The role of biochar on alleviating ammonia toxicity in anaerobic digestion of nitrogen-rich wastes: A review

Yafan Cai[a,c*], Mingming Zhu[d], Xingyao Meng[b], John L. Zhou[e], Huan Zhang[f], Xia Shen[g], Xiaofen Wang[h]

[a] School of Chemical Engineering, Zhengzhou University, Kexue Dadao 100, 450001 Zhengzhou, China

[b] Beijing Technology and Business University, State Environmental Protection Key Laboratory of Food Chain Pollution Control Beijing 100048, China.

[c] Department of Biochemical Conversion, Deutsches Biomassforschungszentrum Gemeinnützige GmbH, Torgauer Straße116, 04347 Leipzig, Germany

[d] Centre for Climate and Environmental Protection, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, UK

[e] Centre for Green Technology, University of Technology Sydney (UTS), Broadway, NSW 2007, Australia

[f] College of Engineering, Nanjing Agricultural University, Nanjing 210014, China

[g] Key Laboratory of Agricultural Soil and Water Engineering in Arid and Semiarid Areas, Ministry of Education, Northwest A and F University, Yangling, Shaanxi, 712100, China

[h] College of Agronomy and Biotechnology/Biomass Engineering Center, China Agricultural University, China

*Corresponding author: Yafan Cai

E-mail address: caiyafan@zzu.edu.cn

Abstract: Ammonia inhibition is one of the biggest obstacles hindering the development of anaerobic digestion (AD) of substrates with very high ammonia nitrogen concentration. Due to high specific surface area, porosity, conductivity and functional groups, biochar has been suggested as an additive in AD to alleviate ammonia inhibition. In this article, the effect of biochar addition on the ammonia inhibition was reviewed. A literature search was undertaken to summarize the key physiochemical properties of biochar that have significant impacts on ammonia nitrogen concentration. The performance of biochar on the biogas production and microbial community in AD with high ammonia nitrogen was discussed, with a focus on the working mechanisms of biochar. Biochar shows a great potential in alleviating ammonia inhibition in AD. Biochar absorbs ammonia nitrogen by chemical adsorption (electrostatic attraction, ion exchange, and complexation) and physical adsorption. The absorption efficiency, mainly affected by the properties of biochar, pH and temperature of AD, can reach 50 mg g^{-1} on average. The biochar addition can buffer pH by reducing the concentrations of VFAs, alleviating ammonia inhibition. Biochar enhances the direct interspecies electron transfer (DIET) pathway by acting as an electron carrier. In addition, biochar can release trace elements, increasing the bioavailability of trace elements which in turn improve the ability of microorganisms to resist high concentration of ammonia nitrogen.

Keywords: Ammonia inhibition; Anaerobic digestion; Biochar; Microbial community

1. *Introduction*

Anaerobic digestion (AD) is a mature and effective technology for the treatment of organic wastes and production of biogas and energy (Yang et al., 2021a). However, in processing nitrogen-rich wastes, such as livestock manure (Zhou et al., 2021), food waste (Chuenchart et al., 2020) and sludge (Yuan et al., 2016), ammonia is produced at a high concentration, leading to instability, low efficiency and even failure of the AD system, known as ammonia inhibition (Zheng et al., 2021). Recently, the issue of ammonia inhibition has gradually received attention due to the need of processing nitrogen rich-material in AD (Cai et al., 2021a). To alleviate ammonia inhibition, a number of strategies have been proposed in the literature including: 1) adjustment of temperature or pH to turn NH_3 into NH_4^+, thereby reducing the toxicity of ammonia nitrogen (Karlsson and Ejlertsson, 2012); 2) supplement of methanogenic archaea with high resistance to ammonia nitrogen or acclimation under high ammonia nitrogen concentration (Yan et al., 2021); 3) removal of ammonia nitrogen by converting ammonia nitrogen to N_2 by nitrification or denitrification (Kwon et al., 2019); 4) addition of nutrients such as trace elements to enhance the ability of microorganisms to resist high ammonia nitrogen concentration (Cai et al., 2021b). Although these methods could alleviate ammonia inhibition to a certain extent, their application to large-scale treatment of nitrogen-rich substrates are still far from commercialization due to high cost and low operability.

