EGM biochar doses of 1% and 5%, respectively. This dose-dependent increase confirms that the addition of EGM



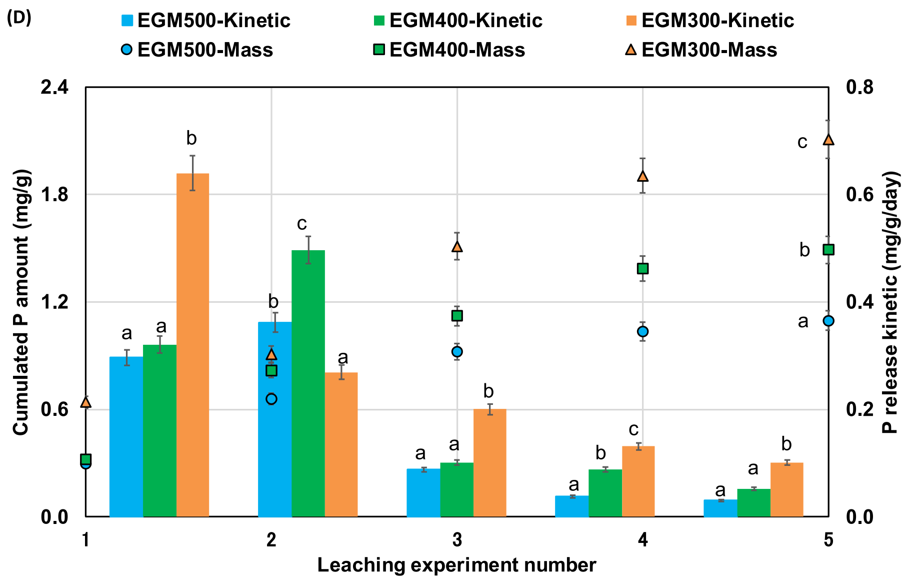




**Fig. 2.** (*continued*).

biochars to an agricultural soil could contribute to its nitrogen enrichment with bioavailable forms. At the end of this first experimental phase, the release kinetics of nitrates were low and indicate that almost all of the exchangeable nitrates were leached (Fig. 3a–b).

After the artificial addition of nitrates (32.2 mg), the measured concentrations at the outlet of the columns highly increased for all soil treatments. At the end of this second phase, the leached cumulated amounts were estimated at 21.6, 22.5 and 31.0 mg for untreated soil, and soil amended with 1% and 5% biochar, respectively. The calculated ratios of these masses by the artificially added nitrates mass were to 0.67, 0.70 and 0.96 (Table 4). This highlights that higher is the biochar dose, lower is the $NO_3^-$ retention efficiency and confirms preliminary batch assays (data not shown) that EGM500 was inefficient in removing $NO_3^-$. It is important to underline that due to both its important solubility in water and its negative charge, nitrate ions are generally very mobile and therefore could be easily leached and slightly retained. Similar results were reported by Iqbal et al. (2015) when studying the efficiency of adding forest-slash biochar to compost in the retention of $NO_3^-$, $PO_4^{3-}$ and organic carbon in a bioretention system.

