Reactivity towards Na of biochars produced from date palm residues with different oxygen proportions during pyrolysis

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Reactivity towards Na of biochars produced from date palm residues with different oxygen proportions during pyrolysis

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Abstract. The use of biochar produced from the rachis of date palm leaves could help fight soil salinization while using under-utilized crop residues. To improve the specific surface area of the biochars produced and therefore their adsorption capacity, the addition of oxygen (3 and 7%) during pyrolysis was tested. The amount of Na adsorbed was relatively low (between 15 and 20% of Na added) whatever are the biochar considered (produced with or without O_2). The release of this adsorbed Na in contact with water was quite important, from 100% for the lowest concentrations of Na added to 30-40% for the highest concentrations added, highlighting a low retention of Na by the biochars studied and a limited impact of the presence of O_2 during pyrolysis.

1. Introduction

Date palm cultivation is one of the main agricultural production systems in the dry areas of North Africa and Middle east (Younis et al. 2023). It generates a high amount of residues (Sizirici et al. 2021) which are currently poorly valorised. In these regions, salinization is one of the main causes of soil degradation. It is notably due to poor-quality irrigation water and high evaporation (Kavvadias et al. 2024). To limit this impact, organic amendments like biochars can be used to adsorb sodium due to their high cation exchange capacity (Ippolito et al. 2020). The properties of biochar are recognized to be mainly influenced by feedstock type and pyrolysis temperature (Usman et al. 2015). The composition of the pyrolysis atmosphere and especially the presence of O_2 is also recognized to influence the biochar properties with an increase of their mesoporosity (Li et al. 2019). A few studies (Rostamian et al. 2015; Nguyen et al. 2022) have been carried out on the capacity of biochars to retain sodium present in solution, but those studies did not focus on biochars derived from date palm residues and they did not study the release of the adsorbed sodium which can contribute to soil salinization.

The aim of this study was twofold: (i) to assess the capacity of biochars derived from date palm residues to retain and then release sodium and (ii) to study the impact of the presence of O_2 during pyrolysis on this retention/mobilisation.

2. Materials and methods

2.1 Biochar production

The residues that are used to produce biochar were the rachis of dry date palm leaves collected in Murcia region (Spain). The pyrolysis was performed at ENSTIB (Ecole Nationale Supérieure des

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Technologies et Industries du Bois, Épinal, France) in collaboration with LERMAB (Laboratoire d'Études et de Recherche sur le Matériau Bois, Lorraine University). The residues were first dried at 90 °C for 48 h. Pyrolysis time was 2 hours at 450 °C after pre-heating to 150 °C, with the temperature rising at a rate of 5 °C per minute up to 450 °C. Three different biochars were produced under N_2 flux with different proportions of O_2: 0, 3 and 7%, respectively BC0, BC3 and BC7. The biochars were ground to a size below 200 µm and then dried at 65 °C for 10 hours before use.

2.2 Biochar characterisation
Biochars were dried at 105 °C to remove water then placed in an oven at 550 °C for 8 h. After the loss on ignition step, 0.25 g of ash was mineralised with a mixture of HCl and HNO_3 (3.5 ml HCl 35% + 1.2 ml HNO_3 70% + 7 ml HNO_3 10%). The mineralisation step was performed in triplicate. After samples digestion, Ca, K, Mg and Na concentrations were measured using inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo Scientific). The physisorption of dinitrogen at 77 K was performed at Institute Jean Lamour (University of Lorraine) on the biochars <200 µm using Micromeritics ASAP2020 adsorption apparatus. The samples were outgassed for 12 h at 350 °C before analysis. The specific surface area (SSA) was calculated using the Brunauer-Emmett-Teller (BET) method, completed with the Rouquerol correction.

2.3 Rinse / Adsorption / Desorption experiments
To avoid the release of Na present in the biochar during the adsorption/desorption experiments, duplicate samples of each biochar were rinsed until the amount of Na released was considered negligible. The rinses were performed with 10 g of biochar mixed with 200 mL of ultrapure water and shaken for 4 hours. The suspension was then centrifuged for 30 minutes at 3500 rpm, after which around 150 mL of supernatant was removed and for the next rinse, 150 mL of ultrapure water was added, then the same protocol was repeated. Five rinses were performed. Finally, the biochar samples were dried in an oven at 65 °C.

