



A re-analysis of NH_4^+ sorption on biochar: Have expectations been too high?

Simon Weldon^{a,b,*}, Bert van der Veen^c, Eva Farkas^b, Nazlı Pelin Kocatürk-Schumacher^{b,d}, Alba Dieguez-Alonso^e, Alice Budai^b, Daniel Rasse^b

^a Faculty of Environmental Sciences and Natural Resource Management, Norwegian University of Life Sciences, NMBU, 1430 Ås, Norway

^b Norwegian Institute of Bioeconomy Research (NIBIO), Division of Environment and Natural Resources, Høgskoleveien 7, 1432 Ås, Norway

^c Norwegian Institute of Bioeconomy Research (NIBIO), Division Food Production and Society, Høgskoleveien 7, 1432 Ås, Norway

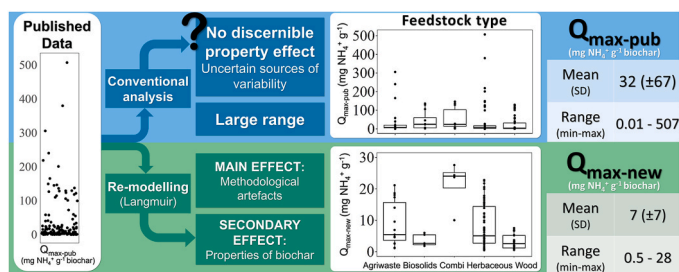
^d Faculty of Science and Technology (REALTEK), Norwegian University of Life Sciences (NMBU), 1432 Ås, Norway

^e Institute of Fluid Dynamics and Thermodynamics, Faculty of Process and Systems Engineering, Otto-von-Guericke University Magdeburg, Universitätsplatz 2, DE-39106, Magdeburg, Germany

HIGHLIGHTS

- NH_4^+ sorption capacity of biochar highly variable in literature.
- Re-analysis showed analytical methods as key source of variability.
- NH_4^+ sorption capacity of biochar is more limited than previously believed.
- Modification of biochar results in modest absolute increases in sorption capacity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Handling Editor: Grzegorz Lisak

Keywords:

Biochar
Ammonium
Sorption capacity
Langmuir
Cation Exchange Capacity

ABSTRACT

Sorption of nutrients such as NH_4^+ is often quoted as a critical property of biochar, explaining its value as a soil amendment and a filter material. However, published values for NH_4^+ sorption to biochar vary by more than 3 orders of magnitude, without consensus as to the source of this variability. This lack of understanding greatly limits our ability to use quantitative sorption measurements towards product design. Here, our objective was to conduct a quantitative analysis of the sources of variability, and infer which biochar traits are more favourable to high sorption capacity. To do so, we conducted a standardized remodelling exercise of published batch sorption studies using Langmuir sorption isotherm. We excluded studies presenting datasets that either could not be reconciled with the standard Langmuir sorption isotherm or generated clear outliers. Our analysis indicates that the magnitude of sorption capacity of unmodified biochar for NH_4^+ is lower than previously reported, with a median of $4.2 \text{ mg NH}_4^+ \text{ g}^{-1}$ and a maximum reported sorption capacity of $22.8 \text{ mg NH}_4^+ \text{ g}^{-1}$. Activation resulted in a significant relative improvement in sorption capacity, but absolute improvements remain modest, with a maximum reported sorption of $27.56 \text{ mg NH}_4^+ \text{ g}^{-1}$ for an activated biochar. Methodology appeared to substantially impact sorption estimates, especially practices such as pH control of batch sorption solution and ash

Abbreviations: CEC, Cation Exchange Capacity; HTT, Highest Treatment Temperature; Agri. Waste, Agro-industrial waste; Combi, Biochar mix with other feedstock, minerals or organic compounds; N, Nitrogen; C.I., Confidence Intervals; GLM, Generalised Linear Model; GLMM, Generalised Linear Mixed Model.

* Corresponding author. Norwegian Institute of Bioeconomy Research (NIBIO), Division of Environment and Natural Resources, Høgskoleveien 7, 1432 Ås, Norway.

E-mail address: simon.weldon@nibio.no (S. Weldon).

<https://doi.org/10.1016/j.chemosphere.2022.134662>

Received 22 December 2021; Received in revised form 8 April 2022; Accepted 17 April 2022

Available online 18 April 2022

0045-6535/© 2022 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

removal. Our results highlight some significant challenges in the quantification of NH_4^+ sorption by biochar and our curated data set provides a potentially valuable scale against which future estimates can be assessed.

1. Introduction

Biochar has received significant attention in the last 20 years as a tool to mitigate climate change and as a green technology to valorise waste products for utility in agriculture and waste management. The study of the *Terra Preta* in the Amazonas has been a driving force behind the current interest in biochar (Lehmann, 2007). The high content of pyrogenic C and the high nutrient holding capacity of these soils has raised hope that biochar application to soil could deliver similar benefits over short timescales (Glaser et al., 2001, 2015). Biochar has been recommended as a tool to both reduce N loss in soils (Al-Wabel et al., 2018) and as media in waste reclamation to stabilise and recover waste N (Huang et al., 2018). Based on its ability to retain nutrients, biochar has also been studied as a component in compound fertilisers (Dong et al., 2019).

With respect to mineral N retention on biochar, evidence suggests that biochar is a better sorbent for NH_4^+ than NO_3^- (Zhang et al., 2020; Jellali et al., 2022). This is because biochar has a net negative charge at agriculturally relevant pH (>6) and is therefore more suited for the retention of cations such as NH_4^+ . Ammonium is a highly important mineral N form, notably because it is generally the most abundant N compound found in organic wastes such as manure (Portejoie et al., 2004; Montégut et al., 2016). Both the retention capacity and the retention mechanism of biochar for NH_4^+ are of critical importance to the efficacy of biochar products. High capacity sorbents are required to recover and recycle waste NH_4^+ and deliver it to plants in a bio-available form. It is therefore crucial to better understand the key drivers of the sorption capacity of biochar for NH_4^+ , as exemplified by the numerous studies dedicated to this research (Zhang et al., 2020).

