Article

An Effective Biochar Application for Reducing Nitrogen Emissions from Buffalo Digestate Storage Tank

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Abstract: Open manure storage contributes to the release of ammonia (NH_3) into the atmosphere. Tank floating covers represent an effective technique to reduce NH_3 emissions and biochar has been gain attention as a floating cover and as manure additive. Nevertheless, the mechanisms involved in the process still need to be elucidated since they are influenced by the biochar specific properties, application methods and dose. This work aims to study: (i) the biochar adsorption performances in an NH_3 aqueous solution under conditions relevant to manure storage and (ii) the effect of different biochar application methods and dosage on NH_3 emissions from buffalo digestate storage. The results show that a 43% reduction in NH_3 emissions can be achieved by using biochar as a floating cover of 2 cm rather than as an additive. Moreover, the results show that the biochar produced at 550 °C acts as an adsorbent material for both NH_4^+ and NH_3, by being adsorbed on the biochar surface in the form of NH_4^+ after H^+ abstraction from the acid groups. A minimum cover height of 2 cm is required to give compactness and provide an additional resistance to the gas transfer, which is even more relevant than the adsorption in reducing NH_3 emissions.

Keywords: ammonia emissions; floating cover; manure management; biochar application

1. Introduction

Manure storage is one of the pillars of building systems on modern farms. Proper storage facilities are required to handle the increasing volumes of manure due to intensive livestock farming operations [1], which accounted for an annual European production of 1400 million tonnes of manure in 2013 [2].

Open manure storage is a common practice; however, the continuous N losses, mainly of ammonia (NH_3), require farmers to take measures to save nutrients and reduce environmental risks [3] in compliance with EU Directive 2016/2284, also known as the National Emission Ceilings (NEC) Directive, such as by applying additives to manure or covering storage tanks.

Biochar is the carbon-rich solid product of biomass pyrolysis [4]. In general, biochar has been shown to be effective in reducing gas emissions from manure composting and in recovering nutrients from wastewater due to its sorption capacity [5]. However, it is only recently that biochar has been explored both as a manure additive [6] and a floating cover for storage tanks [7–9], thanks to its tuneable porosity, pH and surface chemistry [10]. Indeed, by acting on the pyrolysis conditions, depending on the initial feedstock composition, it is possible to direct the process toward conditions producing biochar with favourable characteristics for reducing ammonia emissions [11,12]. Kalus et al. [6] summarized the positive effects of biochar addition to different types of animal manure such as dairy cattle

slurry and poultry litter in terms of reduction in greenhouse gases emission and retainment of nutrients. Similarly, many authors showed promising results when biochar is used as storage tank cover. Holly and Larson [13] reported a reduction of 96% of NH_3 emissions covering the 16 L dairy digestate for a storage period of 7 weeks. Maurer et al. [14] recorded a reduction ranging between 13 and 23% with biochar application on swine manure surface of 2.28–4.56 kg/m^2, respectively. Scotto di Perta et al. [8] found that a 2 cm layer of biochar can reduce up to about 80% of the NH_3 emissions from manure storage tank in lab conditions. Covali et al. [15] obtained an NH_3 emissions reduction of 48% with biochar application on digestate surface.

Biochar interacts with ammonia nitrogen dynamically through different mechanisms: (i) adsorbing NH_4^+ in the liquid phase onto the biochar layer partially immersed in the liquid at the top layer of the tank, (ii) adsorbing gaseous NH_3 devolatilizing from the manure tank, (iii) altering the NH_4^+/NH_3 equilibrium in the top layer of the liquid due to its typically basic pH, and (iv) providing a physical barrier at the liquid–surface interface, which reduces the gas transport between the manure surface and the atmosphere [16]. This is even more effective in the presence of adverse weather conditions (e.g., high wind speed) [16]. As reported by [17] in the presence of NH_4^+, electrostatic interaction and cation exchange are the main mechanisms involved. The presence of oxygen-containing functional groups, the negative charge on the biochar surface and the high Cation Exchange Capacity (CEC) [18] are found to be conductive to NH_4^+ adsorption. A positive correlation between CEC of pig manure derived biochar and NH_4^+ adsorption was found [19]. Although some authors have indicated that there is no direct correlation between the porosity and surface area of biochar and NH_4^+ adsorption [19], the microporous structure of biochar increases its selectivity towards NH_4^+ compared to larger molecules in real wastewater systems [20]. In case of gaseous NH_3 adsorption it was observed that physio-sorption is the prevalent mechanism, with respect to chemio-sorption [21]. Biochar improves its adsorption performance as the presence of oxygen-containing functional groups acidic sites increases [22]. This observation was confirmed also in the case of polymer-based adsorbents (Lee et al., 2017) and Metal Organic Frameworks (MOFs) [23]. pH changes induced on the top layer by the presence of biochar are limited due to the high buffering capacity of manure, thus having negligible effects on the equilibrium shift towards NH_4^+ [24].

