

Perspectives on the Fate of Absorbed Nitrogen in Dairy Farms

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ABSTRACT. The demand for milk rises dramatically due to the increased global population without damaging the standard of living. As a result, the scale of the dairy industry in the world is growing rapidly. Consequently, a concomitant problem that needs to be faced is the environmental impact of the by-products produced during the operation of the dairy farm. Among the substances produced in dairy farms, the most harmful pollutant to the environment is nitrogen (N). In addition, the N pollution from dairy farms is significant and N has a great danger to human health and society. This study provides a systematic review on how to alleviate N pollution from dairy cows during milk production and the removal of ammonia and nitrate from dairy wastewater via biochar adsorption. First, from a physiological perspective, the metabolic pathways of amino acids and ammonia in the rumen, portal-drained viscera, liver, and mammary gland of dairy cows are elaborated, as well as the measures to improve N utilization. In the second part, the progress of research on the removal of ammonia and nitrate by biochar adsorption and the involved mechanisms are summarized. Modified biochar has a significant improvement in nitrate removal due to weakening the repulsive effect of ions. Based on the review of this paper, it can provide relevant theoretical support for future studies on N pollution mitigation from dairy farms.

Keywords: nitrogen, amino acids, nitrate, dairy farm, adsorption

1. Introduction

The environmental impact of the dairy farm has been a long-term concern, particularly the nitrogen (N) excretion (Arriola et al., 2014). A recent study showed that the average amount of N excretion in feces and in urine per cow is 184.0 ± 50.38 g/d and 175.5 ± 66.2 g/d, respectively (Bougouin et al., 2022a). During the storage of feces and urine in dairy farm, N could be rapidly converted to ammonia and emitted into the air, while ammonium and nitrate as the main inorganic forms of N in the manure phase would leach into the soil and groundwater, and a large amount of Nitrous oxide (N₂O) that is a potent greenhouse gas can be produced through nitrification and denitrification (King et al., 2021; Bougouin et al., 2022a). The excess N in cattle manure and urine would lead to serious environmental and social problems, such as eutrophication of lakes and other water bodies, enhancement of PM_{2.5}, aggravation of greenhouse gas emission, destruction of stratospheric ozone, deterioration of soil and surface water due to the increased acidity of precipitation, and aggravation of asthma (Wolfe and Patz, 2002; Bougouin et al., 2022b). The production of N₂O is determined by the concentration of a variety of excreta (e.g., urea,

purine derivatives, creatine and creatinine) while urinary N is dominant (Dijkstra et al., 2013; Wang et al., 2015; Zhao et al., 2019).

Adsorption is a common and predominantly effective process for the removal of pollutants from wastewater (Luo et al., 2021a). The adsorption capacity of the adsorbent generally depends on the property of the adsorbent and the ambient electrolyte conditions (Luo et al., 2021b). Many common adsorbents have been comprehensively studied for their effectiveness in removing N from dairy wastewater, including carbonaceous materials, zeolites, bentonites, ion exchangers, and nanoparticles (Alshameri et al., 2018; Alshabib and Onaizi, 2019). Biochar is a carbon-rich material formed by pyrolysis of biomass in an oxygen-limited environment, and feedstocks used to produce biochar include agricultural and forestry wastes, municipal sludge, animal manure, and other materials (Kanchanalai et al., 2013). The properties of biochar such as the easy availability of raw materials and low production costs make it an emerging and promising material for environmental remediation in recent decades, in addition to its sustainability (Ahmad et al., 2014). Biochar has a high specific surface area, rich pore structure, abundant carbon content, a large number of oxygen-containing functional groups and possesses ion exchange capacity, properties that give it the potential ability for good adsorption properties (Goli et al., 2019). The feedstock and pyrolysis temperature and time of biochar are the main factors that affect the physical

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and chemical properties, adsorption selectivity and capacity of biochar (Hassan et al., 2020). Furthermore, metallic elements in biochar may also play an indispensable role in the adsorption process (Yin et al., 2018). Many studies have used biochar as an adsorbent to remove N (e.g., NH_4^+ and NO_3^-) from dairy wastewater and soil separately or simultaneously by specific and non-specific adsorption combination (Yin et al., 2019; Zhao et al., 2020).