Biochar is a carbon rich material produced from pyrolysis of biomass (Chiappero et al., 2020). Due to the high specific surface area, porosity, conductivity and functional groups (Huang et al., 2021), biochar has been found to be an effective additive in alleviating ammonia inhibition (Wei et al., 2020; Indren et al., 2020a; Xu et al., 2018). In general, the efficacy of biochar in relieving ammonia inhibition mainly benefits from its capacity of adsorption of ammonia nitrogen (Shi et al., 2013), immobilizing microorganisms and enzyme (Wei et al., 2020; Pandey et al., 2020), releasing trace elements (Indren et al., 2020a) and enhancing the direct interspecies electron transfer (DIET) (Ma et al., 2019). The performance of biochar depends on the properties of biochar and biochar addition ratio, and operating conditions (e.g. temperature and pH) of AD and the total ammonia nitrogen (TAN) concentration in AD system. The porous structure of biochar provides a support for microorganisms to grow and survive (Yan et al., 2021). The addition of biochar can also increase the concentration of microorganisms, thereby improving the resistance of the microbial consortium to the high concentration of ammonia nitrogen (Wei et al., 2020). In addition, methanogenic archaea will adapt to the change of TAN concentration with biochar addition (Capson-Tojo et al., 2020). Biochar was also found to act as an electron carrier to promote DIET between bacteria and archaea to enhance methane production, which may be beneficial for biogas production even under high concentration of ammonia nitrogen (Wang et al., 2017). Since some of trace elements (e.g. Fe, Co, Ni, Mo, Zn, Se, Cu and Mn) can alleviate ammonia inhibition (Banks et al., 2012; Cai et al., 2021b), biochar which is rich in trace elements may be conducive to the growth of microorganisms and thus increase their resistance to ammonia nitrogen (Indren et al., 2020a).

Over the past ten years, there were a few papers reviewing the application of biochar in AD but most of them focused on the effect of biochar on biogas production, microbial activities, economic and environmental advantages (Chiappero et al. (2020), Qiu et al. (2019), Fagbohungbe et al. (2017), and Kumar et al. (2021). The present study was aimed to provide a comprehensive review on the effect of biochar addition on the mitigating ammonia inhibition in AD system, particularly in processing nitrogen-rich wastes. A particular attention was paid to the working mechanisms of biochar and interactions between biochar and microbial communities during AD process with high concentration of ammonia nitrogen.

2. ***Production and characteristics of biochar***

Since the properties of biochar play a key role in the formation and destruction of ammonia nitrogen in AD, this section provides a brief overview of the production and characteristics of biochar. The detailed review on this topic can be found in literature (Weber et al., 2018). Biochar is produced from biomass pyrolysis under inert environment and high temperature condition (400-900 °C) (Sun et al., 2018; Zhang et al., 2019a). The physiochemical properties of biochar including elemental composition, ash content, porosity (the percentage of pore volume to the total volume of biochar), specific surface area and pH can play significant role in alleviating ammonia inhibition. For instance, ash content, pH and hydroxyl groups affect the surface charge of biochar (Tan et al., 2020). Porosity and specific surface area have an impact on the growth of microorganisms. The effect of pyrolysis temperature on the key physiochemical properties of biochar are summarized and presented in Figures 1 and 2. The content of C increases while the content of H and O decreases as the pyrolysis temperature increases. The pyrolysis temperature does not show noticeable effect on N content. The ratio of H/C, N/C, and O/C can represent the number of hydroxyl, amino and carboxylic groups, respectively, which can affect adsorption capacity of ammonia nitrogen on the biochar (Li et al., 2017). As shown in Figure 2, wood vinegar ($pH < 7$) is gradually produced and carbon is gradually mineralized as temperature increased. Therefore, pH and ash content of biochar gradually increase with temperature. In addition, the increase of temperature often leads to the formation of micro and meso-pores, leading to higher porosity and specific surface area.

