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Biomass-Derived Carbonaceous Adsorbents for Trapping Ammonia

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Abstract: The preparation of low-cost carbonaceous adsorbents for nitrogen recovery is of interest from agricultural and waste management perspectives. In this study, the gaseous ammonia (NH_3) and aqueous ammonium (NH_4^+) sorption capacities have been measured for different types of carbonaceous chars produced under different conditions. The study includes a comparison of an oak-based hydrochar produced from hydrothermal carbonisation (HTC) at 250 °C with two biochars produced from slow pyrolysis at 450 °C and 650 °C, respectively. The chars were also chemically modified with H_2SO_4, H_3PO_4, H_2O_2, and KOH to investigate the potential for sorption enhancement. The highest sorption capacities for NH_3 were observed for the hydrochars with typical uptake capacities ranging from 18–28 mg g^{-1} NH_3. Sorption capacity for oak biochars is significantly lower and ranges from 4–8 mg g^{-1} for biochars produced at 450 °C and 650 °C, respectively. Hydrochar showed a substantially higher sorption capacity for NH_3 despite its lower surface area. The $CaCl_2$ extractable NH_4^+ following ammonia adsorption is incomplete. Typically, only 30–40% of the N is released upon washing with $CaCl_2$ in form of NH_4^+. Post chemical modification of the chars resulted in only limited enhancement of char NH_3 and NH_4^+ sorption. H_3PO_4 treatment showed the greatest potential for increasing NH_3/NH_4^+ sorption in biochars, while KOH and H_2O_2 treatment increased NH_3 sorption in the hydrochar. As only marginal increases to char surface area were observed following char treatment, these findings suggest that char surface functionality is more influential than surface area in terms of char NH_3/NH_4^+ sorption.

Keywords: hydrochar; biochar; activation; ammonia; ammonium; adsorption

1. Introduction

Nitrogen species are present in several agricultural and industrial wastewater effluents, where excessive quantities contribute to eutrophication. Furthermore, NH_3 emission into the atmosphere can result in nutrient deposition in nutrient sensitive ecosystems, formation of light–scattering aerosols resulting in haze, and visibility impairment and formation of inhalable aerosol particles which have health concerns [1]. Activated carbon has been the standard adsorbent used for recovering a variety of species owing to its well-developed pore structure and high surface area [2–4]. However, due to the high costs associated with traditional activated carbon, alternative waste-derived feedstocks have been considered, ranging from agricultural by-products and industrial waste materials [2,3]. Subsequent thermal and/or chemical activation of such feedstocks via incorporation of metal salts or oxidizing agents result in more cost-effective adsorbents [3,5]. To be considered suitable however, such alternative feedstocks are required to be abundant, carbon-rich, and possess appreciable pore development [3].

Hydrochars and biochars show potential as suitable alternatives to traditional activated carbon as they are carbon-rich and can be produced from a wide range of feed-stock although they are likely to require modification to enhance their nutrient sorption capacities [6]. Studies have demonstrated that adsorption using biochar is roughly consistent with Langmuir and Freundlich adsorption isotherm models, although uncertainty in adsorption mechanisms exist due to different pyrolysis reaction conditions and the fact that the presence of Brønsted and/or Lewis acid sites on the adsorbent surfaces enhance NH_3 sorption [7,8]. In the former case, protonation of NH_3 occurs as NH_3 dissociates in water or via acid-base neutralization reactions with carbonyl and phenolic OH^- groups to form NH_4^+ complexes [4,5,9–11]. Conversely, the donation of lone pair electrons from N atoms to cationic adsorbent sites such as metal species can occur at Lewis acid sites [9,10,12,13]. NH_3 adsorption capacities have been studied for various biochars and have reported no direct correlation of pyrolysis reaction temperature or significance of surface area once activated [14,15]. Moreover, NH_4^+ adsorption capacities have been reported to be greater in biochars produced at low temperatures between 300 to 400 °C, possibly due to their higher proportion of acid functional groups [16,17] including high pH [18]. However, a study also found biochars with higher NH_4^+ adsorption capacities with increasing pyrolysis temperatures [19]. Though, different feedstock materials were used in the preparation of the biochars examined.

These studies have shown that biochar sorption mechanisms still require further investigation and suggest that hydrochars from the hydrothermal carbonisation (HTC) process are likely to possess greater ability for NH_3/NH_4^+ sorption compared to biochars, given their higher proportion of acidic functional groups. On the other hand, the higher surface areas of biochars may compensate for their lower acidic functionalities since some studies have reported that high adsorbent surface areas and pore volumes increase NH_3/NH_4^+ removal efficiencies [10,19,20]. Moreover, the high surface areas of some biochars may provide more sites for the loading of acidic or cationic species which increase the number of Brønsted and Lewis acid sites respectively.

Studies in the literature directly comparing ammonia sorption of hydrochar and biochar are limited and show mixed results. An emissions and growth study showed that hydrochar lowered NH_3 emissions compared to biochar which was attributed to the greater acidity of hydrochar [21]. Contrarily, it was found that hydrochar and biochar increased the emissions of NH_3 when applied as a soil amender with the addition of pig slurry. Moreover, hydrochar had a reduced ability to absorb NH_4^+, which was attributed to its increased hydrophobicity and pH buffering capabilities [22]. Both studies used the same hydrochar and biochar production approach and both used *Miscanthus* as a feedstock although it is speculated that the production of hydrochar was not performed in subcritical water but was rather steam treated, akin to the autoclaving process.

This study is therefore aimed at contributing to the growing research on factors influencing char NH_3 and NH_4^+ sorption. In particular, understanding the difference in behaviour between hydrochar and biochar and investigating the potential for enhancing sorption using post chemical modification. Owing to their low levels of contaminants, hydrochar and biochars derived from bark-free holm oak wood were evaluated before and after treatment with various chemical agents. It is anticipated that this study will contribute to growing research on the factors influencing nitrogen recovery by adsorbents derived from a wider range of agricultural residues.

