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TECHNICAL NOTE

Fenton oxidation of biochar improves retention of cattle slurry nitrogen

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Abstract

Nitrogen (N) losses during fertilization with livestock slurry, mainly in the form of ammonia (NH_3), can cause environmental problems and reduce fertilizer efficiency. Leonardite, which is characterized by oxygen-rich functional groups and low pH, has been found to decrease losses of slurry N. However, leonardite, as a byproduct of open-cast lignite mining, is not a renewable resource. The objective of this study was to modify biochar by chemical surface oxidation in order to find a sustainable but similarly effective substitute for leonardite. Biochar was produced from spruce sawdust in a pyrolysis oven at a maximum temperature of 610 ˚C. Then the biochar was oxidized using the Fenton reaction, with a ratio of Fe^{2+}/H_2O_2 of 1:1,000, as a source of highly reactive HO· radicals to introduce oxygen-rich functional groups to the biochar surface. The ammonium (NH_4^+) adsorption capacity of biochar, oxidized biochar, and leonardite was tested in ammonium sulfate [$(NH_4)_2SO_4$] solution, pH-adjusted $(NH_4)_2SO_4$ solution, and cattle slurry. The results showed that biochar had the highest total NH_4^+ adsorption of 1.4 mg N g^{-1} in $(NH_4)_2SO_4$ solution, whereas oxidized biochar had the highest reversible NH_4^+ adsorption of 0.8 mg N g^{-1}. In the pH-adjusted ammonium solution, all materials reduced NH_3 emissions by ≥90%, and oxidized biochar reduced NH_3 emissions by 99.99%. In contrast, leonardite reduced NH_3 emissions the most in cattle slurry, and oxidation of biochar increased the reduction in NH_3 emissions from 22 to 67% compared with non-oxidized biochar. In conclusion, biochar oxidized by means of the Fenton reaction greatly decreased NH_3 emissions by increased adsorption of NH_4^+ in cattle slurry compared with non-oxidized biochar, indicating the great potential of oxidized biochar for reducing N losses during slurry application.

1 | INTRODUCTION

Nitrogen (N) is one of the most essential nutrients for plant growth. Livestock slurry, containing easily available carbon (C) and ammonium (NH_4^+), is a traditional organic fertilizer. However, it has been reported that up to 29% of the slurry-N

Abbreviations: BET, Brunauer–Emmett–Teller; CEC, cation exchange capacity; CM, carbonaceous material.

can be emitted to the atmosphere via ammonia (NH_3) volatilization during the fertilization process (Bouwman et al., 2002). During nitrification, NH_4^+ can be converted to nitrate (NO_3^-), which is highly mobile in soil and can pollute water bodies through leaching. Part of the N can also be converted to nitrous oxide (N_2O) by nitrification and denitrification, which contributes to global warming (Reay et al., 2012; Zhang et al., 2015).

In addition to agricultural management practices, such as adjusting fertilizer placement and application rates (He et al., 2014; Pan et al., 2016), many studies have attempted to add soil amendments, such as carbonaceous material (CM), to improve N retention (Lehmann et al., 2011; Pitman, 2006; Spokas et al., 2012). Previous studies have shown that leonardite, an oxidized form of lignite, has the potential to mitigate slurry-N loss due to its acidity and high cation exchange capacity (CEC) (Cao et al., 2022; Manzoni & Porporato, 2009). However, because leonardite originates from near-surface mining of lignite, it is not a sustainable resource. Therefore, sustainable sources of CM, such as biochar, could provide a suitable alternative and increase acceptance in practice.

Biochar is a readily available and renewable resource, and its benefits as a soil amendment have attracted the attention of a growing number of researchers over the past few decades (Schmidt et al., 2021). The composition and effectiveness of biochar varies depending on the raw material, pyrolysis temperature, and time or rate of heating (Ippolito et al., 2020). Biochar produced by slow pyrolysis of wood cuttings and rice husks at 600 ˚C for 10 h adsorbed up to 60% of the NH_4^+ from anaerobic pig slurry digestate at an application rate of 30 kg m^{-3} slurry, while its adsorption capacity was related to contact time, pH, NH_4^+ concentration, and biochar particle size (Kizito et al., 2015). Biochar produced from corn cobs, grapefruit peels, and banana stems by pyrolysis at 200 ˚C for 21 d retained 90% of NH_4^+ of an ammonium sulfate [$(NH_4)_2SO_4$] solution due to oxygen-rich functional groups (Cai et al., 2016).