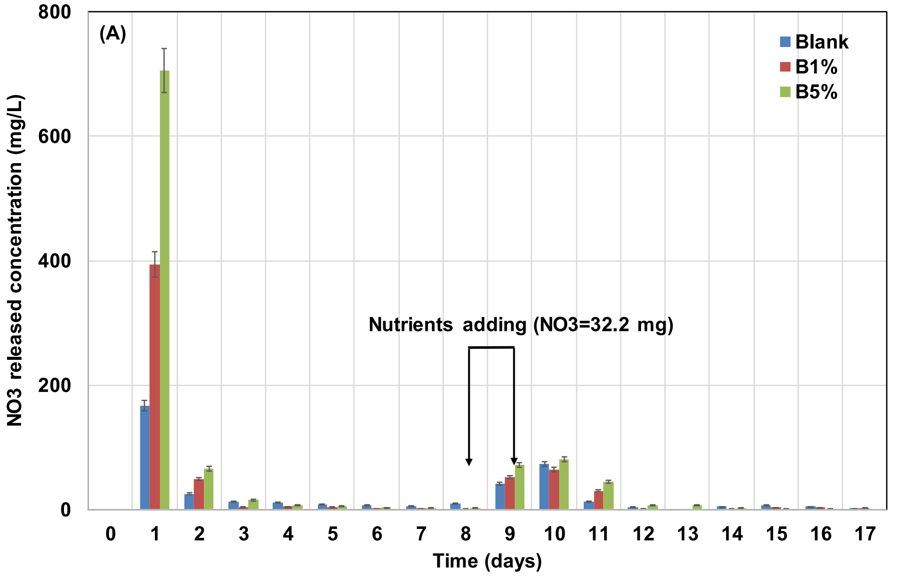



**Fig. 3.** Nitrates ($NO_3^-$) daily leached concentrations (A) and cumulated amounts (B) from the three soil treatments (0%, 1% and 5% EGM500 biochar) under dynamic conditions. At days 8 and 17, means of cumulated amounts with the same lowercase letters are not statistically different at $P \leq 0.05$.

**Table 4**
Effect of EGM biochars adding at different doses to the agricultural soil on nutrients leaching (AM: Synthetically added mass; RM: released mass; P1: phase 1; P2: phase 2).

| Nutrient | AM before P2 (mg) | Blank test | | | EGM500 adding at a dose of 1% | | | EGM500 adding at a dose of 5% comparison to blank test | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | RM-P1 (mg) | RM-P2 (mg) | Ratio RM-P2/AM | RM-P1 (mg) | RM-P2 (mg) | Ratio RM P2/AM | RM-P1 (mg) | RM-P2 (mg) | Ratio RM-P2/AM |
| NO3 | 32.20 | 21.30 | 21.62 | 0.67 | 43.69 | 22.46 | 0.70 | 56.18 | 30.95 | 0.96 |
| PO4 | 22.40 | 10.33 | 15.56 | 0.69 | 10.74 | 12.64 | 0.56 | 13.12 | 22.61 | 1.01 |
| Na | 12.00 | 120.84 | 31.47 | 2.62 | 38.53 | 26.97 | 2.25 | 30.31 | 23.02 | 1.92 |
| Ca | – | 140.64 | 40.14 | – | 120.79 | 48.29 | – | 53.27 | 38.76 | – |
| K | 9.20 | 29.56 | 17.39 | 1.89 | 48.96 | 38.07 | 4.14 | 192.96 | 164.70 | 17.90 |

However, this result is in contradiction with that reported by Beusch et al. (2019) who investigated the effect of adding biochars from trunks and branches of *Prosopis juliflora* (5% v/v) and clays (10%) on the dynamic behavior of $NO_3^-$. They showed that biochar addition induced a significant decrease in $NO_3^-$ leaching (by about 46%) in the first eight months of the experiment compared to unamended soil. This behavior could be, nevertheless, attributed to the physico-chemical properties of the biochar especially its large specific surface area (249.2 $m^2$ $g^{-1}$) and abundant acid functional groups that had favored the effective retention of nitrates. Besides, Cao et al. (2019) studied the effect of adding biochars (derived from apple branches at 700 °C) at doses of 0.5% and 4% to an orchard soil in microcosms. They reported decreases in nitrates leaching ratios of 10% and 69%, respectively. This could be due to a possible dose-dependent increase of the water holding capacity by about 0.7% and 5.6% respectively with the possibility of $NO_3^-$ being trapped in the soil solution within biochar pores (Knowles et al., 2011). It is worth mentioning that nitrate retention is generally favored when biochars are produced at relatively high temperatures, which is not the case for EGM500 (Hale et al., 2013; Hollister et al., 2013). In this context, Yao et al. (2012) pointed out that among 13 produced biochars, the four pyrolyzed at a temperature of 600 °C efficiently removed ions from aqueous solutions. A high adsorption capacity of nitrates by bamboo charcoal produced at a temperature of 900 °C was also reported by Mizuta et al. (2004).

Regarding $PO_4^{3-}$anions, it appears that the biochar presence in the system contributed to a significant dose-dependent increase of the measured concentrations at the outlet of the columns and the cumulated amounts (Fig. 4A–B). Indeed, at the end of the first phase, the cumulated amounts of released $PO_4^{3-}$ increased by about 3.9% and 27.0% for the amended soils with 1% and 5%, respectively as compared to control. It is important to underline that even after eight daily leaching with 146 mL of distilled water per day, $PO_4^{3-}$ ions continued to be released with rates of 1.4, 1.6 and 2.3 mg $d^{-1}$ for control soil and biochar-amended soils at 1% and 5% (Fig. 4-B). This is a very attracting property of the studied EGM biochar since it will allow the plant to have access to available P without significant losses to groundwater (Haddad et al., 2017).