The rinsed biochars were used for the adsorption experiments performed in triplicate. For each experiment, 0.75 g of biochar was added to 30 mL of NaCl solution. Five Na concentrations were used: 45, 175, 350, 700 and 1300 $mgNa.L^{-1}$. A control experiment was also carried out without the addition of Na to estimate the release of Na under the conditions of the adsorption experiments. The suspensions were shaken for 24 h and then filtered using a vacuum pump with 0.7 µm glass fibre filters. The filtrates were collected for analyses. The biochars were dried in an oven at 65 °C and then used for the desorption experiments.

The desorption experiments were performed for the 3 biochars, on the triplicates on which the adsorption experiments were conducted. For that, 0.5 g of dried biochar was added to 20 mL of ultrapure water. The protocol was similar to the one followed for the adsorption experiments with shaking for 24 h, then filtration.

The concentrations of Ca, K, Mg and Na were analysed in the filtrates obtained after the adsorption experiments, using ICP-OES. The pH values were measured in the filtrates after the adsorption experiments. They were 8.36 ± 0.02 for BC0 and of 8.69 ± 0.05 for BC3 and BC7 whatever the NaCl concentration used.

2.4 Statistical analyses
Statistical analyses were conducted to test the effect of biochar type on biochar properties and measured parameters, using one-way analysis of variance in R (version 4.3.1). Post-hoc comparisons were made using the LSD test to identify differences among biochar types.

3. Results and discussion

3.1 Biochar characterisation

The three biochars have basic pH, with a mean value of 9.6 as observed previously by Sizirici et al. (2021) with a pH slightly lower for BC0 compared to BC3 and BC7. The SSA measurements evidenced an increase in the SSA with the increasing quantity of O_2 during pyrolysis, results in agreement with previous observations. Zhu et al. (2018) worked at 700°C with an air flux during thermal treatment ranging from 0 to 90 ml/min which corresponds to O_2 proportions of around 0 to 6%. They demonstrated an increase in the volume of mesoporosity and the value of the SSA with the presence of O_2 between 0 and approximately 3-4%. Amounts of O_2 above 3-4% no longer increased the SSA of biochars.

Table 1. Biochars characterisation

	pH (1st rinse)	Specific surface area ($m^2.g^{-1}$)	Total Ca $g.kg^{-1}$	Total K $g.kg^{-1}$	Total Mg $g.kg^{-1}$	Total Na $g.kg^{-1}$
BC0	8.5	13.5	26.8+/-0.4	26.0+/-0.9	12.6+/-0.2	2.80+/-0.01
BC3	10.1	32.4	17.2+/-0.3	22.8+/-0.4	9.8+/-0.1	1.46+/-0.03
BC7	10.1	73.2	21.2+/-0.2	21.8+/-0.3	11.0+/-0.1	1.29+/-0.00

Total Ca, K, Mg and Na concentrations are higher in BC0 than in BC3 and BC7, with K and Ca concentrations being the highest whatever the biochar considered. To our knowledge, the few studies that have looked at the impact of the presence of O_2 during pyrolysis on the properties of the biochars produced have not worked with date palm residues and have not looked at the impact on the chemical composition of the biochars. The total concentrations measured in this study are of the same order of magnitude as those measured by Usman et al. (2015) working on biochars derived from date palm residues. The main difference is the calcium concentrations, which are twice higher in their study for biochars produced at 400 and 500 °C. Awan et al (2021) studied the chemical composition of four biochars of different origins (wheat straw, lodge pine, Kentucky bluegrass and hemp stalks) and highlighted a significant variability of their composition, with Ca concentrations varying from 0.5 to 17.9 $g.kg^{-1}$, K from 2.2 to 24.2 $g.kg^{-1}$, Mg from 2.5 to 8.2 $g.kg^{-1}$ and Na from 0.3 to 26.1 $g.kg^{-1}$, depending on the nature of the feedstock. The results obtained in this study for Ca, K and Mg are higher than or correspond to the high values of variability presented in the article of Awan et al. (2021). Ippolito et al. (2020) have shown in their review that the chemical composition of biochars is highly variable and is mainly influenced by the feedstock used.

3.2 Biochar rinse

Only the results of the 1st rinse are shown in Figure 1, highlighting a difference between the 3 biochars. The biochar produced in the absence of oxygen (BC0) has the highest levels of Ca, K, Mg and Na in the rinse water which is linked to the higher total content of these 4 elements in this biochar. Figure 1b shows that the proportions extracted are slightly higher for BC0 compared to

BC3 and BC7 for Ca, Mg and K. Whatever the biochar considered, the most abundant element in rinse water was K.