It is known that oxygen-containing functional groups, such as carboxylic acid and keto and hydroxyl groups, promote adsorption of heavy metals and organic molecules (Mandal et al., 2017) and can also adsorb NH_3 either by proton exchange, thereby forming adduct ions, or by chemical reactions, therby forming amines and amides on the surface of biochar (Seredych & Bandosz, 2007). Hydrogen peroxide (H_2O_2) is an oxidant that can change the properties of biochar by introducing oxygen functional groups while only producing H_2O and O_2, which are not harmful to the environment (Huff & Lee, 2016). Several studies have shown that the oxidation of biochar with H_2O_2 improves the removal of heavy metals from aqueous solutions (Wang et al., 2018; Zuo et al., 2016). Huff and Lee (2016) used different concentrations of H_2O_2 to oxidize pinewood biochar and showed that high concentrations of H_2O_2 increased the CEC of biochar. However, the efficiency of this modification is usually very low and requires long reaction times and additional heating (Wang et al., 2016). Therefore, a faster and more efficient oxidation method would be a great advantage.

Core ideas

- Nitrogen losses from manure cause environmental problems.
- Renewable biochar has a great potential to reduce nitrogen losses.
- The Fenton reaction introduces oxygen functional groups on the surface of biochar.
- The Fenton reaction improves the adsorption capacity of biochar for ammonium.

Fenton oxidation is a complex chain of reactions between H_2O_2 and Fe(II) ions in acidic solutions, mainly producing the highly reactive HO· radical, which is one of the most powerful oxidants (Bachi et al., 2013). Xu et al. (2020) reported that Fenton modification of biochar, including iron-promoted pyrolysis and H_2O_2 oxidation, improved adsorption of hexavalent chromium and methylene blue. In contrast, the effect of the Fenton reaction on the NH_4^+ adsorption capacity of common biochar has not been studied. To our knowledge, there is only one study available that reported a Fenton-mediated enhancement of ammonium adsorption of hydrochar, a material that is produced by high-temperature and high-pressure conversion of organic material in an aqueous medium (Belete et al., 2021).

The objectives of this study were to investigate whether the Fenton reaction can directly and effectively oxidize common biochar and enhance the functional groups on the surface for improving the NH_4^+ adsorption capacity of biochar in aqueous solutions and livestock slurry. In this study, we produced biochar from spruce sawdust in a pyrolysis oven and subsequently oxidized the biochar by Fenton oxidation with a Fe^{2+}/H_2O_2 ratio of 1:1,000. Sawdust is a common and abundant byproduct of sawmills and is considered a promising feedstock for biochar and alternative fuels (Beiyuan et al., 2017; Ghani et al., 2013). Then, we compared the NH_4^+ adsorption capacity of biochar, oxidized biochar, and leonardite. We hypothesized that Fenton oxidation would introduce oxygen functional groups to the surface of the biochar and increase the NH_4^+ adsorption capacity of the biochar to the same level as that of leonardite.

2 | MATERIALS AND METHODS

2.1 | Biochar production

The biochar was produced from small particles of spruce sawdust (no. 823 "Siebgut fein") from Holz Ruser. The spruce sawdust was produced in a custom-made pyrolysis oven, and the pyrolysis process was terminated when the flame at the top of the oven changed color from yellow to blue, indicating a change from combustion of organic volatiles to C monoxide (i.e., the completion of wood gasification). The maximum temperature reached during the production process was 610 ˚C.

2.2 | Biochar oxidation

Oxidized biochar was produced by applying the Fenton reaction. For this purpose, 4 g biochar was added to 40 ml of a solution of 30% H_2O_2 and ferrous sulfate ($FeSO_4 \cdot 7H_2O$) with a ratio of Fe^{2+} to H_2O_2 of 1:1,000. The reaction process was intense, with formation of a large amount of foam that lasted for about 10 min. The oxidized biochar was rinsed with deionized water and dried at 65 ˚C for 2 d.