However, to the best of our knowledge, few previous studies have systematically summarized amino acids (AAs) uptake and metabolism in the digestive tract of dairy cows from the perspective of environmental protection and no systematic review has been conducted on the capabilities and mechanisms of biochar for N removal in dairy wastewater. This study comprehensively revealed the metabolic process of N compounds (AAs and ammonia) in cows and the performance of carbonaceous materials adsorption in removing N (e.g., NH_4^+ and NO_3^-) in the treatment of dairy wastewater. This paper presents two main points: summarization of the metabolism of AAs and ammonia in cattle as well as the effect of dairy diet management on the reduction of N emissions from animals; investigation of the removal of N from dairy farm effluent by adsorption of carbonaceous materials and the related mechanism.

2. The Fate of Absorbed Nitrogen in Dairy Cattle

2.1. Rumen Metabolism of Nitrogen

For ruminants, ammonia is mainly produced by the digestion of microbial proteins in the digestive tract, absorbed into the portal vein, and subsequently transported to the liver where it is transformed into urea by detoxification (Souza et al., 2021). Rumen degradable protein (RDP) is the main source of N required for microbial protein synthesis in the rumen, when the dietary RDP exceeds the requirement of rumen microbes. The excess N in the form of ammonia is absorbed by the rumen wall, converted to urea in the liver and excretion via urine (Hartinger et al., 2018). The urinary urea N excretion increased exponentially with the increased intake of dietary crude protein (CP) level, but the amount of fecal N excretion was negative to that of urinary urea N (Batista et al., 2017). Approximately 70 ~ 80% of the rumen microorganisms are attached to the feed particles, of which 30 ~ 50% of the microorganisms can hydrolyze protein into peptides and AAs and are further utilized by the microorganisms. In addition, the aforementioned peptides may be further decomposed into AAs, while are used for protein synthesis or deamination of microorganisms into volatile fatty acids (VFA), carbon dioxide and ammonia. The deamination process is considered to be caused by energy limitation or excessive AAs (Bach et al., 2005). Therefore, balanced nutrition is essential to improve the efficiency of N utilization (Matthews et al., 2019). The rumen microbiota consists of a complex community of bacteria, archaea, protozoa, and fungi (Ribeiro et al., 2017). They can convert complex fibrous substrates into VFA and microbial proteins, which are consumed by the host for maintenance, growth, and lactation (Morgavi et al., 2012). A variety of rumen bacteria are associated with the process of deamination, such as *Butyrivibrio fibrisolvens*, *Prevotella rumi-*

nicola, and *Eubacterium ruminantium* (Bento et al., 2015). Therefore, N utilization in dairy cows is strongly related to rumen microbial metabolic activity. Studies have shown that N digestibility and retention could be improved by changing rumen microbial species (Ribeiro et al., 2017). Recently, metabolic crosstalk between gut microbes and hosts has become a hot topic of related N metabolism research.

A large number of studies have demonstrated that microbes support host physiological metabolism via their metabolites, while host metabolites also have significant effects on microbes (McCarville et al., 2020). And the rumen, as a large mammalian microbial reservoir, theoretically also has crosstalk points, such as the urea cycle in the rumen. Urea is considered to be a metabolic waste in most animals (Hediger et al., 1996; Zhao et al., 2022). Ruminants only about 29% of endogenous urea is excreted in urine, because ruminants have evolved certain regulatory mechanisms to reduce the waste of ingested N by returning urea in the body through saliva or the epithelial wall of the rumen for the protein synthesis by rumen microbes (Batista et al., 2017; Patra and Aschenbach, 2018); On the other hand, the ammonia converted to urea by the liver is about 81% of the digested N, the remaining 19% is not enough to support the production of milk protein, so that there must be a portion of urea N that should be reused (Lapierre et al., 2005). Studies have shown that about 40 ~ 80% of urea is synthesized in the liver (Berthiaume et al., 2001). About 71% of endogenous urea and 35% of ingested total N would re-enter the digestive tract (Batista et al., 2017). In addition to being a precursor to AA synthesis, urea may also be used to regulate the acid environment in the rumen (Arioli et al., 2010). The amount of endogenous urea recovered to the gastrointestinal tract was determined by the relationship between dietary CP and RDP concentration (Hailemariam et al., 2021), also related to various factors such as dry matter intake, feeding frequency, organic matter digestibility and others (Batista et al., 2017; Patra and Aschenbach, 2018).