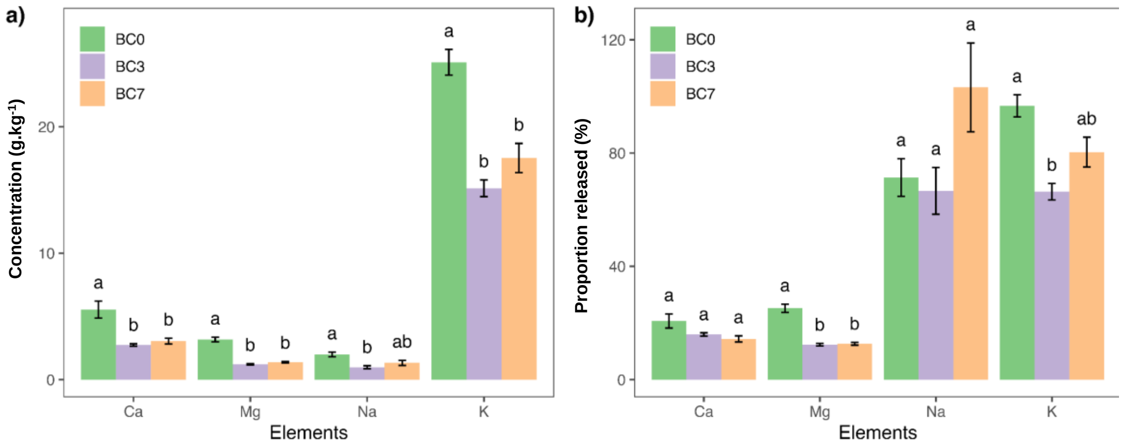

Figure 1. Concentrations measured in the solution of the 1st rinse expressed in $g.kg^{-1}$ of biochar (a) and as a percentage of total concentrations (b). Bars indicate standard deviation of two replicates. Different letters indicate statistically significant differences between biochar types, as determined by the LSD test at $p < 0.05$.

Md Som et al. (2012) worked with biochar produced from palm fronds of oil palm tree. They observed the same trends, with K levels much higher than Ca, Mg and Na levels. Figure 1b evidenced that the four elements studied behave differently during rinsing. Between 60% and 100% of Na and K were extracted during the 1st rinse, whereas only between 10 and 20% of Ca and Mg were extracted. These two divalent cations were therefore more strongly retained within the biochar than the monovalent cations K and Na, which were released as soon as they came into contact with water.

These results showed that the addition of biochar produced from date palm residues to the soil could lead to a significant release of cations into the soil when in contact with water. Nguyen et al. (2022) reached the same conclusion for biochars produced from rice husk, corn stalks, longan branches and coconut coir. They recommended rinsing biochars before applying them to the soil. The release of significant quantities of cations could pose a problem in soils already affected by salinization processes.

Concentrations in the rinse water decreased with each rinse, reaching an average of 0.073 ± 0.019 $g.kg^{-1}$ of biochar for Na at the 5th rinse for the 3 biochars studied. This concentration is considered sufficiently low compared to the concentrations of Na added for the adsorption experiments (levels between 1.83 and 52.7 $g.kg^{-1}$).

3.3 Na adsorption

The adsorption experiments were carried out with 5 different concentrations of Na ranging from 45mg.L^{-1} to 1300mg.L^{-1}. Despite rinsing, significant concentrations of Na were measured in the control experiment (between 0.2 and 0.4 $g.kg^{-1}$). These concentrations were taken into account when calculating the quantity of Na adsorbed. The concentration of adsorbed Na corresponds to the concentration of added Na minus the concentration of Na measured in the solution after 24 hours of agitation corrected for the concentration measured in the control experiments (without Na). The amount of Na adsorbed on the three biochars increased with the concentration of Na in the solution (Figure 2a), but the proportion of adsorbed Na calculated in relation to the total amount of Na added remained more or less constant at around 15-20%.

A fairly high variability in Na concentrations adsorbed on BC0 is observed, compared with the other two biochars. Nevertheless, according to statistical tests, for the lowest Na concentrations in solution (45 and 175 mg.L^{-1}), the quantities adsorbed on BC0 are significantly lower than for BC3 and BC7. The increase in SSA with increasing oxygen content could explain these lower adsorbed quantities for BC0, but a difference between the quantities adsorbed on BC3 and BC7 should be observed, which is not the case in our experiments. Li et al. (2019) demonstrated a significant increase (approximately a factor of 10) in tetracycline adsorption with the addition of O_2, rising from 0% to 4% of O_2 present during pyrolysis, linked to the increase in SSA. However, SSA is not the only parameter governing Na retention, other parameters should also be studied, including porosity size and surface functional groups (Nguyen et al. 2022).