2. Materials and Methods

2.1. Materials

Oak hydrochar was produced using a 600 mL stainless steel Parr 4836 bench-top reactor (Parr, Moline, IL, USA) by heating 10 wt% bark-free holm oak wood (particle size < 1 mm) in distilled water at 250 °C for 1 h at autogenous pressure (approximately 4 MPa). The reactor and its contents were allowed to cool to about 50 °C before recovering the resulting hydrochar from the process water by filtration followed by air-drying. The hydrochar was designated as Oak 250. Biochars were supplied and produced from Oak wood (particle size < 2 mm) were obtained from a commercial pyrolysis plant operated by Proininso S.A. (Málaga, Spain) at 450 °C and 650 °C (henceforth referred to as Oak 450 and Oak 650, respectively). Particles were ground and sieved through 1 mm and 2 mm apertures until homogenous.

2.2. Methods

2.2.1. Acid Treatment

For char chemical modification, as-received analytical-grade reagents were used. Chars were prepared to particle size <2 mm then weighed to 4 g and mixed with 2 g of 99% phosphoric acid in 20 mL distilled water. The mixtures were shaken briefly and left to stand for 24 h at room temperature after which the mixtures were heated for about 15 h at 80 °C in an oven and rinsed with distilled water. Hydrochars and biochars were oven-dried at 80 °C and 100 °C, respectively.

For sulphuric acid treatment, 5 g of char ($\leq$2 mm) was mixed with 100 mL of 0.1 M H_2SO_4 and heated for 3 h at 80 °C after which treated chars were washed with distilled water until a stable pH was attained and oven-dried at 80–100 °C.

H_2O_2 treatment involved soaking 2 g of char ($\leq$2 mm) in 20 mL of 10% H_2O_2 for 48 h at room temperature, followed by heating at 80 °C for 24 h and rinsing with distilled water until the pH was between 6–7 for biochars or close to the hydrochars original pH before oven-drying at 80–100 °C.

2.2.2. KOH Treatment

KOH treatment involved mixing 4 g of char ($\leq$2 mm) in a solution of 2 g KOH and 20 mL of distilled water. The mixture was stirred for 2 h at 75 °C with a magnetic stirrer. Treated chars were subsequently rinsed with HCl followed by distilled water until the leachate pH values ranged between 6–7 for biochars or close to the hydrochars original pH, after which treated hydrochars and biochars were oven-dried for 2 h at 80 °C and 100 °C, respectively.

2.2.3. Agronomical Analysis

Ultimate analyses of biochar and hydrochar samples were determined using a CHN Elemental Analyser (Flash 2000, Thermo Scientific, Waltham, MA, USA). Proximate analysis was performed using a muffle furnace and analysis of char pH, CEC, N_2 BET, surface area, macro-, and micro-nutrient contents have been described elsewhere [23].

2.2.4. Ammonium Sorption Tests

Details of the batch ammonium adsorption tests have been provided in [24]. Briefly, 0.1 g of char ($\leq$850 µm) is mixed with 100 mL of either 43 mg or 450 mg NH_4^+ L^{-1} solution (pH 7) prepared from ammonium chloride salt in deionised water. NH_4^+ sorption capacities for the various treated chars were evaluated at 450 mg NH_4^+ L^{-1} to investigate their potential for NH_4^+ recovery from a representative concentration range encountered in real-case conditions. The mixture was shaken at 160 rpm for 24 h at room temperature. To determine whether losses in NH_4^+ occurred during sorption tests, the same procedure was performed without char addition. As only small amounts of NH_4^+ were lost after sorption tests with such controls, reductions in NH_4^+ after sorption tests were assumed to be entirely due to char sorption. Char NH_4^+ sorption capacity was determined as:

$$q_{e=}\ (C_0 - C_e)\frac{V}{M} \tag{1}$$

where C_0 and C_e = initial and equilibrium ammonium adsorbate concentrations respectively (mg L^{-1}); V = volume of solution (L); M = mass of char (g).

Batch desorption followed a similar procedure as outlined above, where adsorbed NH_4^+ was extracted from chars using 0.01 M KCl and analysed by ion chromatography. This procedure was also performed on chars to determine their native NH_4^+ contents to correct for any NH_4^+ release from the initial char. Desorbability was determined as the ratio of desorbed NH_4^+ to total adsorbed NH_4^+.

2.2.5. Ammonia Sorption Test

Ammonia adsorption was evaluated in a simple batch set-up, slightly modified from the methodology outlined in Taghizadeh-Toosi et al. [11]. Briefly, 60 mL of NaOH was transferred into a 250 mL Schott Duran bottle after which a weighing boat containing about 0.2 g char was carefully placed into the bottle so it floats on top of the solution. The bottle was fitted with a septa and closed to obtain a gas tight seal. Carefully, 25 mL of 0.05 M $(NH_4)_2SO_4$ was injected into the bottle through the septa and gaseous ammonia was produced via the following chemical reaction:

$$2NaOH_{(aq)} + (NH_4)_2SO_{4(aq)} \rightarrow Na_2SO_{4(aq)} + 2H_2O_{(l)} + 2NH_{3(g)} \quad (2)$$

NaOH was present in excess such that a known amount of gaseous NH_3 was produced; in the current case this was 43 mg of NH_3 gas and average headspace volumes were equivalent to about 242.6 mL. After seven days the samples were removed from the bottles and changes to nitrogen content were analysed via elemental analysis. The nitrogen content was adjusted for increased moisture content with respect to the char samples prior to NH_3 sorption. Changes to NH_4^+ content were also determined by ion chromatography after shaking a mixture of the char in a solution of 0.01 M $CaCl_2$ in a 1:20 ratio for 2 h at 160 rpm. The NH_3 sorption capacity of the raw holm oak biomass (from which the biochar and hydrochar were produced) was also evaluated following the same procedure outlined above for comparative purposes, since unprocessed feedstocks are often used as litter material for NH_3 abatement in livestock systems. The NH_3 sorption capacities of Oak 250 were further investigated at various concentrations of NH_3 following the same procedure as outlined above, generating about 450, 1000, and 1500 mg NH_3 by adjusting molar concentrations of $(NH_4)_2SO_4$ and NaOH according to Equation (2).

2.2.6. Assessment of Error and Statistical Analysis

Hydrothermal carbonization experiments were performed until repeatability of hydrochar yields was typically ±3 wt%. Whereas pyrolysis was performed by a commercial plant (Proininso S.A. Málaga, Spain), therefore, yields of biochar were unavailable. Biochar and hydrochar samples were both homogenized prior to use. All absorption tests were performed in duplicate, with selected data being performed in triplicate and products combined for a representative sample for analysis. Metal analysis and ultimate and proximate analysis were performed in duplicate until a maximum standard deviation of ±2% was achieved. Mean values are reported together with standard error ranges and bars in tables and figures. Selected data for sorption of NH_3 on modified chars was also analysed using a one-way ANOVA with a significance level ($\alpha = 0.05$), followed by a Tukey or Dunnett's test for examining each variable as separate. The value of $p < 0.05$ was considered significant. Data for statistical analysis can be found in the Supplementary Materials.