In the case of manure storage tank covers, all mechanisms coexist, and their relative importance depends firstly on the characteristics of biochar. It is therefore necessary to understand the relationship between biochar properties and NH_4^+-N and NH_3 sorption, so that biochar production can be directed towards higher ammonia sorption, or existing biochars with specific properties can be selected for this purpose [25].

However, the method of biochar application also proved important, i.e., as a bio-mix [26] or bio-cover [27]. For example, it is likely that the role of biochar in adsorbing NH_4^+ from the manure top layer or altering manure pH can be minimized by the buoyancy of the biochar on the manure surface and by its hydrophobicity [15], whereas the thickness of the biochar layer can promote its role in adsorbing gaseous NH_3 and creating a physical barrier. Moreover, the relative importance of the physical barrier offered by the biochar layer and the change induced by the biochar in the chemistry and biological activity at the manure–atmosphere interface is a relevant point to be addressed [28].

In this study a commercial biochar has been used to assess the role of the different mechanisms involved in the mitigation of NH_3 emissions from manure digestate storage tank. To this aim, a preliminary evaluation of the biochar adsorption performances in an ammonia aqueous solution under different conditions relevant to manure storage has been carried out. Then, a lab-scale experimental design, including different biochar applications methods and dosage, has been performed to measure the performance of the biochar in mitigating NH_3 emission. To this purpose, buffalo manure digestate storage was simulated, since buffalo breeding plays a central role in southern Italy for the production of top-quality products, such as mozzarella cheese [29].

The results give indications relevant to the development of optimal biochar application methods and support the use of biochar as a smart approach to promote environmental benefits and efficient resource use in the management of modern farms.

2. Materials and Methods

2.1. Characteristics of Materials

2.1.1. Livestock Digestate Characterization

The digestate used in these experiments was collected from a centralized biogas plant(managed by Power Rinasce Srl in S. Maria La Fossa) in Southern Italy (Caserta province, Campania region), receiving buffalo manure from surrounding local livestock farms. This area, together with the province of Salerno, represents 56% of the territory of the Campania region, where the highest number of buffalo heads are concentrated (more than 290,000 in 2019) in the whole of Italy [30].

Representative digestate samples were collected and pH, Dry Matter (DM), Total Ammoniacal Nitrogen (TAN) and Total Kjeldahl Nitrogen (TKN) were measured according to the standard method [31].

2.1.2. Biochar Characterization

Biochar was purchased from Nera Biochar S.r.l and was produced via pyrolysis (30 min) at 550 °C, using as feedstock mixed wood chips from Piedmont: elm tree, ash tree, chestnut and conifers. The choice of using a commercial biochar was dictated by the possibility of applying, after the storage period, the biochar cover mixed with digestate in the field as soil conditioner and fertilizer. This approach would provide significant benefits in the context of regenerative agriculture as recognized in the REDII-Implementing Regulation. Several European countries have aligned their regulations on the application of biochar as a soil conditioner, with the European Biochar Certificate indicating an H/C_{org} value of 0.7, a value met by the biochar used in the present work. The technical specifications provided by the biochar producer reported a C, H, N and ash content equal to 74.6, 2.0, 0.7, and 3.4 wt% dry basis (db), respectively. Oxygen content, calculated as difference, was 19.3 wt% db, whereas pH was ~10 and Brunauer–Emmett–Teller (BET) surface was 350 m^2 g^{-1}.

The concentration of total OH groups was measured adopting the Bohem titration procedure and provided a value of 0.0697 mmol g^{-1}. The pH at point of zero charge (pH_{PZC}) was evaluated using the salt addition method adapting the procedure described in [32]. A 0.1 M solution of $NaNO_3$ at 30 °C was used as an electrolyte. The initial pH (pH_i) was adjusted in a range of 2 to 12 using NaOH and HNO_3 0.1 M solutions. A biochar dose of 5 g L^{-1} was used. The final pH values (pH_f) were recorded in the remaining suspensions after shaking in a magnetic stirrer for 24 h at 400 rpm. The pH_{PZC}, corresponding to the point where the difference between pH_i and pH_f was equal to 0, was 8.38.

2.2. Ammonia Emissions Assessment from Digestate Storage

Digestate storage was reproduced under laboratory conditions, employing cylindrical glass containers of 5 L and 16 cm diameter. To reduce the parameters influencing the emissions, the experiments were conducted inside a climate-controlled room at 20 °C. Temperature and humidity were checked once a day for the whole experimental period. Glass containers were filled with 3.5 L of digestate. Three different biochar application methods were adopted and compared. In the first test, 140 g of biochar, representing 4 wt% of the liquid digestate sample and about 7 kg m^{-2}, were applied on the surface of the digestate to form a cover 2 cm thick; in the second test a similar configuration was adopted using 70 g of biochar forming a cover 1 cm thick; finally, 140 g of biochar was mixed with the liquid digestate and placed in the jar without any cover. Table 1 summarizes the three different conditions considered and their abbreviations.

Table 1. Experimental set-up.

Treatment	N Source	pH	T (°C)	Duration	Replicates	Abbreviation of Treatments
Biochar cover 2 cm thick						2B
Biochar cover 1 cm thick	Liquid fraction of digestate	8–9	20	84 days	3	1B
No cover, biochar mixed with the liquid solution						Bm

Three replicates were made for each treatment for a total of 9 jars.