Concerning leaching kinetics during phase 2, the released amount of $PO_4^{3-}$ increased with the biochar dose in the soil, which indicates that the EGM biochar was not effective in adsorbing the artificially added element. As such, when the agricultural soil was amended with 5% of biochar, approximately all the added $PO_4^{3-}$ (22.4 mg) by-passed the column and was recovered at the outlet of the column (22.6 mg). Similar results were reported by Coleman et al. (2019) who studied the effect of pine biochar addition to woodchips columns at 10% and 30% (v/v) on $PO_4^{3-}$ removal from simulated agricultural drainage under various hydraulic residence times (3; 6 and 12 h). Besides, Haddad et al. (2018) showed that even under a wide experimental conditions (various doses and pH), P retention by a biochar generated from the pyrolysis of a lignocellulosic biomass (raw cypress sawdust) was negligible. They figured out that a chemical modification with $MgCl_2$ was necessary in order to get interesting adsorption capacities of 43.5, 58.8 and 66.7 mg $g^{-1}$ for the treated biochars produced at 400, 500 and 600 °C, respectively. However, Eduah et al. (2020), showed that among six types of biochars, P adsorption depends on both the nature of the used feedstock and the used pyrolysis and adsorption experimental conditions, especially the used pyrolysis temperature and aqueous pHs. The highest adsorption capacity (11.63 mg $g^{-1}$) was observed for an initial adsorption aqueous solution pH of 2.5 for palm kernel biochar produced at a pyrolysis temperature of 650 °C. Furthermore, Chen et al. (2018c) showed that in column mode, Mg-impregnated biochar generated from the slow pyrolysis of cow dung at a dose of 1% decreased P leaching by about 89%. They explained this outcome mainly by a chemical adsorption of P through the formation of Mg–P precipitates.

On the other hand, the properties of the soil to be amended with biochars could be also very decisive in the transport of $PO_4^{3-}$ ions. Chen et al. (2018b) investigated $PO_4^{3-}$ retention by two acidic and two alkaline soils amended with wood chip-derived biochar nanoparticles in column mode. They showed that the amendment of the acidic paddy soil (pH = 6.31) and the red soil (pH = 5.05) increased the retention of P by 24% and 16%, respectively due to the stabilization of Fe/Al oxides and DOC-associated P. On the contrary, in both alkaline Huangmian soil (pH = 8.04) and Chao soil (pH = 7.77), the retention of P was reduced by 23% and 18%, respectively. Besides, Laird et al. (2010) reported that adding hardwood biochar to a loamy acidic soil at a dose of 0.2%, caused a reduction of P release capacity by about 69%, for a total leaching duration of 45 weeks. In the current study, the pH of the agricultural soil is alkaline (see Table 2) and could therefore favor the transport of Fe/Al oxide-associated P in the leaching water. The non-effective retention of nitrates and phosphates by EGM500 biochar should be seriously taken into account when using it as an amendment in combination with N–P-synthetic fertilizers in order to avoid their vertical and lateral migration in the soil.

On the other hand, the experimental results showed that cations dynamics depend on the nature of the target element as well. Accordingly, during the phase 1, $Ca^{2+}$ and $Na^+$ were released from the agricultural soil at relatively higher concentrations than from those treated with biochar at 1% and 5% (Figs. 5–6). At the end of phase 1, the release kinetic of $Na^+$ was relatively low indicating that 8 days were enough to ensure a maximum leaching of its easily exchangeable fraction (Fig. 6). The released Ca and Na amounts by the soil amended with the highest EGM500 dose of 5% were about 62% and 75% lower than the ones observed for the blank test (Table 4). This behavior could be explained by both the richness of the agricultural soil in these two elements and by their retention owing to biochar addition as well. This retention could be also as a result of cation exchange mechanism with other cations initially contained in the added biochar such as ammonium and potassium. Moreover, Na or Ca that are originally associated to chlorides may be transformed into organically bound forms in EGM500 biochar following the release of chlorides during the pyrolysis process or transformed into other forms such as carbonates or oxides which could seriously inhibit their leaching (Wu et al., 2011).