2.2. PDV Metabolism of Nitrogen

Even though ruminants have evolved efficient mechanisms for N reuse, the efficiency of N use in cows is still low with only 25% of ingested N entering the milk (Arriola et al., 2014), while that of pigs and poultry are able to reach 40% or even higher (Nahm, 2002). It has been pointed out that the inevitable sources of N losses from cows are urine and feces, metabolism of AAs after absorption, microbial nucleic acids and undigested protein (Dijkstra et al., 2013).

N metabolites enter the portal vein from the intestinal cavity and are absorbed mainly as AAs and ammonia, accounting for 0.58 and 0.57 of digested N, respectively (Lapierre et al., 2005). As shown in Table 1, different AAs have differences in metabolizable fluxes because of their different proportions in various proteins, ranging from 27 g/d for tryptophan to 208.5 g/d for leucine among the essential amino acids (EAAs). When ammonia enters the liver via the portal vein, it is efficiently converted to urea or glutamine via detoxification (Parker et al., 1995). It has been shown that when protein intake is low, the liver tends

to convert ammonia to glutamine as an amino salvage mechanism (Paulusma et al., 2022), and ruminants can reduce the emission of urea N in urine and increase the proportion of circulation to the rumen when ruminants are supplied with low-protein diets (Batista et al., 2017). Reducing the CP content of diets is considered to be the most effective way to reduce ammonia emissions during breeding (Bougouin et al., 2016; Souza et al., 2021). It has been reported that about 60% of the total N loss occurs after absorption into the body (Arriola et al., 2014). Nitrous oxide (PDV) and the liver are the main sites where AAs metabolic losses occur (Lapierre and Lobley, 2001).

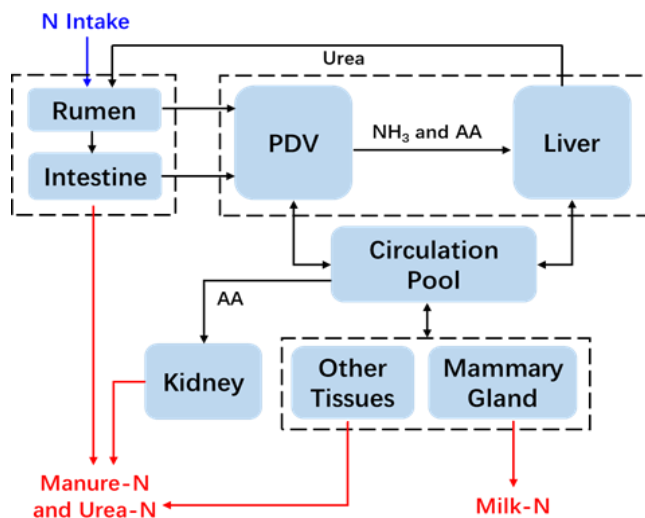


Figure 1. Nitrogen metabolism in dairy cows (CP: crude protein; blue arrow denotes N intake; red arrow represents N excretion).

As shown in Table 1, there are large differences in the metabolic losses of different EAAs within different body parts. The approximate metabolism of dietary N as it enters the cow's body through feeding is depicted in Figure 1.

Free AAs are consumed by PDV tissue when they are absorbed into the small intestine, for example, approximately 35% of the total AAs are oxidized or converted to endogenous secretions when passing through the small intestine (Lapierre et al., 2005). Significant differences in intestinal losses have been reported for different AAs, with glutamine (glutamate) consumption more than 90% and histidine less than 5% in sheep (Berthiaume et al., 2001), and branched-chain amino acids (BCAA), threonine with a certain loss (Lobley and Lapierre, 2003; Souffrant and Metges, 2003) and the differences between AAs are shown in Table 1. The intestine not only degrades glutamine absorbed by the intestinal tract but degrades about 30% of circulating glutamine (Kim and Kim, 2017; Liu et al., 2017). It can be observed that the intestinal consumption of certain AA (including glutamine, glutamate, and aspartate) is huge (Omphalius et al., 2020), the reason may be that the intestine uses them as a major source of energy (Tran et al., 2020). It has been reported that Thr, Phe, Leu and His have the highest PDV clearance constant in EAAs, Val and Met are intermediate, and