Variability in the estimations for the sorption capacity of biochar for NH_4^+ appears extremely high, with published values ranging from 0.01 mg g^{-1} to 518.9 mg g^{-1} . In a review of literature values Zhang et al. (2020) reported an average sorption capacity of 14 and 29 $\text{mg NH}_4^+ \text{g}^{-1}$ biochar for a non-activated and activated biochar respectively. Several reviews have concluded, based on average values, that the sorption capacity of biochar for NH_4^+ is limited (Zhang et al., 2020; Jellali et al., 2022; Rasse et al., 2022). However, biochar has been proposed as a competitive tool for NH_4^+ recovery in waste water treatment based on exceptionally high values reported in the literature (Huang et al., 2018). A logical hypothesis is that it should be possible to link reported high values to specific biochar properties through meta-analysis of the existing literature. However, this does not appear to be the case, as meta-analyses and reviews have failed so far to demonstrate a relationship between sorption capacity for NH_4^+ and biochar production conditions or feedstock (Jellali et al., 2022; Rasse et al., 2022). This lack of positive relationship is potentially due to the diversity of biochar types as well as to differences in the methodologies applied to estimate sorption capacity (Jellali et al., 2022; Rasse et al., 2022). Sorption estimates are known to be influenced by both laboratory methods (Volesky, 2007) and mathematical approaches for modelling the sorption behaviour (Barrow, 2008). In addition, methodological artefacts easily affect estimates of sorption values of solutes to solids (Barrow, 2008; Foo and Hameed, 2010; Tran et al., 2017; Al-Ghouti and Da'ana, 2020; Cherkasov, 2020). All these elements have the potential to confound the interpretation of sorption capacity across studies.

Meta-analysis approaches conventionally deal with high data variability through the use of response ratios, which hinders determination of effect size across studies. Conversely, review often fails to deal with the diversity of methodological approaches underpinning the estimated mean responses. These considerations suggest that understanding the source of variability for biochar NH_4^+ sorption requires to go beyond

meta-analyses and passive reviews of final sorption parameters, and consider the collection and analysis of data in the reporting studies. A reanalysis of published data requires a standard approach, which might only be applicable to a subset of the diversity of biochar NH_4^+ sorption studies.

Because sorption data can be biased both by methodology and the mathematical approach to determining the coefficients, the source of variability can be better assessed and analysed through applying a single standardised methodology on published data. A common approach to the determination of biochar sorption capacity is the application of Langmuir isotherms to measurements derived by batch sorption experiments (Rasse et al., 2022). The Langmuir isotherm is a theoretical model applied to experimental data and it is often used because it provides an estimate for the theoretical maximum sorption capacity of a sorbent. Based on Langmuir remodelling of published datasets, the objective of the present study was to conduct a quantitative analysis of the source of variability for biochar NH_4^+ sorption, and, if possible, infer which biochar traits are more favourable to high sorption capacity of NH_4^+ on biochar.

2. Methodology

2.1. Choice of approach

To understand the relationship between biochar properties and sorption capacity for NH_4^+ , we first needed to develop a constrained dataset of estimates for the maximum sorption potential of biochar.

Although there are several methods for estimating the maximum sorption capacity of biochar for NH_4^+ the most commonly applied is the Langmuir isotherm. The fitting of the Langmuir isotherm requires multiple measurements spanning a range of sorbate concentrations. Since the estimation of the Langmuir coefficients require multiple measurements it is possible to derive an error in the estimate, which is a potentially valuable quality assessment tool. Here we focus specifically on the Langmuir coefficient Q_{max} which is an estimation of the theoretical maximum sorption capacity of a sorbent for a sorbate. The Langmuir model requires measurements that span saturation (Giles et al., 1960; Calvet, 1989; Barrow, 2008), so by definition, we excluded single-concentration studies where the theoretical maximum sorption cannot be ascertained. We also excluded isotherm studies that did not apply the Langmuir model because it potentially indicated that the datasets were not appropriate for such a modelling, e.g., due to an insufficient measurement range. The remodelling step was required in order to 1) standardise the approach for estimating the Langmuir coefficients and 2) provide a measure of uncertainty in order to quality check the estimates.

2.2. Data collection

Our literature search was conducted on the Web of Science with a cut-off date of February 2020 using the search terms: (batch sorption OR isotherm OR Langmuir OR Freundlich) AND (NH_4^+ OR ammonium) AND (biochar OR activated carbon OR pyrogenic carbon OR black carbon). We identified all studies where measurements used to estimate the Langmuir coefficients were provided (in graphic form) either in the main text or in supplementary information.

Remodelling was conducted according to the classical Langmuir approach to model isotherms (Giles et al., 1960). In short, a fixed amount of sorbent is subjected to increasing concentrations of sorbate in a solution, and the amount of adsorbed sorbate (q_e) is calculated according to Equation (1).

$$q_e = \frac{(C_0 - C_e)V}{M} \quad \text{Eq 1}$$

where C_0 (mg L^{-1}) is the initial concentration of the sorbate solution, C_e (mg L^{-1}) is the equilibrium concentration. V (L) is the solution volume and M (mg) is the mass of the sorbent. Isotherm models are plotted as a function of q_e (mg g^{-1}) versus C_e (mg L^{-1}), and we therefore excluded studies where q_e was plotted versus C_0 .

Relevant figures were captured from the reviewed literature as .jpg files and digitised manually using Engauge Digitizer (Mitchell et al., 2020). Units were standardised with q_e in $\text{mg NH}_4^+ \text{g}^{-1}$ biochar and C_e in $\text{mg NH}_4^+ \text{L}^{-1}$ solution.

2.3. Checking for consistency

We checked all studies for data and unit consistency. Following this consistency check, four studies were removed for reasons that include; lack of clarity regarding units, inconsistency between the re-estimated and the published coefficients and non-standard isotherms that resulted in large errors of the estimate (Table S2). This resulted in a quality-checked collection of 125 isotherms in 31 papers (Table S4).

2.4. Data re-modelling

We applied a standard non-linear modelling approach to estimate the Langmuir coefficients Q_{max} and K_L , which represent the theoretical maximum sorption capacity and the adsorption equilibrium constant, respectively (Eq 2). This non-linear modelling approach is preferred to the linearization of the Langmuir isotherm, which is commonly used to simplify coefficient estimation (Eq (3)).

$$q_e = \frac{Q_{\text{max}}K_L C_e}{(1 + K_L C_e)} \quad \text{Eq 2}$$

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_{\text{max}}} + \frac{C_e}{Q_{\text{max}}} \quad \text{Eq 3}$$

Linearization has been shown to introduce bias and therefore result in poor estimates (Barrow, 2008; Foo and Hameed, 2010; Tran et al., 2017; Al-Ghouti and Da'ana, 2020; Cherkasov, 2020). Our own tests on this dataset confirm that estimates derived by linear vs non-linear methods vary significantly (Fig S3 in Supplementary Information). Therefore, we used only the non-linear method for the purpose of this review.

We estimated the non-linear parameters using the *nls* function in the R-package *nls* (Pinheiro et al., 2021; R Core Team., 2021). We set a condition to accept only positive estimates for the coefficients on the basis that negative values for Q_{max} or K_L confound the theoretical assumptions of the Langmuir model. For the sake of clarity in the text, we distinguish between the previously published and our remodelled estimates for Q_{max} with the terms Q_{pub} and Q_{new} , respectively.

We assessed the fit of the isotherms using the standard error of the estimate. We removed all isotherm models where the standard error of the estimates was greater than the value of the estimate, for any of the coefficients. This resulted in the largest functional subset consisting of 116 isotherms in 29 studies (Table S4 in Supplementary Information).