Ammonia emissions and pH values were monitored for the whole storing period of 84 days. To measure the pH, an access tube was placed in each jar in order to place the pH meter probe (MT51302523, Mettler Toledo (https://www.mt.com/it/it/home/products/Laboratory_Analytics_Browse/pH-meter/pH-meters/SG23-Meter.html, accessed on 24 June 2024)) below the manure surface without damaging the superficial layer of the biochar.

Ammonia emissions were measured with the dynamic chamber technique, as described by [9]. Specifically, the containers were closed only during the measurement activity to ventilate the headspace of the container once per minute. The airflow rate was adjusted by a flow meter. The containers were closed using a screw lid designed to let air in and to connect the container to an expansion chamber. The air exchange of 1.5 L min^{-1} was performed with a vacuum pump. Before the ammonia sampling, the pump was turned on for 20 min to create a steady condition. Real-time ammonia detection was run for 15 min with a gas-sensitive semiconductor and electrochemical sensors (Aeroqual, https://www.aeroqual.com/s-series-portable-air-monitors/series-500-portable-air-pollution-monitor, accessed on 24 June 2024).

The fluxes were evaluated as follows:

$$F = Q \ (C_{out} - C_{in}) \ A^{-1},$$ (1)

where C_{in} is the gas concentration of air inlet into the chamber in mg m^{-3}; C_{out} is the gas concentration of air outlet from the chamber in mg m^{-3}; Q is the airflow rate through the chamber in m^3 h^{-1}; and A the area of the emitting surface in m^2.

Simultaneously, as suggested by [14], visual surface monitoring was performed every day, to macroscopically observe the cover performance during the storage period.

NH_4^+ adsorbed by the biochar after each storage trial was indirectly estimated using the method described in [33]. For this purpose, the biochar collected from each jar was mixed for homogenization. About 10 g of biochar were collected and washed with 1 l of distilled water to remove digestate residues from the biochar surface and then dried for 48 h at ambient temperature, avoiding possible ammoniacal nitrogen desorption. Then, 1 g of biochar was separated and dried for two hours at 105 °C to measure the residual moisture content needed for further calculations. At the same time, 5 g of biochar samples underwent desorption tests, adapted from [33], by adding 40 mL of 2 M KCl solution and placing the suspension on a magnetic stirrer for 2 h. Then, the suspension was filtered with a Büchner funnel, and the TAN of the filtered solution was measured. The desorbed NH_4^+ was compared to the potential adsorption capacity of the biochar (see Section 2.3).

2.3. Biochar Adsorption Mechanisms Study

Different adsorption tests were performed on biochar to determine the maximum adsorption capacity (q_{max}) and to assess the ability of biochar in adsorbing NH_4^+ or NH_3 from an aqueous solution resembling the conditions established in the digestate storage

tests 1B and Bm. The conditions of the adsorption tests are summarized in Table 2 and described in Sections 2.3.1 and 2.3.2.

Table 2. Synoptic list of adsorption tests.

Aim	Biochar Condition	Solution	Adsorbed Nitrogen Assessment	pH	T (°C)	Duration	Test
To evaluate the maximum NH_4^+ adsorption capacity	Biochar mixed with a NH_4Cl solution in a closed batch experiment	0, 5, 10, 50, and 100 mg/L of $N-NH_4^+$	Differences in NH_4^+ concentrations before and after the trial	unadjusted	room temperature	16 h	n.a.
To discriminate N adsorption as NH_3 or NH_4^+	Biochar mixed with a NH_4Cl solution, in an open batch experiment	1 g/L $N-NH_4Cl$ aqueous solution	• Differences in NH_4^+ concentrations before and after the trial; • NH_4^+ desorbed from biochar.	8.8	20	48 h	M
	Biochar as cover suspended 1 cm over the surface of a NH_4Cl solution		• Differences in NH_4^+ concentrations before and after the trial; • Detecting possible physisorbed NH_3, purging biochar with N_2; • NH_4^+ desorbed from biochar.				Bc

2.3.1. NH_4^+ Maximum Adsorption Capacity

The maximum adsorption capacity (q_{max}) was detected under laboratory batch adsorption experiments at room temperature using NH_4Cl aqueous solutions at different concentrations, adapting the procedure described in [33]. A quantity of 0.5 g of the dried biochar was added into five Polyethylene (PE) vessels containing 40 mL of solution with 0, 5, 10, 50, or 100 mg/L of $N-NH_4^+$, respectively. Each solution was characterized in terms of initial $N-NH_4^+$ concentration. A biochar suspension in distilled water without NH_4Cl was used as a blank run. The vessels containing the suspensions were closed to avoid evaporation and shaken at 400 rpm in a magnetic stirrer for 16 h. Then, the biochar was separated from the aqueous solution by vacuum filtration with MF-Millipore membrane filters, 3 μm pore size. Finally, the filtered solutions were analysed for determining TAN concentration using the spectrophotometric procedure of the indophenol blue method [34]. Adsorbed nitrogen was determined as the difference between the nitrogen concentration of the aqueous solutions before and after the adsorption tests.