Lys and Arg are the lowest in dairy cows (based on the absorbed AAs) (Hanigan et al., 2004) and when the concentrations of arterial AAs are also taken into account, the clearance rate changes considerably, as shown in Table 1. The kidney can also degrade glutamine in large amounts, and both kidney and liver metabolize glutamine into glutamate and ammonia, which enters the bloodstream or is excreted directly from the body (Wright and Jalan, 2007; Cordoba et al., 2014). It has been suggested that the main net producers of glutamine are skeletal muscle and adipose tissue, while the net uptake occurs mainly in the intestine and kidneys (Stumvoll et al., 1999). The circulating glutamine is synthesized from BCAA and α -ketoglutarate in skeletal muscle, adipose tissue, heart, and placenta (Self et al., 2004), which is inevitably accompanied by a large amount of ammonia metabolism.

2.3. Liver Metabolism of Nitrogen

The liver is thought to be the "gatekeeper" that can control the systemic exposure of most AAs that enter through the gastrointestinal tract, with the exception of BCAA (Paulusma et al., 2022). AAs enter the liver through PDV tissue, and a portion of AAs are lost in the liver in addition to the detoxification of ammonia described above (Hanigan et al., 2001). The liver can metabolize about 45% of the total AAs from the portal vein. For dairy cows, EAAs are generally divided into two main categories: the first is metabolized in the liver in small amounts, including BCAAs and lysine, mainly because of the lack of enzymes associated with their metabolism in the liver, and the second is metabolized in the liver in larger amounts, including histidine, methionine, and phenylalanine, and is able to metabolize 35 ~ 50% of the portal absorption (Wang et al., 2019). The metabolism of non-essential amino acids (NEAAs) in the liver mainly involves their glycoisomerization activities in the liver, especially in the case of fasting (Paulusma et al., 2022).

The main net producers of alanine are muscle and intestine, while the net uptake occurs mainly in the liver for hepatic functions, gluconeogenesis, in conjunction with the catabolism of arginine, and participation in the urea cycle to produce urea. The alanine accounts for approximately 50% of the total AAs intake by the liver (Paulusma et al., 2022). Therefore, a rational feeding management system may be able to reduce AAs metabolism in the liver. Although the liver is hardly directly involved in the deamination of BCAA (this process occurs mainly in muscle tissues) due to the lack of related enzymes, most of the ketoacids produced by other tissues are metabolized by the liver (Paulusma et al., 2022). It has been pointed out that the liver is able to metabolize all AAs in the blood except BCAA and plays a key role in the synthesis of various NEAAs and glucose in the body (Hou et al., 2020). The number of AAs metabolized in the liver appears to be modifiable. The study has shown that when pigs are fed a balanced diet, the number of AAs metabolized by the liver decreases dramatically, and only 5% of urea N is produced by hepatic degradation of AAs (Hou et al., 2020), whereas correspondingly if the supply of metabolic protein is simply increased, it may be possible to increase AAs removal from liver and PDV tissues (Wang et al.,

2019). And increasing the availability of dietary CP was found to increase the concentration of urea N and non-protein N in milk (Reid et al., 2015).

Table 1. The Utilization State of Different AAs in Dairy Cows

AA	Digestible Flow (g/d)	AA Efficiency (%)	Ratio of PDV Use (%)	Ratio of Liver Use (%)	U:O
Arg	115.50	0.72	1.60	7.30	2.45
His	53.95	0.78	4.70	7.30	1.08
Ile	122.00	0.61	7.20	0.70	1.41
Leu	208.50	0.67	8.60	0.70	1.31
Lys	158.50	0.67	8.80	3.90	1.33
Met	48.55	0.71	8.00	10.40	0.96
Phe	125.50	0.54	10.10	12.40	1.07
Thr	117.50	0.58	10.60	4.00	1.19
Trp	27.00	0.77	-	-	0.93
Val	135.00	0.65	5.30	-0.10	1.49

Notes: Digestible flow: AA net digestible flow, is calculated as the sum of digestible flow from rumen-undegraded protein flow and microbial protein (endogenous duodenal flow was not included), data from Fleming et al. (2019b) and Omphalius et al. (2020); AA efficiency = (AA secretion in milk + scurf + metabolic fecal protein)/(digestible flow - AA endogenous urinary secretion) \times 100, data from Omphalius et al. (2020); ratio of PDV use coming from both arterial flux and absorption, data from (Fleming et al., 2019a); ratio of liver use coming from both arterial flux and EAA not used in PDV flux, data from Fleming et al. (2019a); U:O is mammary uptake to milk output, data from Lapierre et al. (2012).