2.5. Biochar properties

We aimed to model the effect of biochar properties on values of Q_{new} . Due to variability in the availability of the specific variables that were provided in the source articles, we performed the modelling on multiple subsets of the data (subsets defined in Table S4, Supplementary Information). The data sub-setting reduced the availability of data at each stage, which impacted the statistical power of our analysis. For this reason we have discussed all results in light of the consistent fixed effects at each stage of sub-setting. The variables included in the model fitting

are reported in Table S3 (Supplementary Information).

We chose source article to represent the apparent effect of study methodology on the response variable and applied this as a random effect. Because we aimed to understand how source article might influence the fit of the biochar parameters, we applied both a Generalised Linear Model (GLM) and Generalised Linear Mixed Model (GLMM), which allowed us to parametrise the model both with and without a random effect. In the fitting of both the GLMs and GLMMs, we chose a gamma distribution with log-link function. We performed model-selection using Akaike's information criterion adjusted for small sample sizes (AICc), and with the *MuMIn* R-package (Barton, 2020). We considered all models within 2 points AICc difference of the best fitting model as fitting the data equally well (Burnham and Anderson, 2002), and discuss the differences between those models in the results. We used the *glmmTMB* R-package (Brooks et al., 2017) to fit the models both with and without source article as a random effect.

3. Results and discussion

3.1. Spread of the values

Our remodelling and analysis of the 116 isotherms included in 29 studies showed that Q_{new} was lower than $20 \text{ mg NH}_4^+ \text{g}^{-1}$ biochar in the majority of studies (Fig. 1, Table S4). Despite our approach to data discrimination our final dataset contained outliers, represented by two studies consisting of 5 isotherms with Q_{new} values approximately 3–10 times the upper quartile of all measurements included in this study. One of the studies reporting these higher values (Fan et al., 2019), estimated a Q_{pub} of 95–116 mg g^{-1} for a commercially produced bamboo biochar

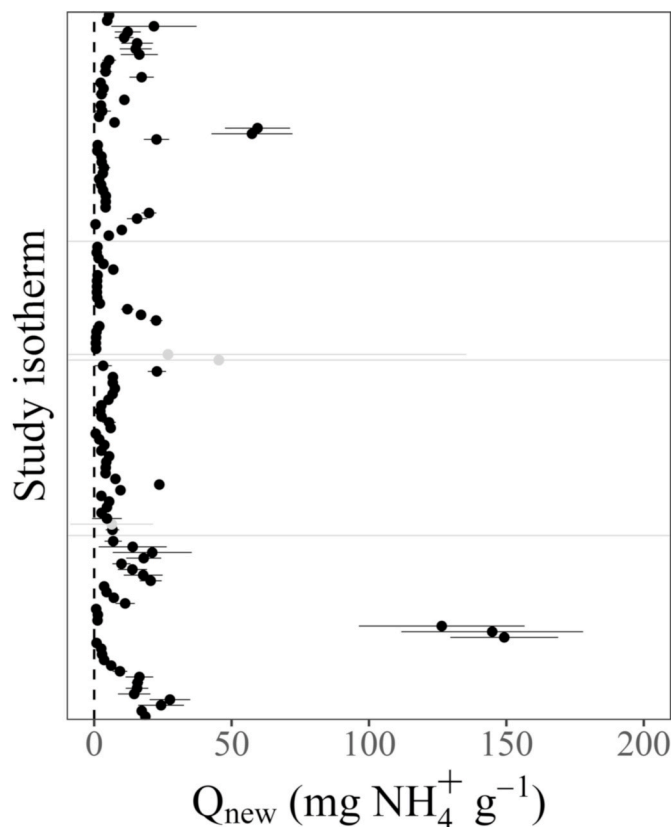


Fig. 1. Q_{new} ($\text{mg NH}_4^+ \text{g}^{-1}$ biochar) values for articles following data discrimination prior to removal of uncertain estimates (subset 2 – see Table S4 Supplementary Information). Each point is an estimate derived from fitting a Langmuir isotherm to data digitised from a single published isotherm. Bars represent 95% confidence intervals and grey colouring represent estimates where the standard error of the estimate was larger than the estimate.

at a highest treatment temperature (HTT) of 370 °C (solution pH was between 3 and 7). This was higher than the 6.8–22.8 mg g⁻¹ Q_{pub} range reported for a bamboo biochar produced at 450 °C HTT (solution pH 6) by Qin et al. (2019). The second outlier study (Yin et al., 2019), estimated Q_{pub} values for a non-activated poplar wood biochar that were approximately 10 times higher than the next two highest estimates for non-activated wood biochar, including a high temperature wood chip biochar (Hailegnaw et al., 2019) and a low temperature oak sawdust biochar (Wang et al., 2015c). Removal of these values from the dataset reduced the mean and standard deviation of the estimates and reduced the difference between the median and the mean (Table 1). We tested whether we could explain these high outlier values by modelling Q_{new} as a function of available biochar properties such as solution pH, activation, biochar HTT, or feedstock. However, inclusion of these outliers in a GLM resulted in a negative estimate for the pH effect on Q_{new} (GLM: Est.-0.05, C.I. -0.16 – 0.06 see Table S5a in Supplementary Information), which is unexpected considering the well documented positive correlation between pH and cation sorption (Fidel et al., 2018). Removing these 2 studies resulted in a positive correlation between pH and Q_{new} as well as a better fitting model (Table S5b in Supplementary Information). This observation supports removing these values from our analysis, but it does not preclude that other variables, not available for analysis, might explain these high values.

A previous quantitative review of the biochar sorption potential for NH₄⁺ estimated average values of 14 and 29 mg NH₄⁺ g⁻¹ biochar for non-activated and activated biochars, respectively (Zhang et al., 2020). In Rasse et al. (2022), the mean for non-activated biochars was 31.5 mg NH₄⁺ g⁻¹ biochar, which is 2 folds higher than the estimate by Zhang et al. (2020) for non-activated chars. The reason for this discrepancy was that the study by Rasse et al. (2022) included values excluded by Zhang et al. (2020) in their analysis. Rasse et al. (2022) identified that the response variable, Q_{max}, was skewed, which informed their decision to interpret the median as a more suitable measure of centre. Applying our current conservative approach, however, we find both a low median and mean estimate for our remodelled estimate of Q_{new} for both non-activated and activated char (Table 1), which reduced the degree of skew in the data, further highlighting the influence of the high estimates on the mean.

Our results suggest that the sorption potential of biochar is low even following activation (Table 1). However, we come to this conclusion because we raise doubts over a number of high estimates. While our study suggests that the most likely explanation for these high values are methodological issues, it is also possible that these chars represent exceptional biochar sorbents. For future studies, values outside the range we identify here should be scrutinised more closely to rule out methodological issues and identify biochars with exceptional sorption capacity.