During phase 2, the re-enhancement of Ca release from the three substrates (Ca was not added in the synthetic solution) might be attributed to a cation exchange phenomenon with other cations such as ammonium and potassium contained

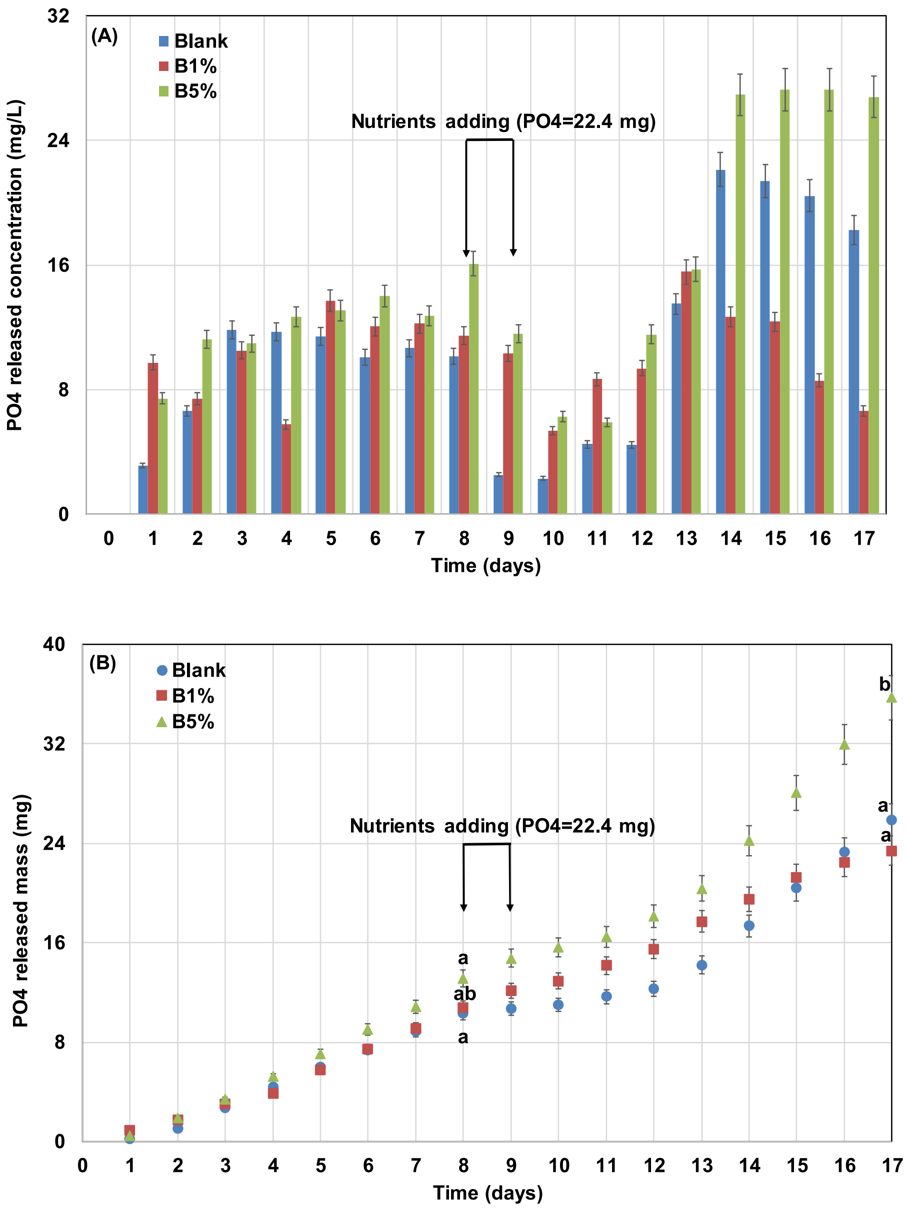
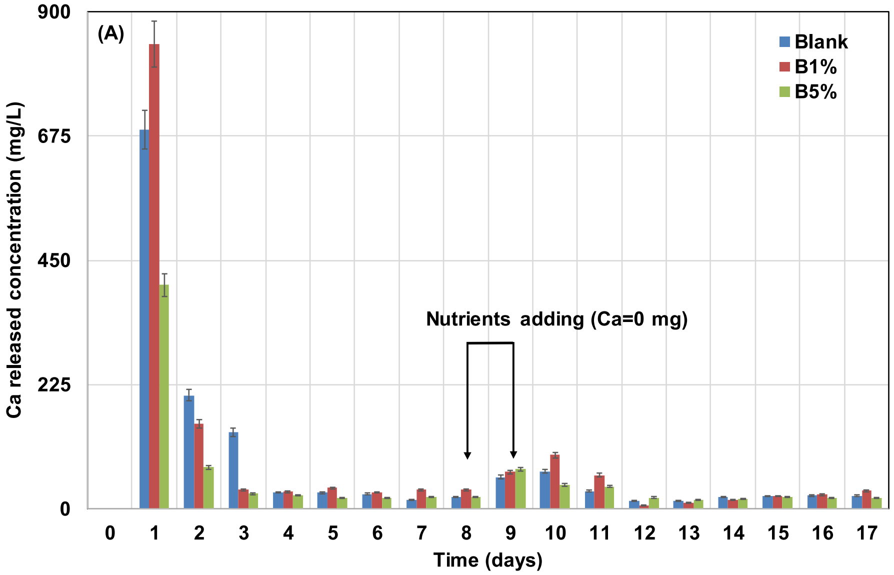