2.3.2. Adsorption Tests Using Different Biochar Application Methods

Two adsorption tests were conducted using an NH_4Cl aqueous solution simulating the conditions established in the manure storage experiments in terms of temperature, pH, NH_4^+ concentration and biochar dosage. Two different biochar application methods were used to assess separately the biochar ability to adsorb NH_4^+ (trial M) and NH_3 (trial B_c). A schematic representation of the two application methods is reported in Figure 1.
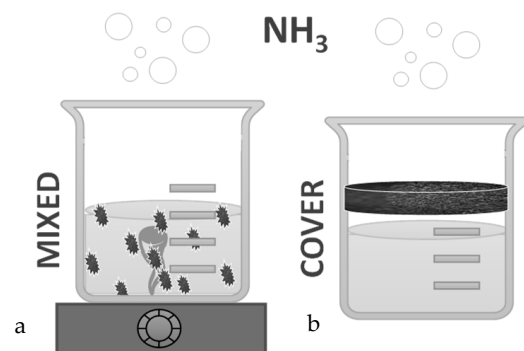

Figure 1. (**a**) Biochar mixed with the liquid solution (M) and (**b**) a biochar layer placed as a suspended cover on the liquid surface (B_c).

Two open beakers were filled with 40 mL of an NH_4Cl aqueous solution with an initial ammoniacal N concentration of 1 g L^{-1} and maintained ad 20 °C using a thermostatic bath for 48 h. The initial pH was adjusted to 8.8 using NaOH, to simulate the digestate conditions. Finally, a biochar load of 4% wt was applied in both experiments. In the first beaker, biochar was added to the liquid solution and continuously mixed on a magnetic stirrer at 400 rpm in order to maintain the biochar in contact with the liquid solution for the duration of the experiment. Under these conditions biochar could adsorb ammoniacal N present in the liquid solution mainly in form of NH_4^+, according to the NH_3/NH_4^+ equilibrium established at 20 °C and pH = 8.8. In the second beaker, biochar was placed on a Teflon grid at the top of the vessel at a distance of 1 cm from the free surface of the solution, which was continuously stirred at 400 rpm. Under this configuration, any contact between the biochar cover and the liquid solution was avoided and only the volatilized NH_3 could be adsorbed by the biochar cover during the experiment. After 48 h the pH was measured in both cases and the experiments were stopped. In the trial M, the biochar was separated from the suspension through vacuum filtration and dried for 48 h at ambient temperature to remove most of the moisture, avoiding possible ammoniacal N desorption. Then, it was subjected to NH_4^+ desorption experiments using the same procedure described in 2.2. The biochar used for the trial B_c was subjected to two subsequent desorption procedures. The first procedure was applied to detect possible physiosorbed NH_3 [21]. This consisted in purging a biochar column with a 3 NL min^{-1} of N_2 flow at 25 °C as described in [22] and detecting the desorbed NH_3 through an FTIR analyser (Sick GME700, detection limits 0–4000 ppm) placed at the end of the biochar column. Then, the purified biochar was retrieved and subjected to the NH_4^+ desorption procedure described in Section 2.2 to detect NH_3 adsorbed in NH_4^+ form on acidic functional groups present on the biochar surface [35].

3. Results

3.1. Storage Tests: Digestate Characteristics, NH_3 Emissions, Surface Monitoring and Biochar Adsorption

After the storage tests, a representative sample of the digestate in each vessel was analyzed in three replicates (Table 3).

Table 3. Digestate characteristics before and after the treatments.

Treatment	DM (g·kg^{-1})	TAN (g·N·$kgDM^{-1}$)	TKN (g·N·$kgDM^{-1}$)
No treatment	46.22 ± 1.23	20.63 ± 0.57	47.46 ± 1.43
2B	62.05 ± 1.23	10.40 ± 1.09	39.28 ± 2.78
1B	66.78 ± 3.94	6.53 ± 0.53	37.75 ± 0.86
Bm	79.84 ± 2.85	6.34 ± 0.22	33.57 ± 1.85

Compared to the initial digestate, the dry matter content increased, highlighting a reduction in the water content of the samples, especially for Bm, whose DM content is almost double the initial value. On the other hand, both TAN and TKN contents were found to decrease after the test. 2B showed the best behaviour, reducing its TAN content by half compared to the initial value.

In Figure 2 the NH_3 emission rates are presented along with pH variations as function of time for the different storage tests performed when applying different biochar application methods.