2.3 | Characterization of CM

The properties of the CM were analyzed by a commercial laboratory (Ruhr Lab GmbH). Proximate analysis of ash and volatile matter content was performed in line with German standards DIN 51719 (1997) and DIN 51720 (2001), respectively. Elemental analysis included C, N, and hydrogen (H) content and molar ratio of H to organic C (H/C_{org}) (performed according to the standard DIN 51732 [2014]); sulfur (S) content (based on the standard DIN 51724-3 [2012]); and oxygen (O) and the molar ratio of O to organic C (C_{org}) carried out in line with the standard DIN 51733 (2016), where C_{org} was derived from the total C content minus the inorganic C (CO_2) content in the CM. Solid surface area was determined by Brunauer–Emmett–Teller (BET) multipoint (N_2) surface area analysis based on the standard DIN ISO 9277 (2014). The main elements from the borate digestion of ash (i.e., calcium [Ca], iron [Fe], potassium [K], magnesium [Mg], sodium [Na], phosphorous [P], S and silicon [Si]) were analyzed according to the standard DIN EN ISO 11885 (E22) (2009).

2.4 | Determination of NH_4^+ retention and release

For the determination of NH_4^+ retention, 500 mg biochar, oxidized biochar, or leonardite were added to 40 ml of $(NH_4)_2SO_4$ solution with 100 mg NH_4^+–N L^{-1} (pH 5.55). The solution was shaken at 200 rpm for 20 h and centrifuged at 3,500 rpm for 10 min (20 min for leonardite, which was applied as powder), and the supernatant was filtered through a 0.45-μm syringe filter (ProSense). The residual sample was rinsed several times with deionized water and then added to 40 ml deionized water to determine the NH_4^+ release of previously retained NH_4^+, shaken at 200 rpm for 20 h, and treated following the same steps as described above for the determination of NH_4^+ retention. All solutions were stored at −22 ˚C until the NH_4^+ content was analyzed by continuous flow analysis (CFA Analyzer FLOWSYS 3-Kanal, Alliance Instruments).

2.5 | Measurement of NH_3 emission

To further investigate the effects of CM on NH_4^+ adsorption, we prepared a pH-adjusted $(NH_4)_2SO_4$ solution containing 0.22% N, corresponding to 2,200 mg NH_4^+-N L^{-1}, and adjusted the pH to 6.8 with 0.01 M sodium hydroxide (NaOH) to resemble the pH and N content of the cattle slurry used below. The different CM (biochar, oxidized biochar, leonardite) were added to the solution at a rate of 50 g C L^{-1} and mixed well, and then NH_3 emission was measured with an infrared laser gas analyzer (G2508, Picarro Inc.) with a dynamic chamber (50 mm high, 50 mm diameter) in closed-loop mode tightly covering each sample for 10 min. The same set of CM was tested in the same way in real cattle slurry with 0.22% N and pH 6.7. After each NH_3 emission test, 10 ml of deionized water was added to the CM+ slurry mixture to measure the pH because the mixture was too thick for direct measurement. The NH_3 emission reduction efficiency was calculated based on the difference in NH_3 emissions from pH-adjusted $(NH_4)_2SO_4$ solution or cattle slurry with and without CM added.

2.6 | Calculations and statistical analysis

All results are expressed as the mean ± SD of at least three replicates. After accounting for statistical requirements (normal distribution and homogeneity of variance), the significance of the differences between treatments was analyzed by one-way ANOVA and Tukey's HSD as a post hoc test at a significance level of $p < .05$ (SPSS Statistics for Windows, Version 25.0, IBM Corp.).

3 | RESULTS

3.1 | Physicochemical properties of CM

Table 1 shows the physicochemical properties of the CM used in this study. The non-oxidized biochar had the highest C

TABLE 1 The physicochemical properties of the organic materials used in this study

Properties	Leonardite	Biochar	Oxidized biochar
pH_{H2O}	4.29	5.27	3.22
Specific surface area (BET), $m^2\ g^{-1}$	1.10	193.04	25.17
C, % w/w_{total}	47.88	72.07	62.12
H, $\%w/w_{total}$	2.93	2.92	3.30
N, $\%w/w_{total}$	0.85	0.15	0.09
S, $\%w/w_{total}$	1.47	0.03	0.01
O, $\%w/w_{total}$	19.37	17.88	28.1
H/C_{org}	0.73	0.48	0.63
O/C_{org}	0.32	0.19	0.35
Volatile matter, % w/w_{total}	41.88	29.96	47.88
Ash, w/w_{total}	15.32	2.54	0.77
Ca as CaO, % w/w_{ash}	20.4	22.0	27.5
Fe as Fe_2O_3, % w/w_{ash}	5.6	19.2	17.0
K as K_2O, % w/w_{ash}	0.4	8.2	6.2
Mg as MgO, % w/w_{ash}	6.7	3.5	4.9
Na as Na_2O, % w/w_{ash}	3.0	0.8	0.8
P as P_2O_5, % w/w_{ash}	<0.1	2.5	3.7
S as SO_3, % w/w_{ash}	23.6	1.5	4.9
Si as SiO_2, % w/w_{ash}	28.5	24.1	19.1