3. Results

3.1. Physicochemical Properties of Untreated Hydrochars and Biochars

The unprocessed (as-received) bark-free oak wood possesses a low ash content of 2.6% and appreciable concentrations of Ca, K, Mg, and P. Its carbon content of 50.8% and molar O/C ratio of 0.6 is within the range frequently reported for agricultural feedstocks. Following thermochemical treatment, a reduction in volatile matter content is evident while ash content increases (Figure 1).

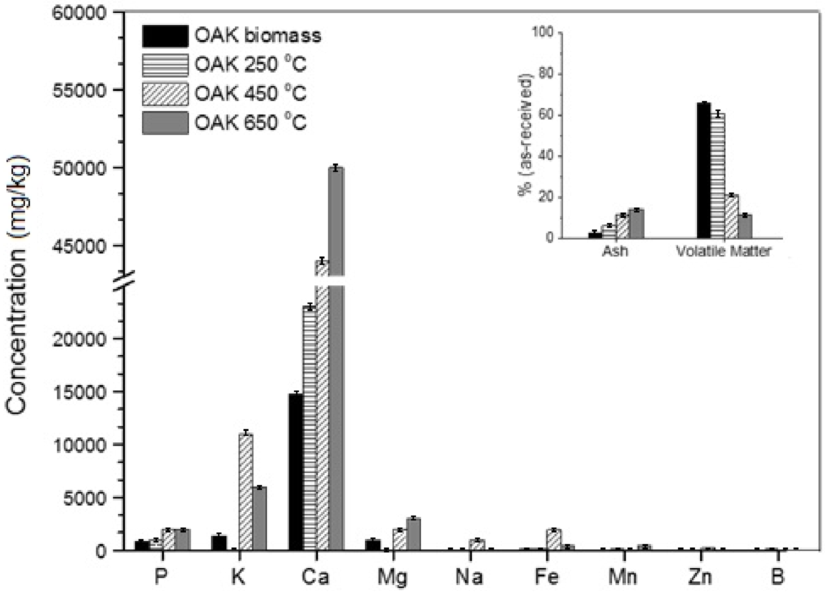

Figure 1. Distribution of the main micro- and macro-mineral contents within oak biomass, hydrochar, and biochars (mg/kg, dry basis). Inset: Ash and volatile content of oak biomass and chars (%wt., as received basis). Based on duplicate data with repeatability typically within ±2%. Error bars represent deviation around the mean.

Other hydrochar and biochar physicochemical properties have been provided elsewhere [24], in which all carbon contents are >50% in accordance with EBC and IBI product specification guidelines. Previous studies have observed that with increasing pyrolysis temperature, relative carbon contents increase and this is also observed in this study, with Oak 650 exhibiting the highest carbon content and surface area, the latter attributed to loss of volatiles with increasing temperature. Differences between the hydrochar and biochar properties are observed: O/C ratios range from 0.2–0.4 and are lowest for Oak 650. Differences in ash content and surface area are also observed with Oak 250 hydrochar having the lowest ash content (6.2%) and surface area (6 m^2 g^{-1}) compared to biochar ash contents and surface areas of 11.7–14.3% and 180–280 m^2 g^{-1}, respectively. Oak 250 hydrochar also possesses the highest CEC as expected of a low temperature char [25] although this trend is not followed in the biochars since the CEC of Oak 650 is greater than Oak 450. A similar trend in biochar CEC was observed in Yuan et al. [26] and, to some extent, in Jassal et al. [27].

3.2. NH_3/NH_4^+ Sorption by Untreated Hydrochar and Biochars

The NH_3 and NH_4^+ sorption profiles of untreated oak biochars and hydrochars are presented in Figure 2 for concentrations equating to (a) 43 mg and (b) 450 mg NH_3/NH_4^+. The different conditions are used to assess the influence of the concentration of N species on sorption capacity and to simulate low to high levels of N species. The increase in total N content after exposure to 43 mg NH_3 is 11.0 ± 0.4 mg g^{-1} for oak biomass and between 0.58–15.4 mg g^{-1} for the resulting chars. These levels are comparable to those reported in the literature; an average increment of 6.7 ± 0.6 mg g^{-1} as reported by Taghizadeh-Toosi et al. [11].

Figure 2a shows that the % sorption efficiency of NH_3 is higher for the hydrochar than for both biochars (45% compared to <10%, respectively), equivalent to 18.8 mg g^{-1} for the hydrochar and <3 mg g^{-1} for the biochars (Table 1). It is also worth noting that the performance of the raw biomass is comparable to that of the hydrochar at the lower levels of NH_3 (Figure 2a) and is significantly higher than the biochar performance. This is less evident at higher NH_3 levels (Figure 2b), however, the sorption efficiency of the raw biomass is still comparable with that of the biochars. NH_3 sorption capacities of the raw feedstock and hydrochar are, in fact, comparable in spite of the lower mineral matter concentrations present in the former (Figure 1). While the % sorption is lower with the higher initial NH_3/NH_4^+ concentration, the same general trend is observed for NH_3 sorption with Oak 250 hydrochar retaining about 20.4 mg g^{-1} more NH_3 than Oak 650 (Table 1). The sorption capacity is approximately a factor of 10 lower as expected.