2.4. Mammary Gland Metabolism of Nitrogen

The mammary AAs clearance rate was used to assess the ability of the mammary gland to remove AAs from the blood, and AAs clearance in the mammary gland refers to the extraction of AAs after blood flow including milk protein synthesis, cellular Table 1. The utilization state of different AAs in dairy cows protein synthesis and catabolism in the mammary gland (Hanigan et al., 1998). An average clearance rate of 43% for EAAs and 30% for NEAAs was observed in cows, with a range from 5% for aspartate to 69% for phenylalanine (Hanigan et al., 1992). During lactation, a large number of AAs synthesis and degradation processes take place in the mammary gland (Wang et al., 2019). Mephram divided EAAs into two groups based on the metabolism in the mammary gland: the first group of EAAs extracted in the mammary gland is similar to the output, i.e. the uptake-to-output ratio (U:O) is almost equal to 1, including methionine, phenylalanine, tyrosine, and tryptophan; the second group of EAAs extracted in the mammary gland is higher than the milk output, including lysine, threonine, arginine and BCAA. The second group of AAs is subdivided into two categories: one (Ile, Leu, Val, and Lys) that the U:O changes with dietary protein supply, while the other does not change (Lapierre et al., 2012). For EAAs with U:O greater than 1, it is thought that catabolism occurs in the mammary gland and is used for NEAAs synthesis, as many NEAAs have U:O less than 1 (Lapierre et al., 2012). The mammary gland extracts only less than 70% of the NEAAs needed for lactation from the circulation. Amino acid efficiencies of utilization vary by different mechanisms in response to energy and protein supplies in dairy cows. The U:O of total AAs in the mammary gland is 96 ~ 105%, indicating a

small metabolic loss of total AAs under normal physiological conditions, but at the same time the U:O of EAAs and NEAAs was 66 ~ 79% and 141 ~ 182%, respectively, indicating that part of EAAs was converted to NEAAs in the mammary gland, in which the removal rate of Leu in the mammary gland was greater than 20% (Omphalius et al., 2019). The rate of BCAA turnover is relatively constant under steady-state conditions, so that at least 20% of the Leu extracted from the mammary gland is catabolized. Lysine uptake by the mammary gland has also been shown to support the synthesis of NEAAs, particularly glutamate and aspartate (Neinast et al., 2019). Methionine metabolism in the mammary gland is thought to synthesize cysteine and provide methyl to mammary cells (Wang et al., 2019). As mentioned earlier, because the total AAs U:O of the mammary gland is about 1, there is almost no loss of total N from the ingested AAs from the mammary gland, and almost all of it is used for milk protein synthesis, although some amount of urea is also excreted in milk (Appuhamy et al., 2011). Urea N in milk is derived from blood and the correlation between milk urea N concentration and blood urea N concentration is high (Broderick and Clay-ton, 1997). On the other hand, the mammary gland appears to have a strong ability to regulate the extraction of a single EAA, and when the supply of multiple single EAA was sharply reduced, the mammary gland greatly increased its affinity for that AA, resulting in no dramatic change in the mammary extraction of the EAA (Guo et al., 2017; Liu et al., 2019). Therefore, it is possible to increase the efficiency of N utilization by adjusting the AAs ratio to regulate the ability of mammary glands to increase the uptake of AAs.

As previously mentioned, the kidneys and other organs, especially the liver, can metabolize excess AAs (or ammonia) into urea. Although a portion of urea N can be returned to the digestive tract to be reused by rumen microorganisms in ruminants, most of the urea is still excreted outside the body through urine, causing N excretion. Moreover, based on the metabolic characteristics of various tissues and organs, the metabolism of ammonia in organs (e.g., liver, mammary gland, and rumen) may be able to be regulated. Therefore, it is possible to achieve the regulation of ammonia emission through nutrition. Compared to the low CP level of the diet, which may decrease milk production, regulation of the energy to N ratio and AAs balance to satisfy the requirement of the rumen microorganism and the body's metabolism is a more desirable N reduction program. Improvement of feeding management procedures can be also achieved by inoculating or adding special additives to change the rumen microbiota.