Note. The percentages of Ca as CaO, Fe as Fe_2O_3, K as K_2O, Mg as MgO, Na as Na_2O, P as P_2O_5, S as SO_3, and Si as SiO_2 are based on borate-digested biochar ash. BET, Brunauer–Emmett–Teller.

content of 72%. Oxidation increased the O content of biochar from 18 to 28% and reduced the pH from 5.3 to 3.2. The BET multipoint (N_2) determination of the specific biochar surface area yielded 193 $m^2\ g^{-1}$, which was 6.7 and 192 times higher than that of oxidized biochar and leonardite, suggesting that the non-oxidized biochar had the largest surface area. Non-oxidized biochar had also the smallest H/C_{org} and O/C_{org} ratios, which are associated with high aromaticity and low degree of oxidation.

3.2 | NH_4^+ retention and release

In the non–pH-adjusted $(NH_4)_2SO_4$ solution with 100 mg NH_4–N L^{-1}, the non-oxidized biochar showed the highest NH_4^+ retention capacity of 1.4 mg N g^{-1} biochar, which was significantly higher than that of the oxidized biochar (0.9 mg N g^{-1}) (Figure 1). In contrast, oxidized biochar had the highest exchangeable NH_4^+ content (0.8 mg N g^{-1}) of all CM (i.e., three times higher than that of biochar and 1.6 times higher than that of leonardite).

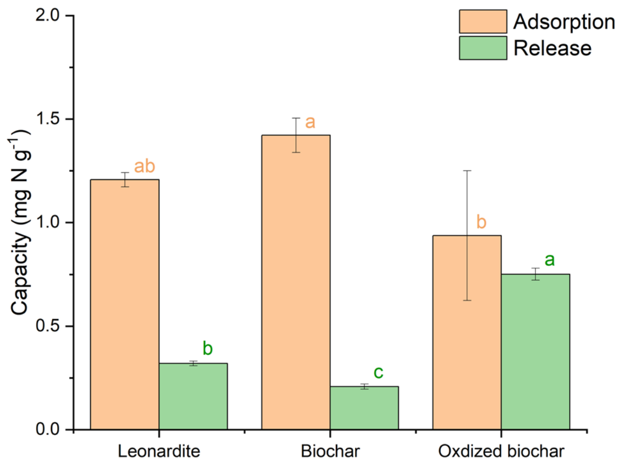

FIGURE 1 The NH_4^+ retention capacity of carbonaceous materials in aqueous $(NH_4)_2SO_4$ solution and NH_4^+ release in deionized water. The error bars show the SEM of each treatment ($n \geq 3$). Different lowercase letters indicate significant differences at the $p < .05$ level between treatments

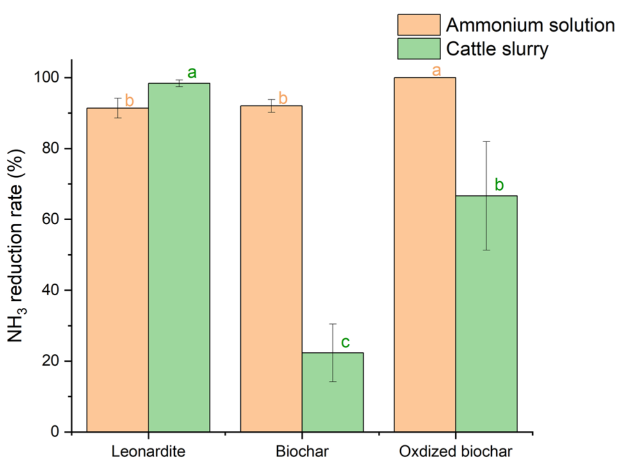

FIGURE 2 The NH_3 reduction rates of carbonaceous materials in pH-adjusted ammonium solution and cattle slurry (pH 6.8 and 6.7). The error bars show the SEM of each treatment ($n = 3$). Different lowercase letters indicate significant differences at the $p < .05$ level between treatments

3.3 | Reduction of NH_3 emission

In the pH-adjusted $(NH_4)_2SO_4$ solution, all CM reduced NH_3 emissions by >90%, with the highest reduction efficiency of 99.99% for oxidized biochar (Figure 2). For cattle slurry, the NH_3 emission reduction efficiency was in the following order: leonardite (98%) > oxidized biochar (67%) > biochar (22%) (Figure 2). The pH values of the slurry mixtures with and without CM were in the following order: leonardite (6.22) < oxidized biochar (6.69) < biochar (6.92) < cattle slurry (6.95).