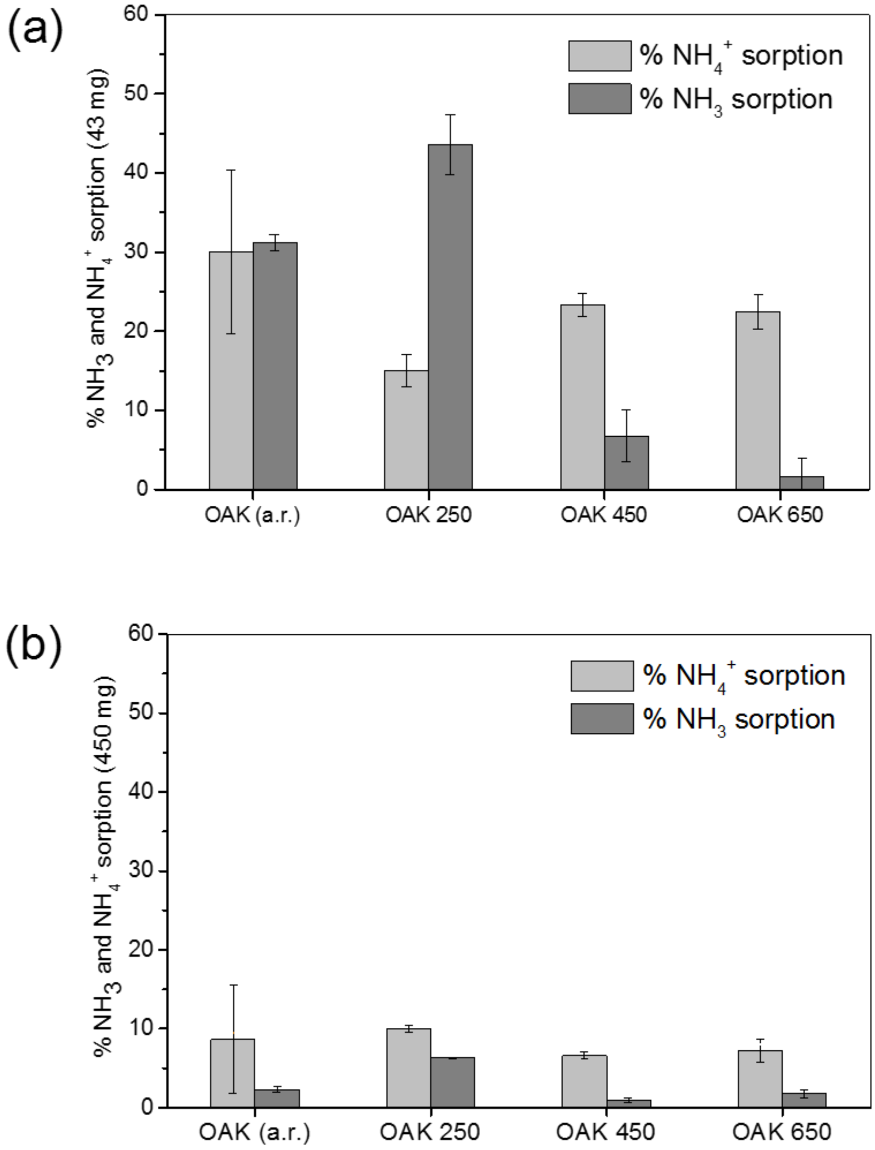

Figure 2. NH_3 and NH_4^+ removal efficiencies of unprocessed oak biomass (as received) and oak chars at approximately (**a**) 43 mg NH_3 and 43 mg NH_4^+ L^{-1} (**b**) 450 mg NH_3 and NH_4^+ L^{-1}. Based on duplicate data and error bars represent deviation around the mean.

Table 1. Char sorption and release profiles for gaseous NH_3 and aqueous NH_4^+.

Char	**NH_3 Sorption ($mg\ g^{-1}$)**	**$CaCl_2$-Extractable NH_4^+ ($mg\ g^{-1}$)**	**NH_4^+ Sorption ($mg\ g^{-1}$)**	**NH_4^+ Desorbed ($mg\ g^{-1}$)**
	[a] 43 mg NH_3		43 mg NH_4^+ L^{-1}	
OAK 250	18.8 ± 1.6	7.2 ± 0.3	6.0 ± 0.5	0.0 ± 0.0
OAK 450	2.9 ± 1.4	1 [b]	9.2 ± 0.2	1.1 ± 1.6
OAK 650	0.7 ± 0.9	1 [b]	8.9 ± 0.8	0.0 ± 0.0
	[a] 450 mg NH_3		450 mg NH_4^+ L^{-1}	
OAK 250	28.5 ± 0.3	6.1 ± 0.8	45.1 ± 1.7	9 [a]
OAK 450	4.3 ± 1.2	2.68 ± 0.04	29.9 ± 1.8	12 [a]
OAK 650	8.1 ± 2.2	2.1 ± 0.1	32.7 ± 6.7	11 [a]

[a] 43 and 450 mg NH_3 generated based on Equation (2); [b] single analyses reported while other values are reported as mean uptake ± standard deviation; undetected NH_4^+ concentrations reported as zero.

Figure 3 illustrates the NH_3 sorption capacities for Oak 250 over a range of NH_3 concentrations. The analysis was found to be statistically significant F(4,4) = 60.57, $p = 0.00086$. A Tukey test was further implemented to demonstrate all the treatments were significantly different. The hydrochar shows a change in NH_3 sorption with increasing NH_3 concentration indicating that while a greater capacity is attained at higher initial NH_3 concentration, the % sorption capacity reduces substantially and suggests that while sites are available for NH_3 sorption even at 1500 mg NH_3, its removal efficiency is greatly reduced. NH_3 sorption appears to start levelling off at higher concentration suggesting a maximum sorption in the order of about 45 mg g^{-1} NH_3 for the hydrochar.

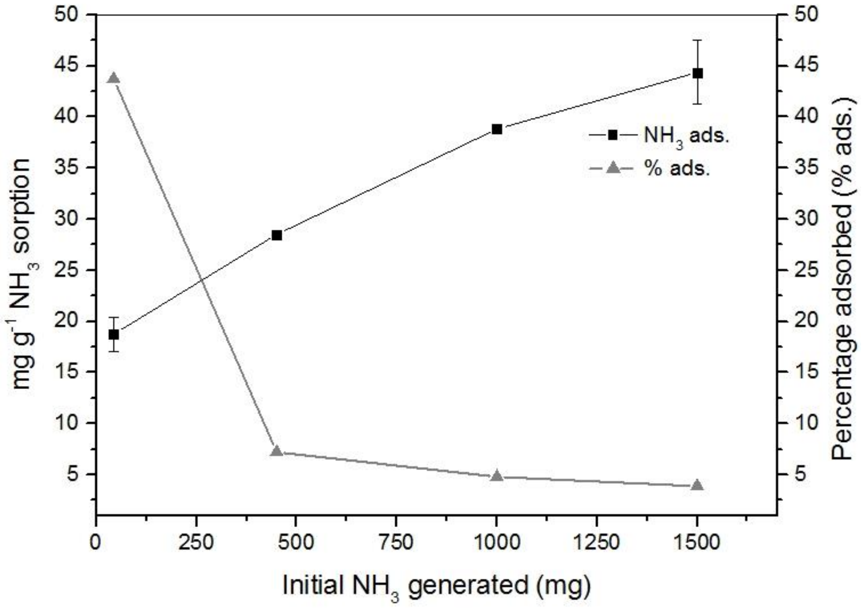

Figure 3. NH_3 sorption capacities for Oak 250 hydrochar at 43, 450, 1000, and 1500 mg NH_3 gas generated according to Equation (2). Error bars represent deviation around the mean. For statistical analysis please refer to Supplementary Material Table S3.