**Fig. 4.** Orthophosphates ($PO_4^{3-}$) daily leached concentrations (A) and cumulated amounts (B) from the three soil treatments (0%, 1% and 5% EGM500 biochar) under dynamic conditions. At days 8 and 17, means of cumulated amounts with the same lowercase letters are not statistically different at $P \leq 0.05$.

in the added synthetic solution (Fig. 5). A similar trend was also observed for $Na^+$ where significant increase of released amounts was observed at the outlet of the columns. These amounts were approximately 2.6, 2.3 and 1.9 times higher than the Na mass added by the synthetic solution (Fig. 7 and Table 4). Comparable trends were reported by Beusch et al. (2019) when they studied the effect of biochars and clays addition on nutrient release and retention at field scale. Moreover, Novak et al. (2009) observed an increase of $Na^+$ and $Ca^{2+}$ leaching by about 111% and 48%, respectively when aggressing the impact of pecan shell biochar addition on a Norfolk loamy soil at dose of 2%.

Regarding potassium release, which exists in the EGM biochar at high content (Table 1), the cumulated amounts at the end of phase 1 were positively correlated with biochar fraction in the soil (Fig. 7). Accordingly, the cumulated released amount from the soil treated with 5% of EGM500 biochar was 193 mg, which is about 553% higher than that leached from the agricultural soil (blank test) (Table 4). It is worth mentioning that even at the end of the phase 1, the release kinetics of $K^+$ from the soil treated with 5% EGM500 biochar remain relatively important (19.5 mg $day^{-1}$), which is about 5- and 12-fold higher than the ones corresponding to the assays with 1% and 0% (control soil). These outcomes are



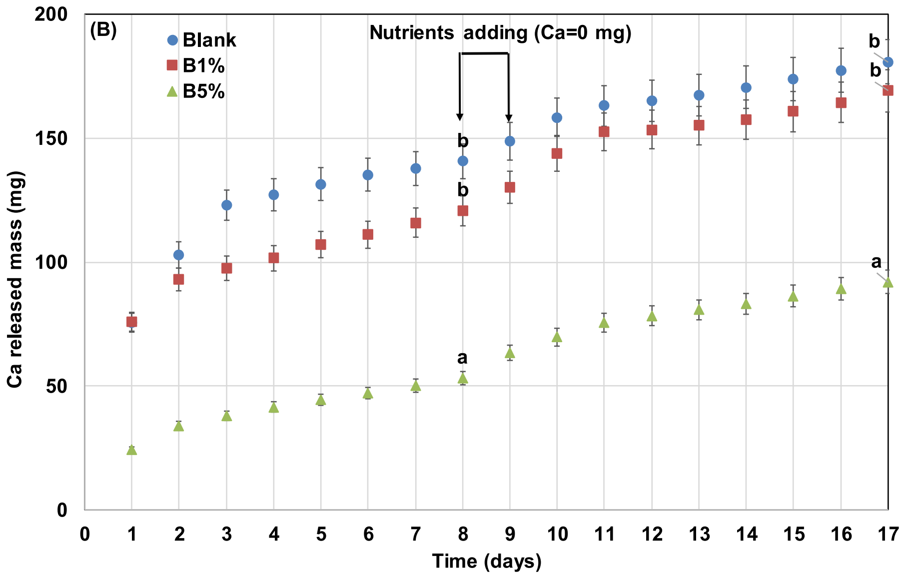




**Fig. 5.** Calcium (Ca) daily leached concentrations (A) and cumulated amounts (B) from the three soil treatments (0%, 1% and 5% EGM500 biochar) under dynamic conditions. At days 8 and 17, means of cumulated amounts with the same lowercase letters are not statistically different at $P \leq 0.05$.