3.2. Relationship between Q_{new} and biochar properties

To explain variations in Q_{new} we extracted the most consistently reported data that quantified biochar properties. This included specific surface area, specific pore volume, CEC, and elemental analysis. However, even for these important properties of the biochar, we found considerable variability in the frequency of reporting. For example, CEC

was quantified in only 8 of the 28 studies. Although specific pore volume and specific surface area were quantified by 12 studies consisting of 48 isotherms, measurements were conducted with two different methods, i. e. N₂ or CO₂ adsorption, which are known to quantify different pore sizes and therefore produce substantially different estimated values (Maziarka et al., 2021). The most consistently quantified biochar properties were the elemental contents of O, N, and C, quantified in 13 studies consisting of 72 isotherms. Taking advantage of this larger data pool, we chose to include the molar ratio (O + N):C as an explanatory variable. The molar ratio O:C is used frequently as a proxy for the abundance of polar functional groups on the surface of biochar (Al-Wabel et al., 2013; Budai et al., 2014). These functional groups are largely responsible for the CEC of biochar (Xiao et al., 2018; Hassan et al., 2020) making this variable a potentially valuable proxy for CEC.

While fitting the GLM we identified several outliers in the value (O + N):C that we traced back to isotherm measurements conducted on eggshell biochar that had an exceptionally high ash content (98% ± 0.5) (Xu et al., 2019). For this biochar type the interpretation of (O + N):C, as a proxy for negatively charged functional groups on a carbon matrix, is confounded by the abundance of mineral C and O in the ash component of this biochar. This observation highlights the potential confounding effect of mineral oxygen content of ash for the popular interpretation of the molar ratio (O + N):C.

We found that both pH (GLM: Est. 0.13, C.I. 0.00–0.25) and activation (GLM: Est. 0.91, C.I. 0.48–1.33) of the biochar had a positive relationship with Q_{new} in the model, while biochar HTT (GLM: Est. -0.001, C.I. -0.001 – 0.0001) had a negative relationship with Q_{new}. (Tables S5b, d, in Supplementary Information). We tested the effect of study methodology on our results by running the models both with and without source article as a random effect. Without a random effect, the variable feedstock appeared to be an important explanatory variable with Wood biochar resulting in significantly lower estimates for Q_{new} than Agri. Waste, Herbaceous, and Combi biochars in both data subsets (Fig. 2 & Table S5b,d in Supplementary Information). However, inclusion of source article as a random effect removes the effect of feedstock, highlighting that feedstock is often study specific. For example, only two studies in our dataset compare wood biochar with other feedstock types (Li et al., 2018; Xu et al., 2019).

Estimates for the effect of activation on Q_{new} were relatively large, positive, and consistent throughout all models (Table S5 b,c,d in Supplementary Information). The activation methods applied in the available literature can be loosely categorised based on 2 different approaches. Either, use of oxidants, in the form of acids (Boopathy et al., 2013; Wang et al., 2016; Zhu et al., 2016; Mia et al., 2017; Vu et al., 2017, 2018; Khalil et al., 2018), or combination of the biochar with minerals (Wang et al., 2015a; Ismajli et al., 2016; Chen et al., 2017; Gong et al., 2017; Chandra et al., 2020; Xiao et al., 2020). The largest estimates (Q_{new} > 20 mg g⁻¹) included 2 studies applying mineral treatments pre-pyrolysis (Ismajli et al., 2016; Chandra et al., 2020) and a single study applying a HNO₃ treatment post pyrolysis (Vu et al., 2017). Compared with the highest estimate for a non-activated char 22.8 mg NH₄⁺ g⁻¹ biochar (Qin et al., 2019), activation resulted in the highest overall estimate of Q_{new} at 27.6 mg NH₄⁺ g⁻¹ biochar (Xiao et al., 2020). However, the relatively small difference in Q_{new} between the best-performing modified and non-modified biochar show that

Table 1

Spread of remodelled sorption coefficients for maximum theoretical sorption capacity Q_{new} values (mg NH₄⁺ g⁻¹ biochar) summarised by quartiles, median and mean with standard deviation for activated and non-activated biochar. (Subset: 1 (top) and subset 2 (bottom), see Table S4 in Supplementary Information).

		Quantiles					Mean	(Sd)
		0%	25%	50%	75%	100%		
Including outliers (Source article n = 29; Isotherm n = 116)	activated	0.93	2.39	7.24	17.24	59.44	11.61	(12.24)
	not activated	0.49	2.59	4.22	10.96	149.23	11.77	(25.89)
Excluding outliers (Source article n = 27; Isotherm n = 111)	activated	0.93	2.06	6.96	17.04	27.56	9.96	(8.4)
	not activated	0.49	2.57	4.20	9.52	22.82	6.51	(5.92)

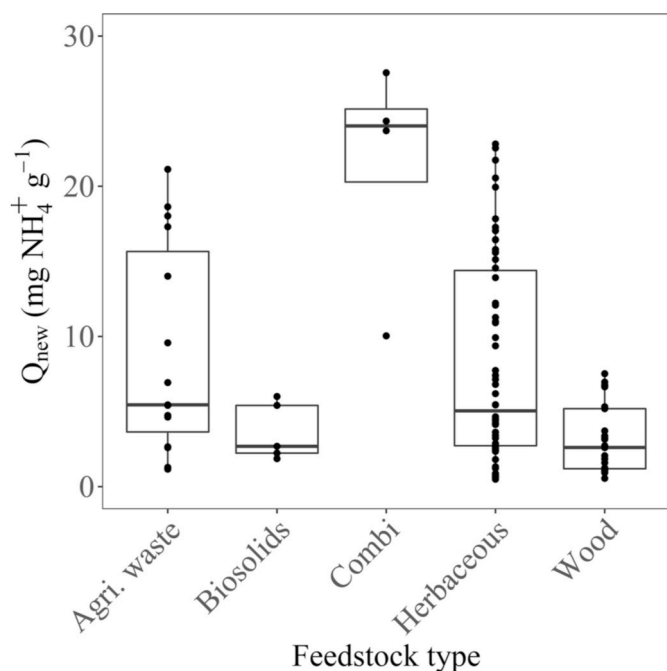


Fig. 2. Distribution of Q_{new} values by feedstock. Data are for non-activated biochar only. Based on data subset 4 (Table S4 in Supplementary Information) following discrimination process and after removal of outliers.

activating biochar may only provide relatively minor net benefits, potentially at the cost of a more expensive biochar production process.