Subsequent washing of the chars in $CaCl_2$ does not release the entire adsorbed N (Table 1). Typically, 30–40% of the N is released upon washing with $CaCl_2$ in the form of NH_4^+. As observed by Taghizadeh-Toosi et al. [11,14], no changes in NO_3^- contents are observed in oak hydrochar or biochars following ammonia sorption tests. $CaCl_2$-extractable ammonium contents are highest for the hydrochar and generally decrease in proportion to ammonia gas concentration exposure. Following exposure to 1000 and 1500 mg gaseous NH_3, only 6.7 ± 0.3 and 8.6 ± 2.0 mg of NH_4^+ are respectively recoverable per gram of Oak 250 hydrochar. Taghizadeh-Toosi et al. [11] similarly observed that 2 M

KCl-extractable NH_4^+ represented only a fraction of the increase in char total N following exposure to NH_3. As $CaCl_2$-extractable ammonium is considered plant-available [28,29], these results suggest that hydrochar may be the most beneficial in terms of release of N in soils or soil amendment products. Further investigations are required to confirm whether more ammonium is recoverable with serial extractions using 2 M KCl and water [30], although N species other than inorganic N may be present in post-NH_3 sorption chars [14] which are not easily recoverable with such extractants. For instance, Petit et al. [31] showed that ammonia retention in the form of amines is also possible. Studies by Thorn and Mikita [32] on ammonia fixation by organic matter, suggested that organic matter rich in phenolic and hydroxyl groups are capable of retaining ammonia in the form of heterocyclic nitrogen (indole, pyrrole, pyridine).

The NH_4^+ sorption profiles for the hydrochar and biochars are also presented in Figure 2a,b at initial concentrations (C_0) of 43 and 450 mg NH_4^+ L^{-1}, respectively. Char NH_4^+ removal efficiencies range from 15.1–23.3% at 43 mg L^{-1} and decrease to 6.6–10% at 450 mg L^{-1}. The trends are less clear for the sorption of NH_4^+. There is less distinction between the different samples for NH_4^+ sorption and there is little statistical difference between the raw biomass and the different chars. At lower levels of NH_4^+ (Figure 2a), Oak 250 hydrochar demonstrates a lower capacity for NH_4^+ sorption compared to NH_3 whereas for the biochars, the opposite is true. For higher levels of NH_4^+ (Figure 2b), the hydrochar sorption is comparable to that of the biochars. In both cases, the capacity of the chars for sorption of NH_4^+ is higher than for NH_3. This suggests that surface functionality is an important consideration in retention of NH_3/NH_4^+. While the biochars have a higher surface area, this does not equate to a higher NH_3 adsorption compared to the hydrochar, indicating that functionality is more important than surface area for NH_3. The levels of NH_4^+ sorption by the biochars increases over three-fold compared to NH_3. This is thought to be related to the presence of mineral matter in the chars which is enhanced in the higher temperature biochars (Figure 1). The levels of inorganics in the chars are often attributed to higher levels of sorption. Zhang and Wang [33] recovered >60% NH_4^+ partly due to the biochar composites being enhanced with Mg and PIn this study, the higher temperature biochars contain higher levels of ash than the raw biomass and hydrochars, however, the raw biomass shows a significant level of sorption capacity compared to the hydrochars and biochars. Detailed analysis of the inorganic content of the chars and raw feedstock indicates there is no obvious correlation between % NH_4^+ sorption and char ash, P, Mg, or Ca content. NH_4^+ release from chars are also low following desorption tests.

The levels of NH_4^+ sorption in this study are comparable to reports in the literature for biochar. Wang et al. reported 12.1–16.1% removal efficiencies of untreated and La-treated 300 °C biochars (C_0 = 25.7 mg NH_4^+ L^{-1}) [25]. Other studies have reported higher NH_4-N removal efficiencies however: 37.3% sorption by activated phytoremediation plant char (C_0 = 39 mg NH_4^+ L^{-1}) in Zeng et al. [34] and 62–83% sorption by Brewer's grains-sewage sludge biochar (C_0 = 100 mg NH_4^+ L^{-1}) in Zhang and Wang [33]. 0.01 M KCl was used to determine the readily recoverable NH_4^+ post-sorption from the chars and a selected number were also extracted with 0.01 M $CaCl_2$ to compare performance of both extractants. NH_4^+ desorption was found to be <10 mg g^{-1} in both cases thus the desorbability ratio ranged between a factor of 0.2–0.4.

Previous studies have reported a positive relationship between NH_4^+ sorption and char CEC, surface area, oxygen content and metal content [9,12,33–35]. In this study, NH_4^+ sorption followed a similar trend to CEC, yet the amounts of NH_4^+ retained by the chars at both 43 and 450 mg NH_4^+ L^{-1} are substantially higher than predicted by their corresponding CEC values, recalculated as $NH_4^+{}_{eq}$ to estimate maximum theoretical NH_4^+ sorption capacities (Table 2). Some studies have also observed that CEC underestimates NH_4^+ sorption capacity [14,27,34,36]; this discrepancy has been attributed to physical sorption of N into the char pores as opposed to ion exchange [27], or to conversion of NH_4^+ into organic nitrogen [36]. Conversely, Nguyen and Tanner [37] observed maximum NH_4^+ sorption by a zeolite to be substantially lower than the CEC-predicted values.

Table 2. Elemental content and CEC values for a selection of treated chars.