3. The Fate of Excreted Nitrogen in Dairy Farm

3.1. Ammonium and Nitrate Removal by Biochar

Ammonium and ammonia are the main inorganic forms of N in dairy wastewater. In addition, the interconversion of ammonium and ammonia is dependent on the pH and temperature of the surrounding environment. According to Emerson et al. (1975), ammonium (NH_4^+) is the predominant form when the ambient pH is less than 8.2 and the temperature is below 28 °C. Up to now, many scholars have studied the effect of biochar

with different feedstocks and production temperatures on the removal efficiency of ammonium N ($\text{NH}_4^+\text{-N}$). For example, kinetic experiments on $\text{NH}_4^+\text{-N}$ adsorption by pine wood chip biochar, wheat straw biochar (Cai et al., 2018), peanut shell biochar, cotton straw biochar (Gao et al., 2015) and giant reed biochar have been completed (Yang et al., 2018). Through extensive studies, it has been found that the capacity of biochar for $\text{NH}_4^+\text{-N}$ varies widely with an average value of 11.19 mg N/g. The maximum adsorption of $\text{NH}_4^+\text{-N}$ in pine wood chip biochar pyrolyzed at 300 °C and 550 °C was 5.38 and 3.37 mg N/g, respectively (Hou et al., 2016). Cui et al. (2016) conducted biomass of 22 plant species in artificial wetlands at 500 °C pyrolysis was performed, and the maximum adsorption of 7.71 mg N/g was the best performance of plantain biochar. In general, most of the reported biochar had a sorption capacity of less than 20 mg N/g for $\text{NH}_4^+\text{-N}$. Improving the cation exchange capacity of biochar and changing the surface functional groups of biochar can improve the adsorption capacity of NH_4^+ .

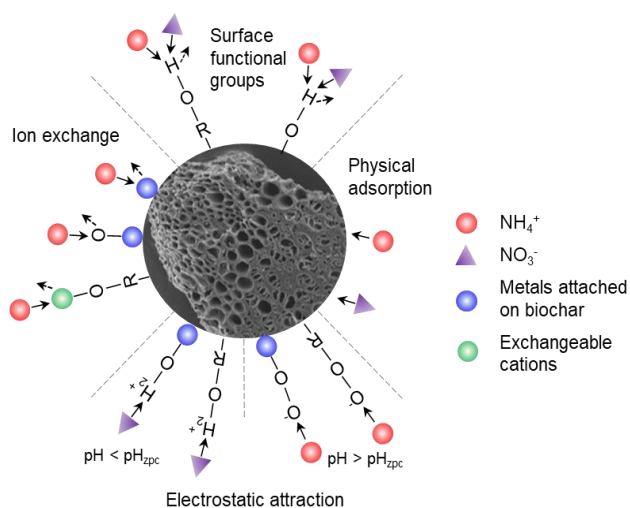


Figure 2. The adsorption mechanism of biochar for NH_4^+ and NO_3^- .

Numerous studies have shown that the sorption capacity of unmodified biochar for nitrate is negligible. No adsorption of nitrate was observed for biochar produced from corn stover, and oak (Hollister et al., 2013). It is possible that this phenomenon is due to the negative charge on the biochar surface and the classical repulsion of nitrate production. Kameyama et al. (2012) tested the nitrate adsorption performance of sugarcane bagasse-derived biochar and found that a small amount of nitrate was adsorbed by the biochar. This finding may be due to the elevated pyrolysis temperature. Higher pyrolysis temperatures can cause changes in the physicochemical properties of the biochar surface, for example, higher surface area and a lower number of oxygen-containing functional groups (Ahmad et al., 2014). An increase in surface area increases the adsorption sites of biochar on nitrate, while a decrease in oxygen-containing functional groups decreases the repulsive force between biochar and nitrate. Therefore, it is imperative to modify the biochar to reduce the electrostatic repulsion between biochar