mainly attributed to the high intrinsic content of K in the EGM500 biochar. These findings highlight the importance of using EGM500 biochar as an effective biofertilizer for agricultural soils. Indeed, the leached K concentrations are so much higher than those observed for biochars derived from several lignocellulosic biomasses such as trunks and branches of Fabaceae tree species (Beusch et al., 2019), waste willow wood (Agegnehu et al., 2015), rice husk, wood, coconut shell (Widowati et al., 2014), and also sewage sludge (Yuan et al., 2016).

For the second leaching phase, a significant increase of K leaching was observed for all soil treatments (Fig. 7). At the end of this phase, the cumulated amounts of leached K were much higher than the input of the synthetic solution (9.2 mg). Eventually, these amounts were about 17.9, 4.1 and 1.9-fold higher than the added K mass of the synthetic solutions for treatments 5%, 1% and 0% biochar, respectively (Table 4). This proves that K retention by the agricultural soil as well as by the added biochar was negligible. Moreover, the higher is the biochar rate in the soil, the most important is the leached $K^+$ amounts. Consequently, the leached K from the 5% biochar treatment during this second phase (164.7 mg) was about 847% and 333% higher than those leached by the agricultural soil and that amended with 1% biochar, respectively. This proves that, similarly to the current batch assays, $K^+$ ions are easily leachable from EGM biochars, which could be