In these experiments, a steady increase in the quantity adsorbed as a function of the quantities added was observed without reaching a plateau (figure 2a). These experiments therefore do not allow us to define the maximum quantity of Na that the biochars can adsorb. The quantity adsorbed for the highest concentration of Na added (1300mg.L^{-1}) was 6.7 g.kg^{-1} for BC0, 9.0 g.kg^{-1} for BC3 and 8.7 g.kg^{-1} for BC7.

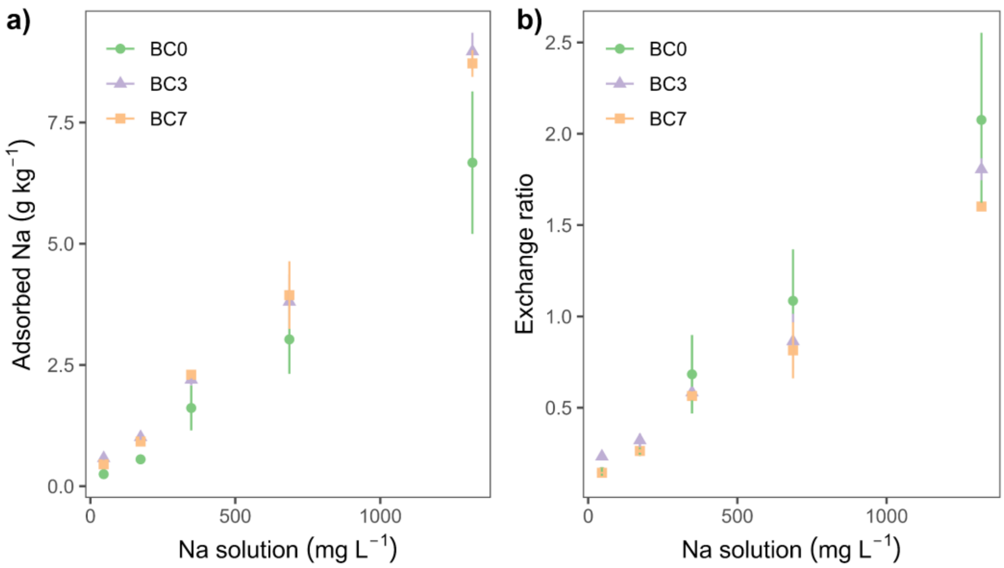

Figure 2. Concentrations of Na adsorbed on the biochars expressed in g.kg^{-1} of biochar (a) and exchange ratios calculated between adsorbed Na and total released Ca, K and Mg (b) Bars indicate standard deviation of three replicates.

These results are comparable with those obtained by Nguyen et al (2022). In their study, for a Na content in solution of 1438 mg.L^{-1}, close to our high point at 1300 mg.L^{-1}, the quantities adsorbed varied between 5 and 25 g.kg^{-1} depending on the biochar considered (different feedstocks were used). Rastamian et al. (2015) worked on chemically activated biochar (rice husk as feedstock), and therefore obtained higher adsorbed quantities (for a Na concentration in solution of 1400 mg.L^{-1}, adsorbed Na was 15 g.kg^{-1}) than those obtained in this work. The quantities of Na adsorbed on biochar are thus of the same order of magnitude in the few studies that have been carried out. They depend on the feedstock used and the conditions under which the biochar is produced.

With increasing Na concentrations in solution, and thus increasing concentrations of adsorbed Na, an increase in Ca, K and Mg concentrations was observed in solution (data not shown). These elements are therefore released during Na adsorption suggesting an exchange between Na and the three cations. Exchange ratios (Figure 2b) were calculated as the ratio between the concentration of Na adsorbed and the sum of the concentrations of Ca, K and Mg released. A ratio of less than 1 means that the quantity of Na adsorbed is less than the quantity of Ca, K and Mg released, so there is an exchange of ions but also a release of Ca, K and Mg linked to the contact of the biochar with water. A ratio greater than 1 means that the amount of Na adsorbed is higher than the amount of Ca, K and Mg released, so Na is adsorbed by ion exchange but also via another process. An increase in the exchange ratio is observed with increasing Na concentrations in solution, with a ratio well above 1 only for the highest Na concentration in solution (1300 mg.L^{-1}). The same trend was observed in the study of Nguyen et al. (2022) and the ratios obtained were comparable in both studies. At similar concentration of Na in solution (around 1300-1400 mg.L-1), the ratio calculated is between 1.6 and 2.1 for the three biochars of this study and is between 0.2 and 4.2 for the biochars studied in Nguyen et al. (2022). The same processes are therefore involved in the adsorption of Na on these biochars prepared with different feedstocks and under different conditions with, as suggested by Nguyen et al. (2022), a combination of ion exchange and physical adsorption.