Char	**CEC**	**^{b} $NH_4^+{}_{eq}$**	**C**	**H**	**N**	**S**	**^{a} O**
	(cmolc kg^{-1})	**(mg g^{-1})**	**(%)**	**(%)**	**(%)**	**(%)**	**(%)**
OAK 250	88.3 ± 9.7	15.9	67.9	6.5	1.4	0.1	24.1
OAK250-H_2SO_4	81.1 ± 4.7	14.6	61.3	4.9	0.4	0.04	33.4
OAK 250-H_3PO_4	86.8 ± 4.7	15.6	60.2	4.8	0.3	0	34.6
OAK 250-H_2O_2	102.4 ± 7.3	18.4	56.1	4.5	0.3	0	39.1
OAK 250-KOH	102.0 ± 8.2	18.4	62	4.9	0.4	0	32.7
OAK 450	59.4 ± 8.1	10.7	65.7	2.7	0.6	0	31
OAK 450-H_2SO_4	66.3 ± 15.6	11.9	73.6	4.8	0.5	0	21.1
OAK 450-H_3PO_4	103.5 ± 33.0	18.6	70	4.1	0.4	0	25.5
OAK 450-H_2O_2	147.2 ± 6.9	26.5	71.3	3.9	0.5	0	24.3
OAK 450-KOH	141.0 ± 13.2	25.4	77.7	2.8	0.6	0	19
OAK 650	76.6 ± 0.7	13.8	76.5	1.4	0.8	0	21.3
OAK 650-H_2SO_4	106.8 ± 18.7	19.2	62.9	2.4	0.6	0	34.2
OAK 650-H_3PO_4	126.3 ± 63.9	22.7	50.5	3.6	0.5	0	45.4
OAK 650-H_2O_2	71.2 ± 7.4	12.8	63.7	2.3	0.5	0	33.5
OAK 650-KOH	132.3 ± 11.2	23.8	68.3	1.9	0.7	0	29.2

[a] Oxygen content determined as difference between % C, H, N and S from 100 (dry basis); [b] $NH_4^+{}_{eq}$ refers to the maximum equivalent char NH_4^+ sorption capacity since 1 $cmol_c$ kg^{-1} = 0.18 mg NH_4^+ kg^{-1} char; char. CEC expressed as average of duplicates ± standard deviation.

3.3. Physicochemical Properties of Modified Hydrochars and Biochars

Table 2 lists the elemental content and CEC of the modified chars and indicates a decrease in carbon and nitrogen content for all the treatments of Oak 250 hydrochar and Oak 650, and a corresponding increase in oxygen content. The carbon content for the Oak 450 chars increase possibly due to the relative decrease of inorganic content following treatment [34,35] while oxygen contents decrease. These findings are in general agreement with Zheng et al. who observed increases in carbon, hydrogen, and nitrogen for acid-washed biochars with a corresponding decrease in oxygen content [38]. This anomaly could be related to the relative ease of leaching of inorganics and the difference in reactivity of the surface towards decarboxylation and hydrolysis. Similar observations were reported by Latham et al. after acid and base treatment during hydrothermal treatment of sucrose [39]. The nitrogen contents of the untreated chars are presented in Table S1 and range from 4.3–5.5 mg N g^{-1} char. The N contents of the treated chars generally decrease with the exception of KOH treated biochars, which result in slight increases in N (for example an increase in N d.3–6.3 mg N g^{-1} for Oak 450 treated in KOH and 5.5–7.0 mg N g^{-1} for Oak 650 treated in KOH). The relative increase in N content following KOH treatment is speculated to be primarily due to loss of carbon, while the reduction in N is possibly due to modification disrupting N-containing compounds in the biomass thus increasing N release.

Acid treatment has varying effects on char CEC: the CEC of the treated hydrochars are generally higher than the biochars, due to increased surface functionality. There is little change in CEC for the hydrochar treated with H_2SO_4 and H_3PO_4, whereas all other treatments increase char CEC. For instance, following H_2O_2 treatment, a two-fold increase in the CEC of Oak 450 is observed although the increase for Oak 250 hydrochar is less. Previous studies [40,41] have attributed this effect to an increase in oxygen functional groups resulting from the oxidation of aromatic carbon and an increase in carbonyl groups. What is also apparent is that the increase in CEC cannot be attributed to changes in surface area since H_2O_2 treatment results in a drastic reduction in surface area (>50%) for both oak biochars [24].

Changes in functionality following char modification has been investigated using FTIR. The FTIR spectra can identify changes in the relative abundance of carbonyl, hydroxyl, and other reactive functional groups as shown in the Supplementary Material (Figure S1, Table S2). However, no major differences in functional group intensities are observed, suggesting that chemical treatment does not alter char functionality substantially. A slight relative increase in the intensity of carbonyl functional groups (1700 cm^{-1}) is observed following H_2O_2 treatment.

3.4. NH_3/NH_4^+ Sorption by Treated Hydrochar and Biochars

The NH_3 sorption capacities of the treated chars are shown in Figure 4 using a fixed concentration of 43 mg of NH_3. The NH_3 sorption for Oak 250 hydrochar and modified hydrochar are shown in Figure 4a, for Oak 450 biochar in Figure 4b and for Oak 650 biochar in Figure 4c. The results show that NH_3 sorption is higher for the hydrochar than for the two biochar samples, in agreement with initial testing. There was a significant difference between the means of the different treatments F(4,5) = 21.43, $p = 0.0024$. Treatment with H_2O_2 and KOH appear to have the largest impact on increasing NH_3 sorption in Oak 250 hydrochar whereas, treatment with H_2SO_4 and H_3PO_4 have little impact on sorption capacity (Figure 4a). The individual evaluation with Dunnett's test demonstrated that the treatments with H_2SO_4 and H_3PO_4, do not exhibit a significant effect, whereas the treatments with H_2O_2 and KOH do exhibit a significant effect. Secondly, in the case of Oak 450 there was a significant difference between the means of the different treatments F(4,5) = 12.10, $p = 0.0088$. Dunnett's test demonstrates that all the treatments (H_2SO_4 and H_3PO_4, H_2O_2, and KOH) exhibit a significant effect. Modification of Oak 450 with acid and peroxide appear to enhance sorption capacity resulting in a three-fold increase in NH_3 sorption from about 6.8% to 20.5% NH_3 removal efficiency. Modification of Oak 650 produces negligible enhancement of sorption capacity with the exception of H_3PO_4 treatment which shows a four-fold enhancement. Thirdly, in the case of Oak 650 there was no significant difference between the means of the different treatments F(4,5) = 1.88, $p = 0.2522$. Dunnett's test here demonstrates that none of the treatments exhibit a significant effect.