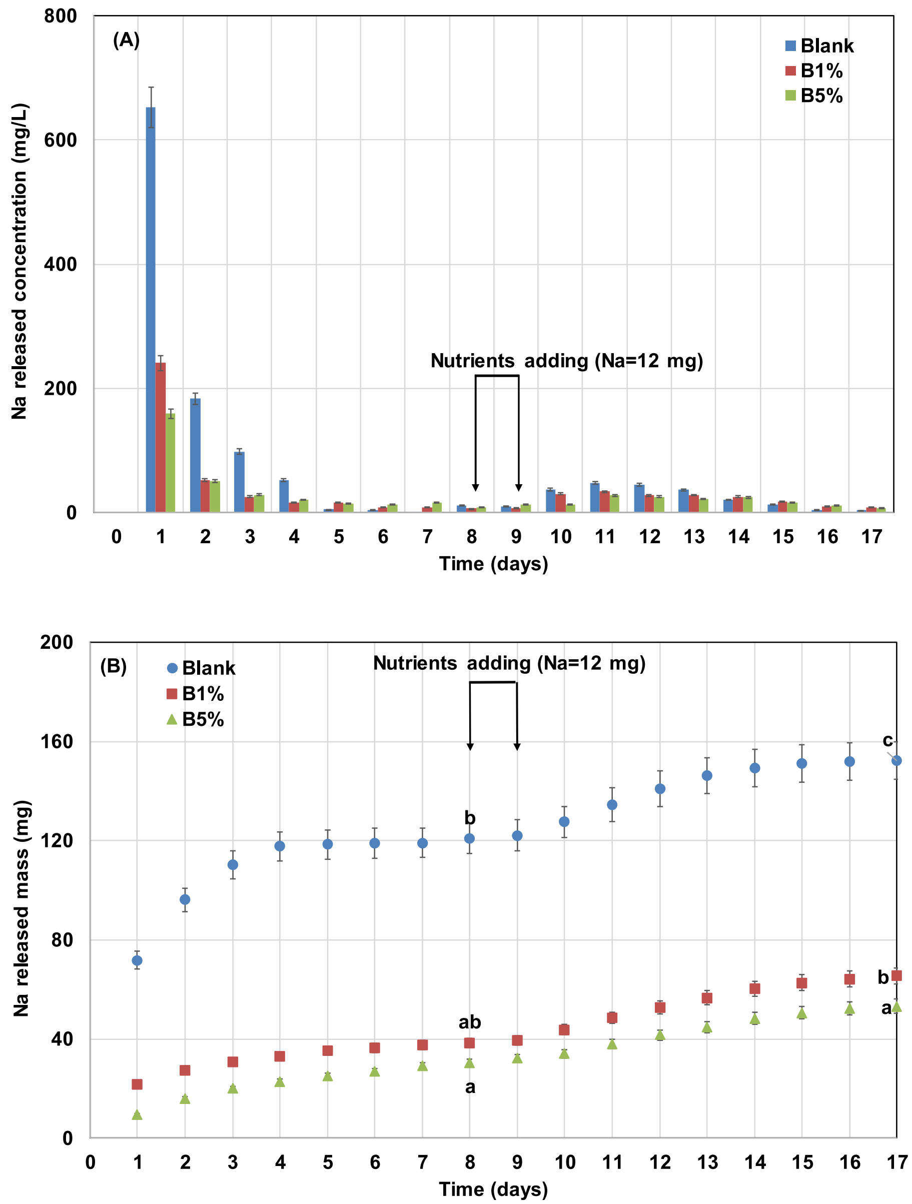
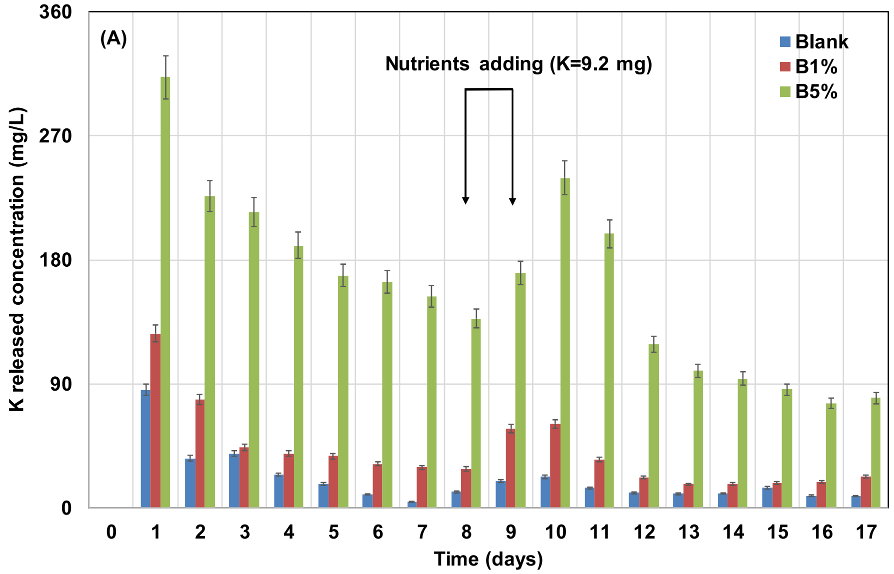



**Fig. 6.** Sodium (Na) daily leached concentrations (A) and cumulated amounts (B) from the three soil treatments (0%, 1% and 5% EGM500 biochar) under dynamic conditions. At days 8 and 17, means of cumulated amounts with the same lowercase letters are not statistically different at $P \leq 0.05$.

considered as an interesting supplementary source of nutrients. Furthermore, the $K^+$ release rate was very slow, since even after 18 days, it continued to be released at relatively high rates: 3.2 and 11.4 mg day$^{-1}$ for 1% and 5% biochar in soil respectively (Fig. 7-B). This property is an important asset for plant growth and yield as well as for the preservation of groundwater resources against pollution.

Similar trends were reported by Widowati et al. (2014) when they investigated the leaching and uptake of nitrogen and potassium from a potted degraded soil cultivated with maize and amended with biochars derived from various lignocellulosic biomasses (rice husk, wood, coconut shell) at increasing doses (0, 15, 30 and 45 t ha$^{-1}$). They showed that coconut shell biochar provided the highest concentrations of leached K due to its high initial content in this element (2.0 and 5.1 times higher than the wood and rice husk, respectively). Furthermore, leached K concentrations were significantly correlated with biochar dose in the soil (Widowati et al., 2014). Moreover, Novak et al. (2009) studied the impact of adding pecan shell biochar (2%) to a Norfolk loamy soil in PVC columns for 67 days and recorded an increase of K by about 478%. It is important to underline that depending on the used biochar type and/or soil conditions, other studies have reported no significant effect on K leaching (Beusch et al., 2019) or even a leaching reduction after biochar amendments