3.4 Na desorption

The desorption experiments were carried out after the adsorption experiments on the samples spiked with 5 concentrations of Na ranging from 45 mg.L^{-1} to 1300 mg.L^{-1} as well as on control experiment.

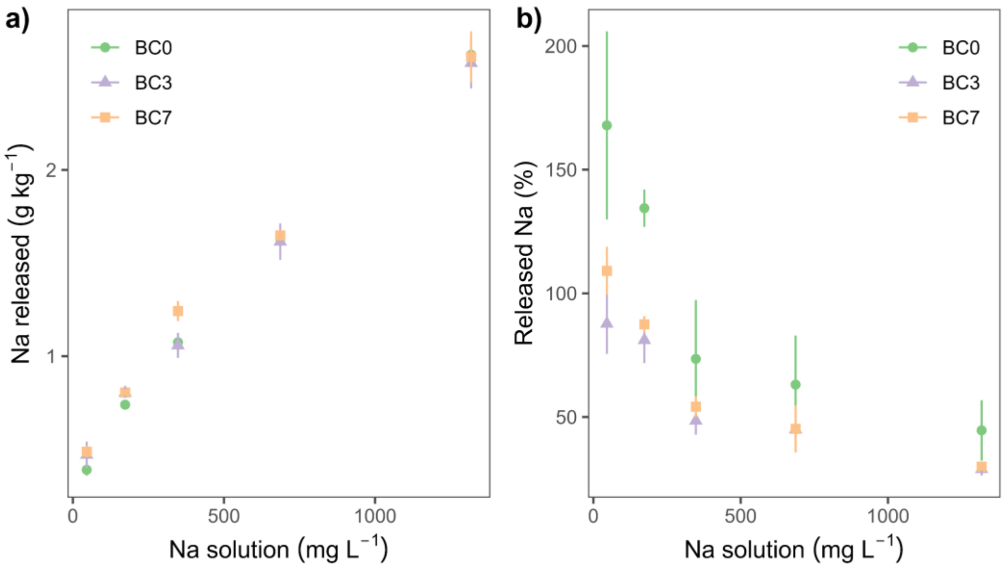

Figure 3. Concentrations of Na released during desorption experiments as a function of Na concentrations added for adsorption experiments expressed in g.kg^{-1} of biochar (a) and as a percentage of Na concentration adsorbed (b). Bars indicate standard deviation of three replicates.

The amount of Na desorbed increase with increasing Na concentrations added and therefore with the increase in Na concentrations adsorbed (Figure 3a). However, the proportion of desorbed Na relative to the quantity adsorbed decreased with increasing added concentrations (Figure 3b). The proportions of Na desorbed decreased from 158 to 39% of the Na adsorbed for BC0 and from an average of 95 to 29% for BC3 and BC7 with the increase of Na concentration in solution. The proportions of Na desorbed are quite high for the three biochars, which seems consistent with the proposed sorption processes i.e. ion exchange and physical adsorption. Based on statistical tests, in just one experiment, the one with Na concentrations in solution of 175mg.L^{-1}, the desorbed Na content is significantly lower and the proportion desorbed significantly higher, for BC0 than for the other two biochars. For all other points, no significant difference was observed. For the lowest concentrations of Na added (45 and 175 mg.L^{-1}), the quantities desorbed for BC0 were greater than the quantities adsorbed. So, despite 5 successive rinses and adsorption experiments, there was still a release of sodium initially present in the biochars.

To our knowledge, no comparable work has been published on the desorption of Na adsorbed on biochar. Gong et al. (2019) worked on biochar produced from rice straw at different temperatures and highlighted very different desorption rate depending on the element considered (NH_4, K, P).

4. Conclusions

This study revealed a significant release of Ca, K, Mg and Na when the biochars were in contact with water. Five rinses were necessary to stabilise these releases, which nevertheless remained non negligible. The proportions of Na adsorbed on the 3 biochars studied were of the order of 15-20%, i.e. fairly low, whatever the added Na content, and the proportions of Na desorbed in contact with water were high. These results therefore highlight the low retention of Na by the biochars studied. The biochar produced without O_2 (BC0) appeared to retain the least Na, but the differences between the 3 biochars were small, and the impact of the presence of O_2 during pyrolysis on Na adsorption is not very marked. Other studies should be carried out with biochars produced at different temperatures or from different feedstocks to assess their ability to limit soil salinisation.

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