For all the treatments, the ammonia emission rates decreased gradually, tending to zero approximately after 84 days. Initially, for 1B and 2B, NH_3 emissions were very close to zero until the day 2 and 5, respectively, when an increase in the emission rates was reported, from 0.8 to 4.9 mg NH_3 m^{-2} h^{-1} and from 0.4 to1.5, respectively. Differently, for Bm the emission rate was high even at the beginning of the test and monotonically decreases over time. The test 2B was characterized by a lower cumulative NH_3 emission (10.38 ± 0.57 g NH_3 m^{-2}),

while the cumulative NH_3 emissions are 14.98 ± 0.43 and 18.08 ± 1.31 g NH_3 m^{-2} for 1B and Bm, respectively. All treatments were significantly different ($p < 0.05$).
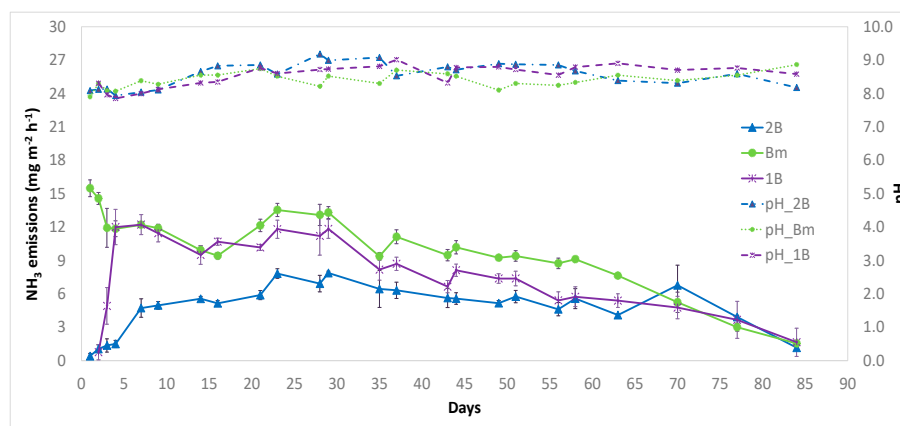

Figure 2. NH_3 emission rates and pH as function of time for 2B (2 cm biochar layer), 1B (1 cm biochar layer) and Bm (biochar mixed with digestate).

No significant difference was found for the pH trend during the experiment, which varied between 7.9–9.2, 7.9–9 and 7.9–8.9 for 2B, 1B and Bm respectively.

The surface of the digestate in each type of storage test changed substantially during the study. The 1B cover started breaking in the middle of the vessel and sinking after 21 days (in one of the replicates) consistently with the thinner and less resistant biochar layer (Figure 3a). At the same time, a slight increase in ammonia emissions was observed in one sample, from an average of 9.9 on day 16 to 13.1 g NH_3 m^{-2} in the following days. During the following weeks, the other replicates went through the same process, resulting in an average emission rate of 11.8 g NH_3 m^{-2}.
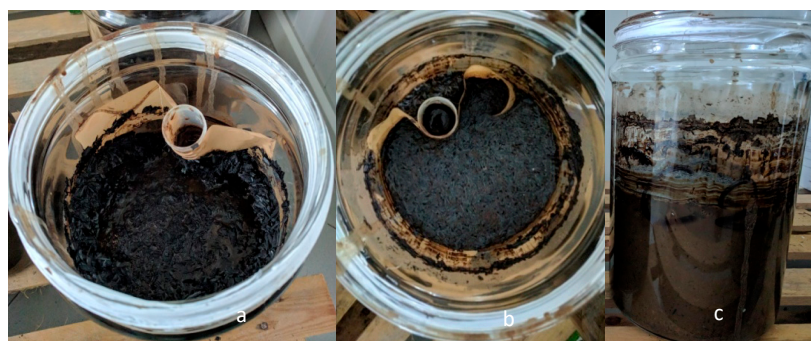

Figure 3. (**a**) The 1B cover breaking and sinking after 21 days; (**b**) Biochar floating and forming a crust after 3 weeks; (**c**) Volume reduction consequent to water evaporation after 50 days.

After the first 21 days, Bm showed the formation of a crust made up of biochar previously mixed into the digestate (Figure 3b). The biochar started floating and formed a crust that thickened as time goes by. In this test, a reduction of the digestate volume/level was also noted, consistently with the water evaporation (Figure 3c) and the consequent increase in DM content at the end of the trial (Table 3).

The 2B cover remained almost intact until week 9. At the same time, a pick of 6.8 mg NH_3 m^{-2} h^{-1} in the NH_3 emission rate curve was observed; then the biochar cover started to be increasingly submerged by the liquid.

Biochar ammonia adsorption during the storage tests was assessed applying a N-NH_4 desorption procedure. As a matter of fact, biochar from the test 2B desorbed 0.122 mg N-NH_4 g^{-1}$_{biochar}$, while biochar from 1B desorbed 0.069 mg N-NH_4 g^{-1}$_{biochar}$, consistently with the lower amount of thickness of the latter. A similar amount of adsorbed N was

observed for Bm, which accounts for 0.075 mg $N-NH_4$ $g^{-1}_{biochar}$, although the biochar amount in this test is the same as the test 2B.