and nitrate, and common modifications include protonation and the addition of metals. Additionally, the use of concentrated hydrochloric acid can be effective in improving the nitrate adsorption capacity of biochar, due to the dissolution of some solids by the concentrated acid, which increases the specific surface. In this study, HCl-modified pine residue biochar showed the highest enhancement of nitrate adsorption with 9.74 mg N/g compared to 2.58 mg N/g for the unmodified biochar. The authors hypothesized that this enhanced adsorption was the result of a significant increase (about 10-fold) in surface area after HCl modification (Chintala et al., 2013). Lanthanum-impregnated (La) wood chip pyrolysis biochar was also found to significantly increase the NO_3^- adsorption capacity of oak wood chip biochar from 2.02 mg N/g (unmodified) to 22.58 mg N/g. The authors hypothesized that the increase in alkaline functional groups in La-modified biochar was responsible for the enhanced nitrate removal (Kanchanalai et al., 2013). In another study, the MgO-modified biochar nanocomposite increased the NO_3^- adsorption capacity to 95 mg N/g by immersing the biomass feedstock in MgCl_2 solution prior to pyrolysis (Wang et al., 2015).

3.2. Mechanisms of Nutrient Removal by Biochar

The adsorption mechanism of biochar for NH_4^+ and NO_3^- is shown in Figure 2. The surface of biochar contains more oxygen-containing functional groups (e.g., $-\text{OH}$ and $-\text{COOH}$), which are mainly due to the high temperature during pyrolysis. Due to the more negative charge on the surface of biochar, biochar has a certain affinity for NH_4^+ and repulsion for nitrate, which minimizes the electrostatic attraction of NO_3^- to biochar. Biochar with a higher O/C ratio may have a higher NH_4^+ adsorption capacity because of the formation of chemical bonds or electrostatic interactions between O-containing functional groups on the surface of biochar and NH_4^+ . Protonation and deprotonation of surface functional groups are influenced by the pH of the solution and can significantly affect the bonding of oxygen-containing functional groups to NH_4^+ , thus affecting the adsorption of NH_4^+ by biochar. Biochar (600 °C) was much less efficient in removing NH_4^+ at lower pH (Kizito et al., 2017), which could be due to the protonation of functional groups ($\text{C}=\text{O}$ and COO^-) on the surface of biochar, which leads to a weakened formation of ionic bonds between NH_4^+ and biochar. According to previous findings, biochar with lower pyrolysis temperatures may have higher cation exchange capacity (CEC), which leads to higher NH_4^+ adsorption capacity (Yang et al., 2018). This may be due to the fact that NH_4^+ is adsorbed on the surface sites of biochar by substituting other cations with lower affinity. A similar conclusion was reached by Gai et al. (2014), who found that biochar pyrolyzed at lower temperatures (400 and 500 °C) had higher CEC than those pyrolyzed at higher temperatures (600 and 700 °C). and the highest removal of NH_4^+ was observed in experiments in biochar with the highest CEC. In addition to the pyrolysis temperature, the biochar CEC was closely related to the feedstock properties. For example, the CEC and NH_4^+ removal rates of corn straw derived biochar were significantly higher than those of wheat straw-derived biochar (Gai et al., 2014). The addition of metal modification

could enhance the CEC of biochar and thus increase the adsorption of NH_4^+ .

4. Conclusions

The N produced in pastures cannot be ignored. Although ruminants have unique metabolic mechanisms that can improve N utilization, the N utilization efficiency is still less than 30%. According to the present study, the reduction of N emissions from dairy farms should focus on two aspects: (1) improving the dairy metabolism to reduce N emission; (2) treating N emissions to reduce diffusion into the environment. For the first point, mainly by changing the structure of the diet to better match the maintenance and production needs of cows, so that as much of the N ingested by the cow is used for production rather than wasted in conversion between nitrogenous compounds or even excreted; it is also possible to improve the rumen environment and thus the rumen microbial metabolism through additives, which is more conducive to the digestion and absorption of N rather than excreted in the feces. Therefore, the development and discovery of promising feed ingredients will also be the focus of future research. For the second point, most studies have focused on the adsorption of biochar, but the results of studies on the adsorption of biochar on N in wastewater are not uniform. Biochar achieves N removal mainly through ion exchange and biochar surface functional group interactions. Biochar modification can significantly improve the removal of N from wastewater. Therefore, the development of cost-effective, environmentally friendly and field applicable biochar adsorbents is a reliable pathway to achieve N emission reduction. When two points are satisfied simultaneously by cattle managers, it should theoretically be possible to significantly reduce nitrogen excretion from cattle farms.

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