4 | DISCUSSION

4.1 | Effect of Fenton oxidation of biochar on NH_4^+ retention and release

Fenton oxidation increased the oxygen content by 10 percentage points and reduced the pH of the biochar from 5.3 to 3.2 (Table 1), indicating that oxygen functional groups were introduced to the surface of the biochar (Cheng et al., 2008). However, oxidation did not increase the amount of NH_4^+ retained from the $(NH_4)_2SO_4$ solution compared with biochar. One reason could be that the increasing volatile matter (Table 1) in the oxidized biochar blocks the pores and then reduces the surface area (Table 1), thus limiting the adsorption of NH_4^+ during the pore filling process (Ambaye et al., 2021; Bourke et al., 2007). Another important reason for the lower NH_4^+ retention rate of oxidized biochar may have been its low pH value. A high degree of protonation of the oxygen functional groups in the acidic $(NH_4)_2SO_4$ solution might have led to a neutral or even positive surface charge that reduced the electrostatic attraction of NH_4^+ (Kizito et al., 2015; Novak et al., 2010). This is supported by studies that have shown that protons and some metals, such as aluminum (Al) and Fe, occupy exchange sites at low pH, which then limit the adsorption of NH_4^+ on biochar (Halim et al., 2013; Sarkhot et al., 2013; Wang et al., 2015).

The higher NH_4^+ retention capacity of biochar may be due to its superior BET surface area (Table 1), which would be less influenced by pH. The high surface area of biochar may be related to its low H/C_{org} ratio, with values <0.7 indicating a mostly aromatic structure (Kuhlbusch & Crutzen, 1995). The high degree of aromaticity indicates that the aliphatic alkyl and ester groups shielding the aromatic core are completely destroyed, and the nanopores within the aromatic C structures increase the surface area (Chen et al., 2008; Sun et al., 2016; Xiao et al., 2016). Chen et al. (2008) found that the surface area increased significantly when the H/C ratio was <0.5, and this was confirmed by our results, with a surface area of biochar of 193 m^2 g^{-1} at an H/C_{org} ratio of 0.48. Wei et al. (2020) produced a series of biochars from herbal residues at different pyrolysis temperatures and investigated their adsorption mechanisms. They found that when the H/C ratio was <0.5, the number of surface acidic groups was <70 cmol kg^{-1}, and the retention mechanism was dominated by pore filling (i.e., absorption). However, when the H/C ratio was >0.5, the number of surface acidic groups increased with increasing H/C values, and chemical bonding at the surface played the dominant role (i.e., adsorption). In our study, the non-oxidized biochar with an H/C_{org} ratio of 0.48 had a high NH_4^+ retention capacity in acidic solution due to its higher absorption capacity (i.e., filling of microcavities) compared with leonardite and oxidized biochar, which were characterized by higher adsorption capacity (i.e., physicochemical bonding at the surface).

In this study, deionized water was used to determine the NH_4^+ release rate of biochars, showing the different NH_4^+ retention strengths of different biochars. After shaking for 20 h, the non-oxidized biochar released the lowest amount of NH_4^+ into deionized water, which further supports the assumption of a strong physical retention of NH_4^+ in the microcavities of the biochar (Saleh et al., 2012). In contrast, oxidized biochar exhibited a greater NH_4^+ release in deionized water than non-oxidized biochar and leonardite, indicating that the retention of NH_4^+ by oxidized biochar was not as strong as for biochar due to the more reversible cation–anion interactions (adsorption) of NH_4^+ and negatively charged functional oxygen groups at the surface of the oxidized biochar. This finding suggests that oxidized biochar may be more suitable for increasing the CEC of the soil than non-oxidized biochar, making retained NH_4^+ more easily available to plants and microorganisms in the soil than non-oxidized biochar. In contrast, non-oxidized biochar could be more effective in retaining nitrate by simple absorption of soil solution containing nitrate in the microporous structure of the biochar, which is particularly pronounced in biochar produced at high temperature (especially >600 ˚C) (Ippolito et al., 2020).