We included solution pH in our modelling because sorption in solute systems is known to be pH dependent (Fidel et al., 2018). Similar to activation, the effect of solution pH was consistent and positive in all models (Table S5d in Supplementary Information). Although we identify a positive correlation between solution pH and Q_{new} , the effect of pH on $\text{NH}_4^+/\text{NH}_3$ speciation is known to result in reduced sorption at high pH due to the lower sorption affinity of NH_3 (Hu et al., 2020). However, our results show consistently higher estimates for Q_{new} in studies where solution pH was higher than the pK_b of ammonium (Fig. 3b), which may, at least partially, be attributed to ammonia volatilisation. NH_3 is an important component of N loss in agricultural systems (Sha et al., 2019). NH_3 volatilisation can result in substantial N losses at high pH, which are generally not quantified in sorption studies (Kizito et al., 2015; Wang et al., 2015b; Esfandbod et al., 2017). NH_3 can also chemisorb to biochar surfaces under ambient conditions forming amine groups (Hestrin et al., 2019). Both mechanisms may confound interpretation of the Langmuir

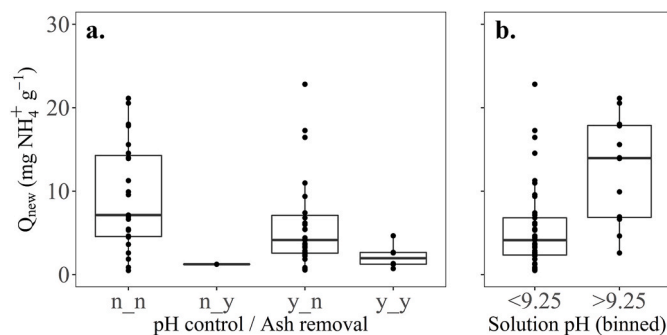


Fig. 3. a: Q_{new} as a function of pH control and ash removal excluding activated biochar. X axis labels denote groupings based on whether a study performed pH control of batch solutions (yes/no) and/or removed the ash from the biochar prior to sorption analysis (yes/no). b: Q_{new} as a function of solution pH that was binned to represent pH above and below the pK_b of ammonium (pH 9.25). Points in both figures show individual measurements.

isotherm where the assumption is that the change in concentration of the sorbate: 1) directly reflects the amount being sorbed on the biochar through conservation of N mass in the system, and 2) is a function of reversible sorption mechanisms on the surface of the biochar. The loss due to volatilisation, in particular, is not only a function of pH, but also of the salt content of the solution, solution temperature, and the equilibrium between the partial pressure of NH_3 in solution and in the immediate environment at the solution surface. This highlights how methodology can affect the interpretation of NH_4^+ isotherms, including the temperature of the solution, the type of vessel used (related to vessel headspace and closed vs open containers) and if the biochar ash was removed prior to sorption experiments or not.

Despite clear evidence that pH has implications for biochar sorption of NH_4^+ (Vu et al., 2018), we found a significant variability in the methodology applied towards pH control throughout the literature. Biochar is strongly alkaline due to both the predominantly negatively charged carbon surfaces and to the ash content (Fidel et al., 2017). Biochar ash, in particular, is a challenge in sorption experiments due to the potentially high buffering capacity of the secondary carbonates and the confounding effect of competitive cations (Fidel et al., 2013, 2017, 2018). We identified that only a minority of studies removed the ash-forming species from biochar. Our results suggest that retaining these ash-forming species in biochar results in higher estimates of Q_{new} (Fig. 3a), which is contrary to the expectation that cations in ash may compete with NH_4^+ for binding sites. Alternately, higher estimates of Q_{new} in the presence of ash may have several explanations. For example, co-precipitation of NH_4^+ with mineral components of the biochar ash can result in the formation of insoluble minerals such as struvite (Yin et al., 2018; Fan et al., 2019). Such mechanisms are dependent on the composition of the ash component, which varies with feedstock type (Chintala et al., 2013; Xiao et al., 2018). The potentially high buffering capacity of biochar ash could also make pH control of sorption solutions more challenging.

Increasing biochar HTT resulted in lower estimates of Q_{new} in all data subsets although the effect size was low and HTT did not consistently appear as an explanatory variable in all of the top candidate models. Biochar HTT is a proxy for a range of biochar properties that change both linearly and non-linearly as a function of pyrolysis temperature (Budai et al., 2014). Oxygen and N-containing functional groups are largely involved in ion exchange mechanisms on biochar surfaces and are the primary source of biochar CEC (Xiao et al., 2018). Due to the paucity of CEC data, we applied the elemental molar ratio $(\text{O} + \text{N})\text{:C}$ as a proxy for this functionality. As previously discussed, eggshell biochar confounded this interpretation due to the large amount of mineral O as compared to that contained in the organic C structure. Excluding biochar made from eggshell from our analysis improved the model fit and resulted in a positive effect of $(\text{O} + \text{N})\text{:C}$ on Q_{new} (GLM: Est. 1.18, C.I. 0.32–2.04. see Table S5d). The ratio $(\text{O} + \text{N})\text{:C}$ seemed to explain similar variation in the response as HTT, which was evidenced by the poorer fit of each variable when both were included in the same model. This is likely because HTT is collinear with $(\text{O} + \text{N})\text{:C}$, although negatively so. Despite the limited number of CEC measurements, CEC was positively

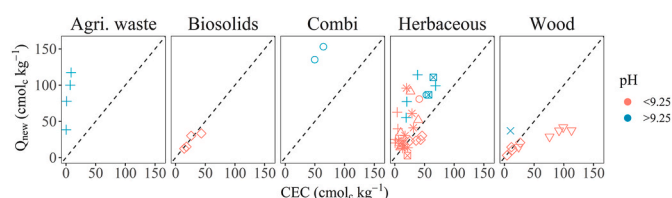


Fig. 4. CEC vs. Q_{new} in $\text{cmol}_c \text{kg}^{-1}$. Symbols refer to study and colour refers to pH. Activated biochars are included and account for 8 of the 53 measurements presented. The dotted line represents a 1:1 ratio between CEC and Q_{new} . (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

correlated with Q_{new} (Fig. 4), but with a high variability in the response. Solution pH appeared to explain some of this variability with a significantly larger difference between measurements of CEC and Q_{new} at solution pH values greater than the pKb of NH_4^+ (Fig. 4 & Fig. S5 in Supplementary Information). This discrepancy between estimates for Q_{max} and CEC has previously been reported in the literature and used as an argument that mechanisms other than ion exchange also contribute to explain Q_{max} (Jassal et al., 2015; Fidel et al., 2018). Although we cannot discard this hypothesis, our results suggest that variability between CEC and Q_{new} could also be a function of methodological choices. Quantification of CEC, as we have already seen with Q_{max} , can also be dependent on methodology, such as pH of solutions and biochar washing prior to measurement (Munera-Echeverri et al., 2018). This may explain why some studies report significantly lower estimates for Q_{max} than for CEC (Fig. 4).