3.2. Biochar Adsorption Mechanisms Study

3.2.1. NH_4^+ Biochar Adsorption Capacity

The effect of the initial concentration of $N-NH_4^+$ (C_0) on the biochar equilibrium adsorption capacity (Q_e) is reported in Figure 4. During the procedure, the pH of the solutions decreased from 6.3 to 5.7 as the $N-NH_4^+$ concentration increased from 5 to 100 mg/L. Biochar addition caused the increase of pH to values higher than 7.5. As shown, the adsorption capacity increased linearly as C_0 increased, indicating that the saturation of the adsorption sites was not achieved in the investigated C_0 range.
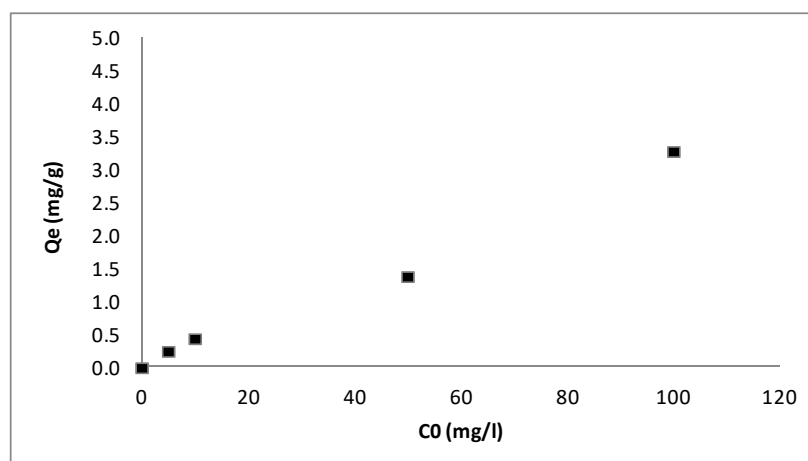
Figure 4. Biochar equilibrium adsorption capacity of NH_4^+ (Q_e) at increasing concentrations of $N-NH_4^+$ (C_0) (T = 25 °C).

3.2.2. Assessment of Biochar Ammoniacal N Adsorption Mechanisms

The results of adsorption tests in aqueous NH_4^+Cl solutions using different biochar application methods are reported in Table 4. The ammoniacal N potentially adsorbed represents the difference between the ammoniacal N amounts in the M and Bc solutions before and after the adsorption tests reported on a biochar weight basis. Concentrations of $N-NH_3$ and $N-NH_4^+$, expressed as $mg/g_{biochar}$, represent the actual amount of the different forms of ammoniacal N measured through the different desorption procedures. More specifically, concentrations of $N-NH_3$ and $N-NH_4^+$ account for physically and chemically adsorbed N, respectively.

Table 4. $N-NH_3$ and NH_4 adsorbed in test 3.

Tests	M	Bc
Ammoniacal N potentially adsorbed (mg $g_{biochar}^{-1}$)	5.1	3.4
$N-NH_3$ (mg $g_{biochar}^{-1}$)	n.d.	n.d.
$N-NH_4^+$ (mg $g_{biochar}^{-1}$)	0.1	1.2

The loss of ammoniacal N in the M test is more than sixfold higher than that in the Bc test. On the other hand, the adsorption of ammoniacal N in form of NH_4^+ is higher in the Bc than in the M test, whereas no $N-NH_3$ adsorption was detected in both tests.

4. Discussion

4.1. Ammonia Emissions

Biochar application during digestate storage reduced NH_3 emission differently depending on biochar application methods and doses in agreement with the literature, where

a wide variation range of NH_3 reduction, from 0 to 96%, was reported for different application methods, doses, biochar characteristics and manure/digestate type. A summary of the literature data is reported in Table 5.

In some studies, mixing biochar with manure [5,28] or using it as a floating cover [14] had no positive effect on reducing NH_3 volatilisation, suggesting that biochar did not significantly alter the pH and N dynamics in the stored manure [14,28], or if an increase in emission was observed, this may be due to the low adsorption capacity of biochar and the high TAN content of the manure [5]. In this study, lower NH_3 emissions were observed for the 2B test (2 cm biochar layer), while in the 1B (1 cm biochar layer) and Bm (biochar mixed with digestate) tests, digestate emitted 44% and 74% of ammonia more than in the 2B case. These results confirm the findings reported by [13], which showed lower ammonia emissions when biochar was applied on the surface, with a maximum reduction with respect to the control of 96% obtained with wood biochar. On the other hand, opposite results were obtained by [15], reporting a greater emission mitigation (52%) in the case of biochar incorporated into digestate with respect to that in which biochar was applied on the surface. However, in this case, a low temperature biochar was used, which is, presumably, richer in oxygen containing functional groups typically involved in ammonia adsorption. In this study, the difference between the tests 2B and Bm, where the amount of biochar applied is the same, can be mainly attributed to the formation of a physical barrier in the test 2B. This hypothesis is confirmed by the final values of ammoniacal N concentrations in the digestate in the two tests which are in good agreement with the ammonia emissions reduction. The effect of the physical barrier is evident also in the highest water evaporation corresponding to the highest dry matter increase in absence of biochar surface layer. The effect of biochar cover in reducing ammonia emissions is more efficient when the mechanical resistance to surface cracks is higher due to the greater thickness, as results when comparing the emissions and the ammoniacal N in the digestate after the storage test in cases 2B and 1B. This observation was also supported by the different ammonia emissions observed in the NH_4Cl aqueous solution resembling the digestate storage tests. In that case, NH_3 devolatilization in Bc is significantly reduced by the presence of the biochar cover, probably due to the achievement of the equilibrium pressure in the headspace at the interface between the free NH_3 dissolved in the solution and NH_3 in air, according to Henry's law [36]. On the contrary, in the M test, ammoniacal N is mostly released due to NH_3 devolatilization, as confirmed by the reduction in pH of the solution from 8.8 to 7.6 observed during the test.