Increases in sorption capacity following acid treatment are expected and supported in the literature. The increase in NH_3 sorption of H_2SO_4-treated biochars is in agreement with the findings of Petit et al. who showed that sulfur-containing groups may be as influential as oxygen functional groups for NH_3 sorption [31]. Similar increases to NH_3 sorption have been reported by Chou et al. and Ritz et al. [42,43]. Such increases likely result from the formation of recoverable ammonium sulphate salts on adsorbent sites possibly following similar reactions to those outlined in Chou et al. [42]. It is also likely that increasing H_2SO_4 concentration up to a certain point could enhance NH_3 sorption capacity, based on findings of Chou et al. [42]. The increase in NH_3 sorption of H_3PO_4 treated biochars is also in agreement with the findings of Oya and Iu. Acid-catalyzed hydrolysis of polymeric units in lignocellulosic materials and labile carbon in biochars result in ketone formation after H_3PO_4 treatment [44,45]. Additionally, the formation of ammonium complexes with H_3PO_4 may have occurred as observed by Oya and Iu whose extensive studies confirmed the presence of $NH_4H_2PO_4$ and/or $(NH_4)_2HPO_4$ depending on H_3PO_4 loading ratio employed [46]. H_2O_2 treatment has a marked effect on NH_3 sorption for the lower temperature chars with H_2O_2-treated Oak 250 and Oak 450 showing an increase compared to the control. Similarly, H_2O_2 modification performed by Gómez-Serrano et al. resulted in an increase in surface OH groups and with increasing treatment time, an increase in carbonyl groups [47]. Increases in NH_3 sorption capacity following H_2O_2 treatment may therefore occur due to interactions between NH_3 and additional carbonyl groups. Similarly, treatment of biochar in KOH can also increase the level of surface OH groups (Figure S1) which may account for the increases in NH_3 sorption by KOH treated Oak 250 and 450 chars.

Figure 5 shows the NH_4^+ sorption following modification. In general, modification of the chars results in either no difference in sorption capacity or a reduction in NH_4^+ sorption capacity for all the chars investigated. This reduction in sorption capacity is particularly apparent for treatment with H_2O_2 and KOH treatment. There is some evidence of enhancement of sorption capacity using acid treatment, however when investigated further using ANOVA tests, there is no significant difference compared to the control. For all modified chars, the release of NH_4^+ is also measured following extraction in 0.01 M KCl. As observed for untreated chars, NH_4^+ release from modified chars are also low following desorption tests. For instance, KOH treated Oak 450 and 650 released 8.5 and 9.7 mg g^{-1}, respectively;

H_2O_2 treated Oak 450 and Oak 650 released 9.4 and 6.7 mg g^{-1}, respectively. As blank sorption tests performed alongside the sample char sorption tests show negligible NH_4^+ losses, it is speculated that NH_4^+ release from chars is low either due to strong interactions between NH_4^+ and the chars.

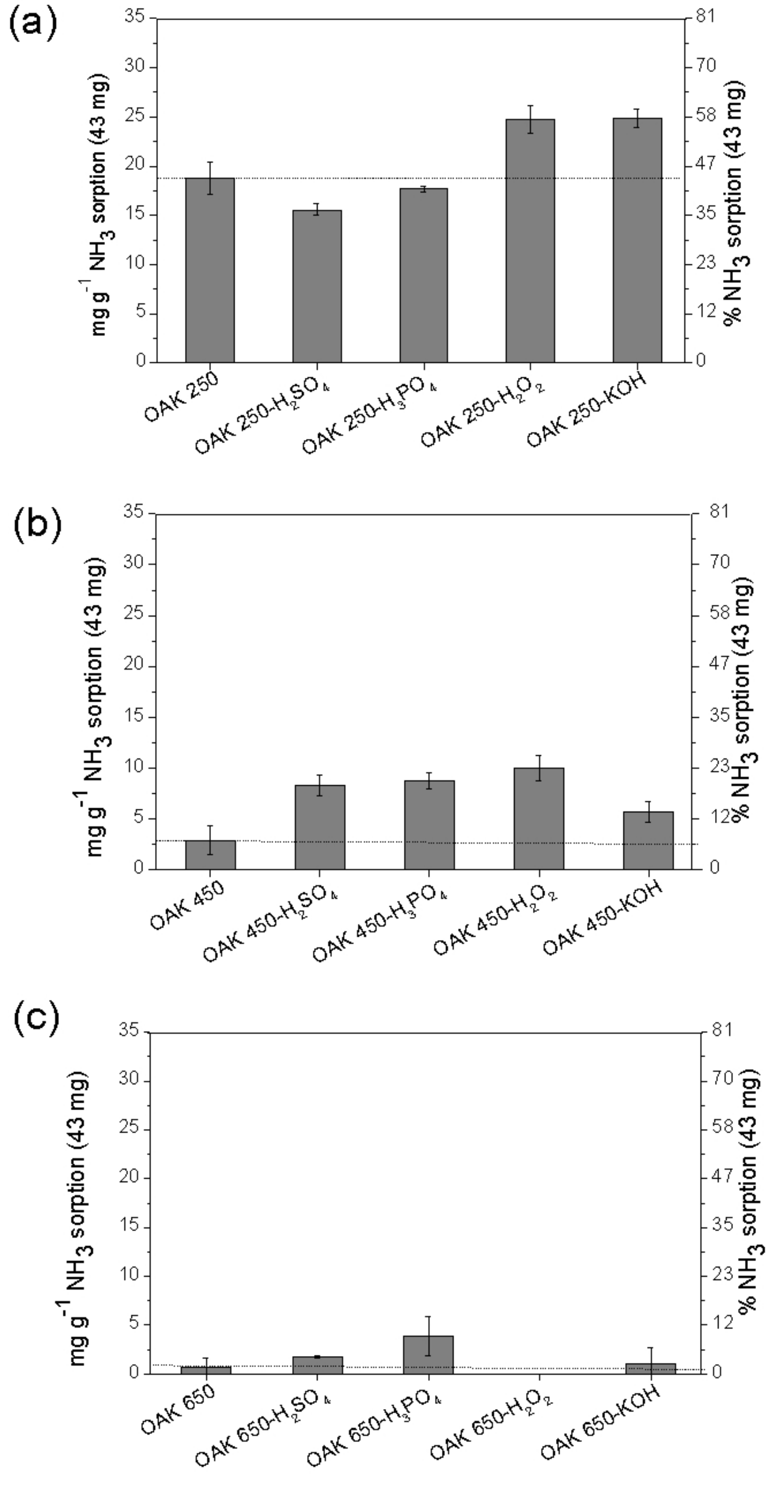

Figure 4. NH_3 sorption by (**a**) treated oak 250 °C hydrochar; (**b**) treated oak 450 °C biochar; and (**c**) treated oak 650 °C biochar d3 mg NH_3 gas generated according to Equation (2). Error bars represent deviation around the mean. For statistical analysis please refer to Supplementary Material Tables S4–S6.