Despite the variance in the data, the average difference between Q_{new} and CEC was $2.7 \text{ cmol}_c \text{ kg}^{-1}$ which is equivalent to $0.48 \text{ mg NH}_4^+ \text{ g}^{-1}$ biochar (Fig. S5 in Supplementary Information). The small size of this difference is consistent with ion exchange being the dominant process for the sorption of NH_4^+ to biochar, as reported by several authors (Fidel et al., 2018; Zhang et al., 2020). This suggests that increasing the density of ion exchange sites is a promising way to increase biochar sorption capacity for NH_4^+ . Maximising surface functional groups can be accomplished through choice of pyrolysis temperature, feedstock, and activation procedure. A meta-analysis by Hassan et al. (2020) found that sorption of ionic nutrients was favoured by the abundance of functional groups which was higher at low pyrolysis temperatures. Hassan et al. (2020) also reported greater abundance of functional groups for grass and manure biochar by comparison with wood biochar. This may explain the negative correlation of Q_{new} with HTT (Table S5 b,c,d in Supplementary Information) and the significantly lower Q_{new} values reported for wood biochars in this study (Fig. 2). Alternatively, this apparent feedstock effect might also be explained by the quantity and composition of the ash, which is also feedstock-specific. As we discussed earlier, activation resulted in some of the highest estimates for NH_4^+ sorption in our curated data set. The activation methods we observed in the literature were focused on methods to enhance the abundance of functional groups on the surface of biochar either through post pyrolysis oxidation with acids and bases (Boopathy et al., 2013; Wang et al., 2016; Zhu et al., 2016; Mia et al., 2017; Vu et al., 2017, 2018; Khalil et al., 2018), or combination of the biochar with minerals (Wang et al., 2015a; Ismadji et al., 2016; Chen et al., 2017; Gong et al., 2017; Chandra et al., 2020; Xiao et al., 2020).

Our ability to determine which biochar properties most influence the sorption of NH_4^+ was limited by the number of studies reporting some of these key factors and the variability in methods for quantification. For example, pore volume and specific surface area are considered important for the sorption of nutrients by biochar (Gong et al., 2019). However, the lack of systematic reporting of these parameters and the variability in quantification methods precluded us from investigating their possible contributions to Q_{new} . Our detailed review of the literature on this topic has emphasised the need to standardise biochar measurement methodologies, as highlighted in previous studies (Bachmann et al., 2016; Singh et al., 2017). Here we observe that methodology related to ash removal and pH control, in particular, appear to exert a significant effect. The results of our modelling exercise also highlight the need to critically assess the significance of outlier values.

4. Conclusions

Based on our standardized analysis of Q_{max} , we show that the range of sorption capacity of fresh, non-activated biochar for NH_4^+ is lower than previously reported. Outside of our curated range of estimates are published values for the sorption capacity of biochar that are exceptionally high. Although our methods highlighted these estimates as uncertain, based on possible methodological artefacts, these biochars

should be a focus of future studies in order to validate whether they are truly exceptional sorbents of NH_4^+ . development of future biochar sorbents will require estimates based on consistent methodologies for the quantification of sorption capacity and associated biochar properties. In particular, studies should consider the potential interaction effect of biochar ash on sorption dynamics and interpret results in light of either the inclusion or exclusion of this component of the biochar.

Author contributions

Simon Weldon: Conceptualisation, Formal analysis, Writing – original draft. **Bert van der Veen,** Formal analysis, Writing – review & editing; **Eva Farkas:** Writing – review & editing; **Nazlı Pelin Kocaturk-Schumacher:** Writing – review & editing **Alba Dieguez-Alonso:** Writing – review & editing **Alice Budai:** Writing – review & editing **Daniel Rasse:** Conceptualisation, Writing – review & editing, 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.

Acknowledgements

This work was supported by the Research Council of Norway through the Carbo-Fertil project NFR281113.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2022.134662>.

References

- Al-Ghouti, M.A., Da'ana, D.A., 2020. Guidelines for the use and interpretation of adsorption isotherm models: a review. *J. Hazard Mater.* 393, 122383.
- Al-Wabel, M.I., Al-Omran, A., El-Naggar, A.H., Nadeem, M., Usman, A.R.A., 2013. Pyrolysis temperature induced changes in characteristics and chemical composition of biochar produced from conocarpus wastes. *Bioresour. Technol.* 131, 374–379.
- Al-Wabel, M.I., Hussain, Q., Usman, A.R.A., Ahmad, M., Abduljabbar, A., Sallam, A.S., Ok, Y.S., 2018. Impact of biochar properties on soil conditions and agricultural sustainability: a review. *Land Degrad. Dev.* 29, 2124–2161.
- Bachmann, H.J., Bucheli, T.D., Dieguez-Alonso, A., Fabri, D., Knicker, H., Schmidt, H. P., Ulbricht, A., Becker, R., Buscaroli, A., Buerge, D., Cross, A., Dickinson, D., Enders, A., Esteves, V.I., Evangelou, M.W.H., Fellet, G., Friedrich, K., Guerrero, G.G., Glaser, B., Hanke, U.M., Hanley, K., Hilber, I., Kalderis, D., Leifeld, J., Masek, O., Mumme, J., Carmona, M.P., Pereira, R.C., Rees, F., Rombola, A.G., de la Rosa, J.M., Sakrabani, R., Sohi, S., Soja, G., Valagussa, M., Verheijen, F., Zehetner, F., 2016. Toward the standardization of biochar analysis: the COST action TD1107 interlaboratory comparison. *J. Agric. Food Chem.* 64, 513–527.
- Barrow, N.J., 2008. The description of sorption curves. *Eur. J. Soil Sci.* 59, 900–910.
- Barton, K., 2020. MuMIn: Multi-Model Inference. R package version 1.43.17. <https://CRAN.R-project.org/package=MumIn>.
- Boopathy, R., Karthikeyan, S., Mandal, A.B., Sekaran, G., 2013. Adsorption of ammonium ion by coconut shell-activated carbon from aqueous solution: kinetic, isotherm, and thermodynamic studies. *Environ. Sci. Pollut. Res.* 20, 533–542.
- Brooks, M.E., Kristensen, K., van Benthem, K.J., Magnusson, A., Berg, C., Nielsen, A., Skaug, H.J., Maechler, M., Bolker, B.M., 2017. glmmTMB balances speed and flexibility among packages for zero-inflated generalized linear mixed modelling. *R J.* 9 (2), 378–400.
- Budai, A., Wang, L., Gronli, M., Strand, L.T., Antal, M.J., Abiven, S., Dieguez-Alonso, A., Anca-Couce, A., Rasse, D.P., 2014. Surface properties and chemical composition of corn cob and miscanthus biochars: effects of production temperature and method. *J. Agric. Food Chem.* 62, 3791–3799.
- Burnham, K.P., Anderson, D.R., 2002. A practical information-theoretic approach. *Model Select. Multimodel Inf* 2, 70–71.
- Calvet, R., 1989. Adsorption of organic chemicals in soils. *Environ. Health Perspect.* 83, 145–177.
- Chandra, S., Medha, I., Bhattacharya, J., 2020. Potassium-iron rice straw biochar composite for sorption of nitrate, phosphate, and ammonium ions in soil for timely and controlled release. *Sci. Total Environ.* 712, 136337.
- Chen, L., Chen, X.L., Zhou, C.H., Yang, H.M., Ji, S.F., Tong, D.S., Zhong, Z.K., Yu, W.H., Chu, M.Q., 2017. Environmental-friendly montmorillonite-biochar composites:

- facile production and tunable adsorption-release of ammonium and phosphate. *J. Clean. Prod.* 156, 648–659.
- Cherkasov, N., 2020. Liquid-phase adsorption: common problems and how we could do better. *J. Mol. Liq.* 301, 112378.
- Chintala, R., Mollinedo, J., Schumacher, T.E., Papiernik, S.K., Malo, D.D., Clay, D.E., Kumar, S., Gulbrandson, D.W., 2013. Nitrate sorption and desorption in biochars from fast pyrolysis. *Microporous Mesoporous Mater.* 179, 250–257.
- Dong, D., Wang, C., Van Zwieten, L., Wang, H., Jiang, P., Zhou, M., Wu, W., 2019. An effective biochar-based slow-release fertilizer for reducing nitrogen loss in paddy fields. *J. Soils Sediments* 1–14.
- Esfandbod, M., Phillips, I.R., Miller, B., Rashti, M.R., Lan, Z.M., Srivastava, P., Singh, B., Chen, C.R., 2017. Aged acidic biochar increases nitrogen retention and decreases ammonia volatilization in alkaline bauxite residue sand. *Ecol. Eng.* 98, 157–165.
- Fan, R., Chen, C.L., Lin, J.Y., Tzeng, J.H., Huang, C.P., Dong, C., Huang, C.P., 2019. Adsorption characteristics of ammonium ion onto hydrous biochars in dilute aqueous solutions. *Bioresour. Technol.* 272, 465–472.
- Fidel, R.B., Laird, D.A., Thompson, M.L., 2013. Evaluation of modified boehm titration methods for use with biochars. *J. Environ. Qual.* 42, 1771–1778.
- Fidel, R.B., Laird, D.A., Thompson, M.L., Lawrinenko, M., 2017. Characterization and quantification of biochar alkalinity. *Chemosphere* 167, 367–373.
- Fidel, R.B., Laird, D.A., Spokas, K.A., 2018. Sorption of ammonium and nitrate to biochars is electrostatic and pH-dependent. *Sci. Rep.* 8, 17627.
- Foo, K.Y., Hameed, B.H., 2010. Insights into the modeling of adsorption isotherm systems. *Chem. Eng. J.* 156, 2–10.
- Giles, C.H., MacEwan, T.H., Nakhwa, S.N., Smith, D., 1960. Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. *J. Chem. Soc.* 111, 3973–3993.
- Glaser, B., Haumaier, L., Guggenberger, G., Zech, W., 2001. The 'Terra Preta' phenomenon: a model for sustainable agriculture in the humid tropics. *Naturwissenschaften* 88, 37–41.
- Glaser, B., Wiedner, K., Seelig, S., Schmidt, H.-P., Gerber, H., 2015. Biochar organic fertilizers from natural resources as substitute for mineral fertilizers. *Agron. Sustain. Dev.* 35, 667–678.
- Gong, H., Tan, Z., Zhang, L., Huang, Q., 2019. Preparation of biochar with high adsorbability and its nutrient adsorption-desorption behaviour. *Sci. Total Environ.* 694, 133728.
- Gong, Y.-P., Ni, Z.-Y., Xiong, Z.-Z., Cheng, L.-H., Xu, X.-H., 2017. Phosphate and ammonium adsorption of the modified biochar based on Phragmites australis after phytoremediation. *Environ. Sci. Pollut. Res.* 24, 8326–8335.
- Hailegnaw, N.S., Mercl, F., Pracke, K., Száková, J., Tlustoš, P., 2019. High temperature-produced biochar can be efficient in nitrate loss prevention and carbon sequestration. *Geoderma* 338, 48–55.
- Hassan, M., Liu, Y., Naidu, R., Parikh, S.J., Du, J., Qi, F., Willett, I.R., 2020. Influences of feedstock sources and pyrolysis temperature on the properties of biochar and functionality as adsorbents: a meta-analysis. *Sci. Total Environ.* 744, 140714.
- Hestrin, R., Torres-Rojas, D., Dynes, J.J., Hook, J.M., Regier, T.Z., Gillespie, A.W., Smernik, R.J., Lehmann, J., 2019. Fire-derived organic matter retains ammonia through covalent bond formation. *Nat. Commun.* 10, 664.
- Hu, X., Zhang, X., Ngo, H.H., Guo, W., Wen, H., Li, C., Zhang, Y., Ma, C., 2020. Comparison study on the ammonium adsorption of the biochars derived from different kinds of fruit peel. *Sci. Total Environ.* 707, 135544.
- Huang, J., Kankanamge, N.R., Chow, C., Welsh, D.T., Li, T., Teasdale, P.R., 2018. Removing ammonium from water and wastewater using cost-effective adsorbents: a review. *J. Environ. Sci.* 63, 174–197.
- Ismadji, S., Tong, D.S., Soetaredjo, F.E., Ayucitra, A., Yu, W.H., Zhou, C.H., 2016. Bentonite hydrochar composite for removal of ammonium from Koi fish tank. *Appl. Clay Sci.* 119, 146–154.
- Jassal, R.S., Johnson, M.S., Molodovskaya, M., Black, T.A., Jollymore, A., Sveinson, K., 2015. Nitrogen enrichment potential of biochar in relation to pyrolysis temperature and feedstock quality. *J. Environ. Manag.* 152, 140–144.
- Jellali, S., El-Bassi, L., Charabi, Y., Uaman, M., Khiari, B., Al-Wardy, M., Jeguirim, M., 2022. Recent advancements on biochars enrichment with ammonium and nitrate from wastewaters: a critical review on benefits for environment and agriculture. *J. Environ. Manag.* 305, 114368.
- Khalil, A., Sergeevich, N., Borisova, V., 2018. Removal of ammonium from fish farms by biochar obtained from rice straw: isotherm and kinetic studies for ammonium adsorption. *Adsorpt. Sci. Technol.* 36, 1294–1309.
- Kizito, S., Wu, S., Kipkemoi Kirui, W., Lei, M., Lu, Q., Bah, H., Dong, R., 2015. Evaluation of slow pyrolyzed wood and rice husks biochar for adsorption of ammonium nitrogen from piggery manure anaerobic digestate slurry. *Sci. Total Environ.* 505, 102–112.
- Lehmann, J., 2007. A handful of carbon. *Nature* 447, 143.
- Li, S.M., Barreto, V., Li, R.W., Chen, G., Hsieh, Y.P., 2018. Nitrogen retention of biochar derived from different feedstocks at variable pyrolysis temperatures. *J. Anal. Appl. Pyrolysis* 133, 136–146.