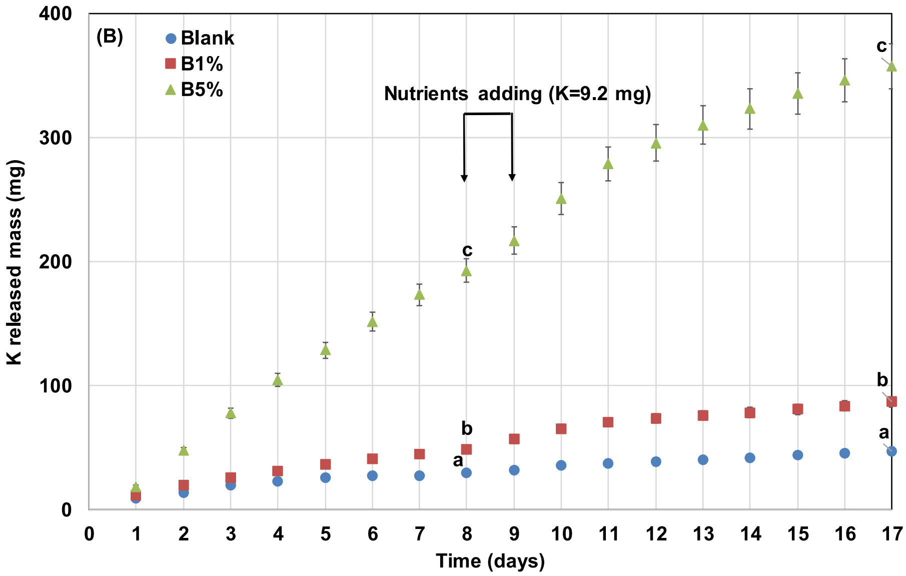




**Fig. 7.** Potassium (K) daily leached concentrations (A) and cumulated amounts (B) from the three soil treatments (0%, 1% and 5% EGM500 biochar) under dynamic conditions. At days 8 and 17, means of cumulated amounts with the same lowercase letters are not statistically different at $P \leq 0.05$.

(Agegnehu et al., 2015). This could be imputed to the relatively high specific surface area, the developed porous structure, and negative surface charge of their used biochars that had probably favored K sorption (Jellali et al., 2016). These discrepancies could be also due to the experimental conditions such as the used column dimensions, water leaching volumes and application rates of biochar.

The relatively high K leached concentrations and amounts and its low adsorption by the used agricultural soil confirms that the use of a dose of 5% of EGM500 as an amendment for alkaline agricultural soils results in important water-soluble and plant-available K ions. Therefore, EGM biochar will constitute an attractive supplementary source for plants growth. This biochar application will reduce the use of chemical fertilizers and the related environmental risks as well as the economic burden on farmers.

## 4. Conclusions

The main purpose of this study was to assess the possible valorization of exhausted grape marc (EGM) biochars as agricultural amendments through nutrient leaching experiments at lab-scale. Outcomes showed that like animal waste feedstock, the increase of pyrolysis temperature converts the contained P in the EGM into a stable phase due to its possible complexation with calcium and/or magnesium. In contrast, K, Na and Ca are converted into a more leachable and plant available forms. Furthermore, the experimental results indicated that these type of biochars could be considered as slow-release fertilizers since significant concentrations of K, P and Ca continued to be released from amended soils with significant rates even after relatively long periods. This property is very interesting for both plant efficient nutrition and environment protection. Further investigation is needed at field-scale in order to evaluate the impact of EGM biochar under realistic pedo-climatic conditions.

## CRediT authorship contribution statement

**Amel Ibn Ferjani:** Investigation, Visualization. **Salah Jellali:** Conceptualization, Methodology, Validation, Investigation, Resources, Writing - original draft, Visualization, Supervision, Funding acquisition. **Hanene Akrout:** Conceptualization, Methodology. **Lionel Limousy:** Conceptualization, Methodology, Supervision. **Helmi Hamdi:** Formal analysis, Validation, Writing - review & editing. **Nicolas Thevenin:** Conceptualization, Methodology. **Mejdi Jeguirim:** Conceptualization, Methodology, Validation, Resources, Writing - review & editing, Visualization, Supervision, Funding acquisition.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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