4.2 | Effect of Fenton oxidation on the reduction of NH_3 emission

In the pH-adjusted $(NH_4)_2SO_4$ solution (pH 6.8) all tested CM reduced NH_3 emissions by >90%. This is consistent with the study of Kizito et al. (2015), where biochar made from rice husks and woody material adsorbed 80% of the NH_4^+ from ammonium chloride (NH_4Cl) solution at pH values between 6.5 and 7.0. In the pH-adjusted $(NH_4)_2SO_4$ solution, the oxidation of biochar significantly increased the reduction efficiency of NH_3 emissions to 99.99%, which supports our assumption that the acidic $(NH_4)_2SO_4$ solution limited the retention of NH_4^+ by oxidized biochar. In neutral solutions, oxygen functional groups are usually deprotonated, and free ions, such as Al and Fe, are precipitated as oxides, and then more adsorption sites of the oxygen functional groups are available for NH_4^+ adsorption (Brady et al., 2008; Wang et al., 2015).

In the cattle slurry, the effect of non-oxidized and oxidized biochar on reducing NH_3 emissions was significantly diminished. The composition of cattle slurry is much more complex than the pure $(NH_4)_2SO_4$ solution. It contains a large number of cations, such as K, Ca, and Al, which can compete with NH_4^+ for adsorption sites, resulting in higher NH_3 emission (Kizito et al., 2015). Although non-oxidized biochar had a much higher BET surface area than oxidized biochar and leonardite, it reduced the NH_3 emissions the least, indicating that it retained the lowest amount of NH_4^+ in the cattle slurry and suggesting that surface area is not a major factor in NH_4^+ adsorption capacity at neutral or even higher pH (Bargmann et al., 2014; Spokas et al., 2012).

Leonardite showed a great effect in reducing NH_3 emissions in both pH-adjusted ammonium solution and cattle slurry, which means that it has sufficient adsorption sites for NH_4^+ and other cations even in cattle slurry. Because oxidized biochar had the highest oxygen content and the lowest pH, we can assume that oxidized biochar had more oxygen functional groups than biochar and leonardite. Nevertheless, the retention of NH_4^+ by leonardite was higher than that of oxidized biochar in cattle slurry. We can only speculate that the reason for this is related to the additional cations in the biochar, which might compete with NH_4^+ for cation exchange sites at the surface of the oxidized biochar. As shown in Table 1, oxidized biochar contained more Ca, Fe, and K than leonardite, and these ions can bind to the oxygen functional groups, resulting in fewer vacant adsorption sites for NH_4^+.

The O/C_{org} values of leonardite and oxidized biochar were similar (0.35 and 0.32) and much higher than the O/C_{org} of non-oxidized biochar (0.19). The O/C_{org} values were found to be positively correlated with CEC because high O/C_{org} ratios indicate a greater abundance of hydroxyl, carbonyl, and carboxyl groups, associated with high CEC (Chen et al., 2008; Glaser et al., 2002). Gai et al. (2014) tested 12 types of biochar with different feedstocks and pyrolysis temperatures and confirmed the previous findings that the O/C ratio was positively correlated with CEC and also with the adsorption capacity for NH_4^+ in NH_4Cl solution.

5 | CONCLUSIONS

Our study demonstrated that the Fenton reaction is a rapid and effective method to increase the NH_4^+ adsorption capacity of biochar. Compared with oxidation with H_2O_2 alone, the Fenton reaction has a much higher oxidation capacity and reduces time and energy consumption, providing an economical and environmentally friendly strategy for biochar oxidation. Biochar produced from spruce sawdust and oxidized using the Fenton reaction exhibited significantly higher reversible NH_4^+ adsorption than the other two CM tested (non-oxidized biochar and leonardite). The oxidized biochar caused also the highest NH_3 emission reduction of 99.99% in $(NH_4)_2SO_4$ solution adjusted to pH 6.8, which resembled the pH of cattle slurry. In real cattle slurry, the Fenton-oxidized biochar improved the NH_3 emission reduction effect significantly compared with non-oxidized biochar, although it remained below the performance of leonardite. Although the oxidation with the Fenton reaction could not boost the biochar all the way up to the level of leonardite, it is an important step toward improving the NH_4^+ retention capacity of biochar as a sustainable resource. To achieve the same effect as leonardite, future studies should focus on further increasing the number of adsorption sites by testing different oxidation conditions and on ways of removing excess cations from the produced biochar to further increase its NH_4^+ ammonium retention capacity.

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AUTHOR CONTRIBUTIONS

Xinyue Cao: Investigation; Writing – original draft. Rüdiger Reichel: Writing – review & editing. Nicolas Brüggemann: Methodology; Writing – review & editing.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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