4.2. Biochar Adsorption Mechanisms

The biochar performance in terms of maximum adsorption capacity was not so notable, due to pH values lower than pH_{PZC} (8.38). Under the conditions of the tests, NH_4^+/NH_3 equilibrium was mainly shifted towards NH_4^+ and the charge distribution on the biochar surface was positive due to pH lower than pH_{PZC}. In these conditions, the ammoniacal N adsorption through cation exchange between NH_4^+ and H^+ on the biochar surface was not favoured due to the high concentration of H^+ in the aqueous solution and the electrostatic repulsion between NH_4^+ and the positively charged biochar surface. However, when the conditions established during the manure storage tests (T = 20 °C, pH in the range 8–9 and ammoniacal N concentration equal to 1 g/L) were reproduced in the NH_4Cl aqueous solution (tests M and Bc), according to NH_4^+/NH_3 equilibrium at 20 °C, free NH_3 concentration ranges between 4 and 29% and when pH is higher than 8.38 the charge distribution on the biochar surface shifts from positive to negative. Different mechanisms can occur under these conditions such as: (i) physio-sorption of gaseous NH_3 in the biochar micropores [37], (ii) reaction of NH_3 at the oxygen groups on the biochar surface leading to the formation of amines and amides [38], (iii) NH_3 protonation at the acid functional groups on the biochar surface followed by NH_4^+ adsorption [38], (iv) NH_4^+ adsorption through cation exchange [37].

Table 5. Biochar application at storage in the literature.

Biochar Characteristics						Liquid Stored Characteristics					NH$_3$ Emissions Reduction (%)	Storage Duration	Ref.
Feedstock Origin	Pyrolisys Temperature (°C)	pH	pH$_{PZC}$	Application	Dose	Type	T (°C)	pH	DM	TKN			
corn stover	500	9.2	8.42	One-Time surface Application / One-Time surface Application / Bi-Weekly surface Reapplication	2 kg/m² / 4 kg/m² / 2 kg/m²	deep pit swine manure	-	-	4.6–8.2%	4340–7350 mg/L	33 / 25 / 53	8 weeks	[39]
red oak	500	7.5	6.75	One-Time surface Application	1.65 kg/m²	swine manure	-	7.47 / 8 / 7.55	2.64% / 4.07% / 2.6%	16.10% / 13.37% / 11.88%	19 / 21 / 39	4 weeks	[24]
corn stover	500	9.2	8.42	One-Time surface Application	2 kg/m²			7.47 / 8 / 7.55	2.64% / 4.07% / 2.6%	16.10% / 13.37% / 11.88%	18 / 21 / 4		
blueleaf (softwood)	450	8.6	–	mixing with manure	0, 2.5, 5, 10, and 25% biochar by volume	liquid swine / dairy slurry / solid poultry manure	21	7.4 / 7.5 / 9.4	49 g/kg / 38 g/kg / 591 g/kg	11.1 mgN/L / 20.4 mgN/L / 44.5 mgN/L	no reduction	21 days	[28]
dynamotive (hardwood)	750	7.4	–			liquid swine / dairy slurry / solid poultry manure		7.4 / 7.5 / 9.4	49 g/kg / 38 g/kg / 591 g/kg	11.1 mgN/L / 20.4 mgN/L / 44.5 mgN/L			
pine	495–505	7.28	–	One-Time surface Application / two surface-applied biochar	2.28 kg/m² / 4.56 kg/m² / 1.14 kg/m² / 2.28 kg/m²	swine manure	12.5	8 / 7.8	8.50% / 7.7%	10.6 g N/L / 9.9 g N/L	no reduction / 12.7 / no reduction / no reduction	30 days / 35 days	[40]
reed canary	300	6.4	–	One-Time surface Application / mixing with manure	5% by weight	digestate	-	8.2	4.06%	6.87%	48 / 52	240 days	[15]
white birch	400	7.7	– / –	One-Time surface Application / mixing with manure	3.6% by weight (5 cm) / 3.6% by weight (5 cm)	Digested dairy manure	20–21	7.7 / 7.7	41 g/kg / 28 g/kg	46 g N/kg / 88 g N/kg	96% / <96%	7 weeks	[13]
cob		9.88	– / –	One-Time surface Application / mixing with manure	2.4% by weight (5 cm) / 2.4% by weight (5 cm)			7.7 / 7.7	27 g/kg / 42 g/kg	54 g N/kg / 50 g N/kg	<<96% / <<<96%		
walnut shell coconut shell coal	500	10.34 7.54 7.61	-	mixing with manure	5% by weight	Liquid pig manure	-	6.16	-	28.0 gN/kgDM	increased the NH$_3$ emissions by 4.00, 3.87, and 1.23 times,	68 days	[5]
wood chips: elm tree, ash tree, chestnut and conifers	550	10	8.38	One-Time surface Application / mixing with manure	7 kg/m² (2 cm) / 3.5 kg/m² (1 cm) / 7 kg/m²	Digested buffalo manure	20	8.1	46.22 g/kg	20.63 g N/kg DM	control / 44% > control / 74% > control	84 days	this study