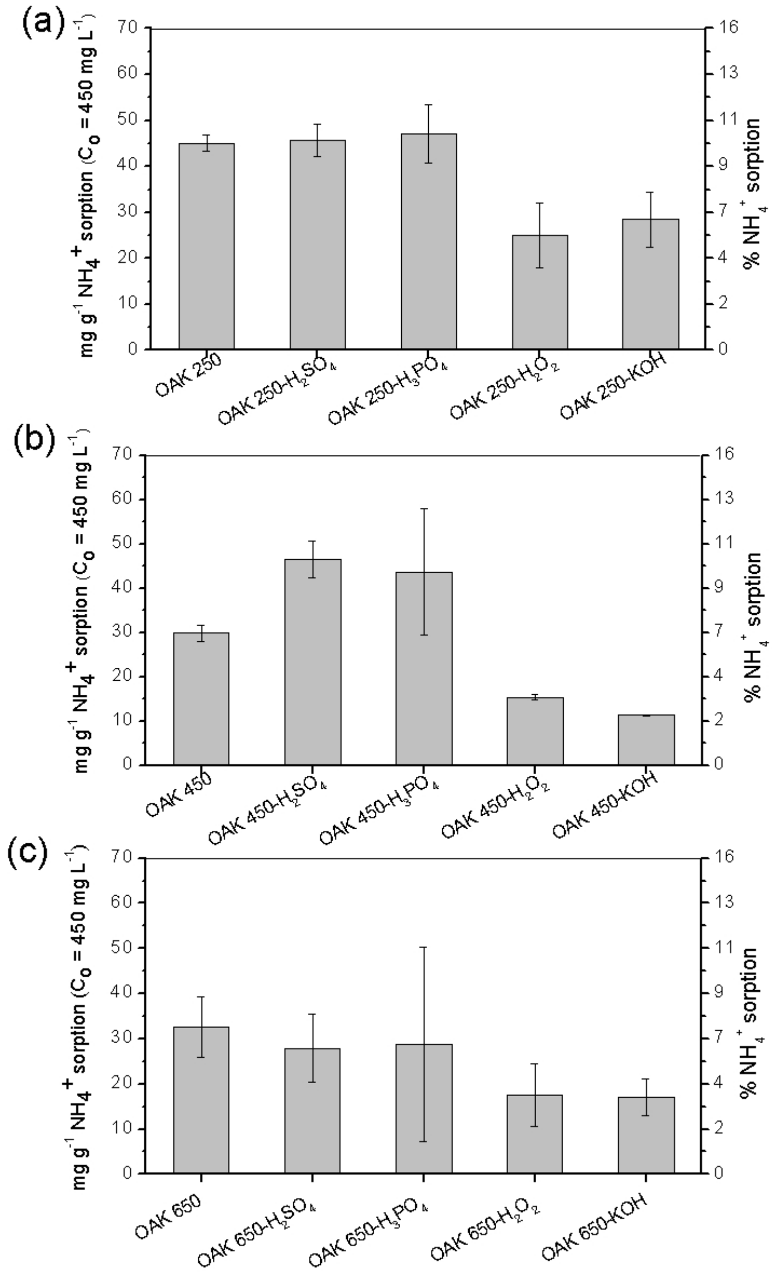

Figure 5. NH_4^+ sorption by (**a**) treated Oak 250 hydrochar; (**b**) treated Oak 450 biochar; (**c**) treated Oak 650 biochar from 450 mg NH_4^+ L^{-1} solution. Based on duplicate data, error bars represent deviation around the mean.

While treatment in H_2O_2 and KOH generally show the highest increase in CEC (Table 2), this is not reflected in sorption experiments. All oak chars experience a reduction in NH_4^+ sorption following KOH and H_2O_2 treatment despite the substantial increases in char CEC (Figure 5). Huff et al. similarly noted that while H_2O_2 treatment increased CEC, methylene blue adsorption capacity decreased, which emphasises that CEC may not be a suitable predictor of char sorption capacity [40].

4. Conclusions

Results from this study show that oak hydrochars possess higher sorption capacities for gaseous NH_3 and aqueous NH_4^+ relative to their corresponding biochars. Post chemical modification of hydrochars and biochars has only limited effect on enhancing sorption capacities. Enhancement is more evident for NH_3 sorption capacity than for NH_4^+ sorption capacity which remains similar and in some cases is reduced compared to the control. Overall, the findings show that char surface functionality is more influential than surface area, thus, modification processes aimed at modifying the former are more beneficial in terms of char NH_3 and NH_4^+ sorption. Of the chemical treatments performed in this study, phosphoric acid appears to show the greatest potential for increasing both NH_4^+ and NH_3 sorption capacities of biochars. Treatment of hydrochars in H_2O_2 and KOH show potential for enhancement of NH_3 sorption but result in a significant drop in NH_4^+ sorption.

The ammonia batch set-up used in this study may be regarded as a useful tool for screening potential NH_3 and NH_4^+ adsorbents although benefits could also arise from the comparison of adsorbent performance in dynamic test conditions or in batch set-ups where humidity is better controlled.

Supplementary Materials: The following are available online at http://www.mdpi.com/2077-0472/9/1/16/s1, **Figure S1.** FTIR spectra of treated and untreated (**a**) OAK 250 (**b**) OAK 450, and (**c**) OAK 650 chars including unprocessed oak biomass (as received) (4000–500 cm^{-1}; arbitrary *y*-axis values); **Table S1.** Char nitrogen content before and after exposure to NH_3; **Table S2.** ATR-FTIR functional group assignment of prominent bands, **Tables S3–S6:** ANOVA analysis for Figures 3 and 4a–c, respectively.

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