- Maziarka, P., Wurzer, C., Arauzo, P.J., Dieguez-Alonso, A., Mašek, O., Ronsse, F., 2021. Do you BET on routine? The reliability of N₂ physisorption for the quantitative assessment of biochar's surface area. *Chem. Eng. J.* 418, 129234.
- Mia, S., Dijkstra, F.A., Singh, B., 2017. Aging induced changes in biochar's functionality and adsorption behavior for phosphate and ammonium. *Environ. Sci. Technol.* 51, 8359–8367.
- Mitchell, M., Muftakhidinov, B., Winchen, T., et al., 2020. Engauge digitizer software. <http://markumitchell.github.io/engauge-digitizer> <https://zenodo.org/record/3941227>.
- Montégut, G., Michelin, L., Brendlé, J., Lebeau, B., Patarin, J., 2016. Ammonium and potassium removal from swine liquid manure using clinoptilolite, chabazite and faujasite zeolites. *J. Environ. Manag.* 167, 147–155.
- Munera-Echeverri, J.L., Martinsen, V., Strand, L.T., Zivanovic, V., Cornelissen, G., Mulder, J., 2018. Cation exchange capacity of biochar: an urgent method modification. *Sci. Total Environ.* 642, 190–197.
- Pinheiro, J., Bates, D., DebRoy, S., Sarkar, D., R Core Team, 2021. *Nlme: Linear and Nonlinear Mixed Effects Models*, pp. 1–153. R package version 3. <https://CRAN.R-project.org/package=nlme>.
- Portejoie, S., Dourmad, J.Y., Martinez, J., Lebreton, Y., 2004. Effect of lowering dietary crude protein on nitrogen excretion, manure composition and ammonia emission from fattening pigs. *Livest. Prod. Sci.* 91, 45–55. <https://doi.org/10.1016/j.livprodsci.2004.06.013>.
- Qin, Y., Zhu, X., Su, Q., Anumah, A., Gao, B., Lyu, W., Zhou, X., Xing, Y., Wang, B., 2019. Enhanced removal of ammonium from water by ball-milled biochar. *Environ. Geochem. Health* 42, 1579–1587.
- R Core Team, 2021. *R: A Language and Environment for Statistical Computing*. R Foundation for Statistical Computing, Vienna, Austria. URL: <https://www.R-project.org/>.
- Rasse, D.P., Weldon, S., Joner, E.J., Joseph, S., Kammann, C.I., Liu, X., O'Toole, A., Pan, G., Kocaturk-Schumacher, N.P., 2022. Enhancing plant N uptake with biochar-based fertilizers: limitation of sorption and prospects. *Plant Soil*. <https://doi.org/10.1007/s11104-022-05365-w>.
- Sha, Z., Li, Q., Lv, T., Misselbrook, T., Liu, X., 2019. Response of ammonia volatilization to biochar addition: a meta-analysis. *Sci. Total Environ.* 655, 1387–1396.
- Singh, B., Camps-Arbestain, M., Lehmann, J. (Eds.), 2017. *Biochar: A Guide to Analytical Methods*. Csiro Publishing.
- Tran, H.N., You, S.-J., Hosseini-Bandegharaei, A., Chao, H.-P., 2017. Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: a critical review. *Water Res.* 120, 88–116.
- Volesky, B., 2007. Biosorption and me. *Water Res.* 41, 4017–4029.
- Vu, M.T., Chao, H.-P., Van Trinh, T., Le, T.T., Lin, C.-C., Tran, H.N., 2018. Removal of ammonium from groundwater using NaOH-treated activated carbon derived from corncob wastes: batch and column experiments. *J. Clean. Prod.* 180, 560–570.
- Vu, T.M., Trinh, V.T., Doan, D.P., Van, H.T., Nguyen, T.V., Vigneswaran, S., Ngo, H.H., 2017. Removing ammonium from water using modified corncob-biochar. *Sci. Total Environ.* 579, 612–619.
- Wang, B., Lehmann, J., Hanley, K., Hestrin, R., Enders, A., 2015a. Adsorption and desorption of ammonium by maple wood biochar as a function of oxidation and pH. *Chemosphere* 138, 120–126.
- Wang, B., Lehmann, J., Hanley, K., Hestrin, R., Enders, A., 2015b. Adsorption and desorption of ammonium by maple wood biochar as a function of oxidation and pH. *Chemosphere* 138, 120–126.
- Wang, B., Lehmann, J., Hanley, K., Hestrin, R., Enders, A., 2016. Ammonium retention by oxidized biochars produced at different pyrolysis temperatures and residence times. *RSC Adv.* 6, 41907–41913.
- Wang, Z., Guo, H., Shen, F., Yang, G., Zhang, Y., Zeng, Y., Wang, L., Xiao, H., Deng, S., 2015c. Biochar produced from oak sawdust by Lanthanum (La)-involved pyrolysis for adsorption of ammonium (NH₄⁺), nitrate (NO₃⁻), and phosphate (PO₄³⁻). *Chemosphere* 119, 646–653.
- Xiao, R., Zhang, H., Tu, Z., Li, R., Li, S., Xu, Z., Zhang, Z., 2020. Enhanced removal of phosphate and ammonium by MgO-biochar composites with NH₃-H₂O hydrolysis pretreatment. *Environ. Sci. Pollut. Res.* 27, 7493–7503.
- Xiao, X., Chen, B., Chen, Z., Zhu, L., Schnoor, J.L., 2018. Insight into multiple and multilevel structures of biochars and their potential environmental applications: a critical review. *Environ. Sci. Technol.* 52, 5027–5047.
- Xu, D., Cao, J., Li, Y., Howard, A., Yu, K., 2019. Effect of pyrolysis temperature on characteristics of biochars derived from different feedstocks: a case study on ammonium adsorption capacity. *Waste Manag.* 87, 652–660.
- Yin, Q., Liu, M., Ren, H., 2019. Removal of ammonium and phosphate from water by Mg-modified biochar: influence of Mg pretreatment and pyrolysis temperature. *Bioresources* 14, 6203–6218.
- Yin, Q., Wang, R., Zhao, Z., 2018. Application of Mg-Al-modified biochar for simultaneous removal of ammonium, nitrate, and phosphate from eutrophic water. *J. Clean. Prod.* 176, 230–240.
- Zhang, M., Song, G., Gelardi, D.L., Huang, L., Khan, E., Mašek, O., Parikh, S.J., Ok, Y.S., 2020. Evaluating biochar and its modifications for the removal of ammonium, nitrate, and phosphate in water. *Water Res.* 186, 116303.
- Zhu, Y., Kolar, P., Shah, S.B., Cheng, J.J., Lim, P.K., 2016. Avocado seed-derived activated carbon for mitigation of aqueous ammonium. *Ind. Crop. Prod.* 92, 34–41.