In this study, the physio-sorption of gaseous NH_3 was not observed (see Table 4) since, as suggested by [17], NH_3 physical interaction with the surface of the biochar is expected to be very weak due to the small size of the molecule. The results of the Bc test indicated that all the volatilized NH_3 is adsorbed on the biochar surface in the form of NH_4^+ after H^+ abstraction (NH_3 protonation) from the acid groups on the biochar surface, whose presence is confirmed by the measured total acidity (0.0697 mmol/g). In this case, only a small reduction of pH from 8.8 to 8.4 is observed from the beginning to the end of the test, in agreement with the low amount of volatilized NH_3. These findings are in good agreement also with [22], which showed similar ammoniacal N adsorption (0.84 mg/$g_{biochar}$) on wood shaving derived biochar produced at 500 °C. As observed by other authors [41,42], the greater the number of acidic functional groups (especially hydroxyl and carbonyl groups), the greater the NH_3 adsorption capacity of the biochar.

Finally, the results of the M test showed that, under the conditions resembling the digestate storage tests, NH_4^+ adsorption through cation exchange was negligible. Indeed, only 2% of the ammoniacal N lost is adsorbed on the biochar surface in form of $N-NH_4^+$, and ammoniacal N is mostly released due to NH_3 devolatilization. This result can be explained considering that the pH reduction from 8.8 to 7.6 determines a shift towards the NH_4^+ form of the ammoniacal nitrogen and a net positive charge on the biochar surface exerting an electrostatic repulsion against the NH_4^+ ions.

These observations are useful in elucidating the mechanisms occurring in the real case of digestate storage tests. In case of biochar cover remaining intact for all the storage test (case 2B), biochar adsorbed higher amount of $N-NH_4$ than biochar mixed with digestate (case Bm), similarly to what has been observed for the tests with NH_4Cl aqueous solutions, thus suggesting that the biochar used in this study has a greater ability to adsorb NH_3 than NH_4^+. Differently from the NH_4Cl aqueous solution in the case of biochar incorporation into the liquid (case M), in the real case of digestate test, given the buffering ability of digestate, the pH of the digestate remained higher and close to the pH_{PZC} under conditions more favourable to NH4+ adsorption. However, in the real case. different ions other than H^+ are in the water solution, which can interact with the biochar, affecting its adsorption selectivity towards ammoniacal N [43], as suggested by the lower $N-NH_4^+$ adsorbed by the biochar in the test Bm compared to the test M (i.e., 0.075 and 0.1 mg g^{-1}, respectively). Moreover, in the real case, the macropores of the biochar, which represent the access routes of ammoniacal N to the adsorption sites, could be obstructed by digestate particles after the mixing of biochar and digestate, thus limiting the adsorption potential of the biochar [13].

When the biochar cover cracks and is submerged by the liquid digestate (case 1B), the adsorption ability is comparable to that of biochar mixed with the digestate, due to the reduced exposure of biochar to gaseous NH_3.

5. Conclusions

In this study, the performance of a commercial biochar in mitigating the ammonia emissions from digestate storage tanks was evaluated and the main mechanisms involved have been discussed. The results of this study suggested that:

- the biochar acts as an adsorbent material, both for NH_4^+ and NH_3;
- the main adsorption mechanism involves NH_3 protonation on the biochar by H^+ abstraction from the acid group's surface to form NH_4^+. The adsorption of NH_4^+ through cation exchange is less relevant, whereas the physio-sorption of gaseous NH_3 does not occur. Moreover, in this case there is not any issue related to digestate pH and to the possible competition with other cations in the liquid digestate;
- when the biochar layer is floating and compact, it introduces an additional resistance to the gas transfer. This aspect is even more impacting than the NH_3 adsorption on the NH_3 emissions reduction. Nevertheless, it would be interesting to investigate biochar activation, which may increase the adsorption capacity of biochar, and test the possibility of further improving ammonia emission reduction.

Overall, the results show that a 43% reduction in NH$_3$ emissions can be achieved by using biochar as a floating cover of 2 cm rather than as an additive. These findings suggests that biochar application as a cover should be preferred to its mixing with digestate, since the mitigation of ammonia emissions is mainly due to the increase of mass transfer resistance and gaseous NH$_3$ adsorption. These thinner layers of biochar were considered to compete with conventional floating cover materials, which require greater thickness (10–20 cm). A greater thickness of biochar could be even more effective, but its economic viability should be investigated. However, further research into the durability of biochar layers in terms of resistance to weathering at farm scale would be of interest. Finally, a systematic study on the effect of surface chemistry is needed to clarify if the findings of this study can be extended to other types of biochars.

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