3. *Ammonia inhibition in AD*

The digestion system often faces the risk of ammonia inhibition when the C/N ratio of substrate is lower than 15 such as livestock manures, food waste, sludge and microalgae (Cai et al., 2021a). NH_3 can penetrate cell structure and cause the imbalance of protons. High NH_4^+ concentration has a potential damage to the enzymes, which are essential to producing methane. Ammonia inhibition will lead to low digestion efficiency due to the low conversion efficiency of VFAs. The reported TAN concentration that can lead to ammonia inhibition is very wide ranging from 2 to 25 g L^{-1} (Poirier et al., 2016; Cai et al., 2021a). There are a number of review papers in the literature discussing ammonia inhibition (Capson-Tojo et al., 2020; Cai et al., 2021a) and we only briefly mention this in this paper. Ammonia inhibition includes complete ammonia inhibition and inhibited steady-state. For the former, the microorganisms in the digestion system completely lose their metabolic activity. Regarding the latter, the digestion performance could remain stable even though it is inhibited by ammonia nitrogen. The literature reports on the digestion system with addition of nitrogen compounds such as NH_4Cl, $(NH_4)_2CO_3$, NH_4HCO_3, urea and $(NH_4)_2SO_4$ to simulate the different TAN concentrations (Yan et al., 2019; Yang et al., 2018; Bonk et al., 2018) suggest that complete ammonia inhibition will happen when TAN concentration is above 15g L^{-1}. In fact, the TAN concentration is rarely greater than 15 g L^{-1} in the actual AD system without extra nitrogen supplement. Therefore, "inhibited steady-state" is the most common ammonia inhibition phenomenon. At inhibited steady-state condition, the pH is higher than 7 because of the high TAN concentration and the accumulation of VFAs happen (Zheng et al., 2021).

Ammonia inhibition will lead to low digestion performance, which was caused by the imbalance of microorganisms (mainly bacteria and archaea) (Cho et al., 2017). Generally, NH_3 is more toxic than NH_4^+ to the digestion system (Cai et al., 2021a). Compared with methanogenic archaea, bacteria are responsible for hydrolysis and acidification are more resistant to high TAN concentration (Capson-Tojo et al., 2020). In general, acetoclastic methanogen dominates in AD process, and acetoclastic pathway is the main methane-producing pathway. The strict acetoclastic methanogen is *Methanosaeta* (Su et al., 2015). The succession of methanogenic archaea's community will happen under ammonia inhibition (Bonk et al., 2018). Due to the special cell morphology and structure, some methanogenic archaea have high ammonia nitrogen resistance (Cai et al., 2021a). For instance, Capson-Tojo et al. (2020) reported that methane production has a high efficiency when the NH_3 concentration is above 1000 mg L^{-1}, due to the succession of methanogenic archaea form *Methanosaeta* to *Methanoculleus*. Interestingly, the succession of methanogenic archaea has a certain sequence along with the increase of TAN concentration. The strict acetoclastic methanogen (*Methanosaeta*) will be replaced by versatile methanogenic archaea (*Methanosarcina*) and then the hydrogenotrophic methanogen (*Methanothermobacter*, *Methanoculleus*, *Methanobrevibacter*, *Methanospirillum*, *Methanolinea*, *Methanomassiliicoccus* and *Methanosphaera*) (Cai et al., 2021a). The hydrogenotrophic pathway will dominate in high concentration of ammonia nitrogen system. The syntrophic acetate oxidation bacteria (SAOB) are essential partner of hydrophilic methanogens. Cai et al. (2021a) showed that SAOB are sensitive to H_2 concentration.

Therefore, the community structure of bacteria will also change along with the succession of methanogenic archaea.

4. *Effect of biochar on ammonia inhibition*

As shown in Table 1, a large number of studies have shown the positive effect of biochar in AD system with high TAN concentration. Biochar addition can increase total yield of methane (Sugiarto et al., 2021; Mumme et al., 2014), the increase in digestion efficiency such as shortening the digestion time (Indren et al., 2020), and the enhancement of biogas quality (mainly methane content) (Shen et al., 2015; Wei et al., 2019). Many factors contributed to the beneficial effect of biochar. Some biochar still contains a large proportion of decomposable-carbon, particularly under low pyrolysis temperature (Figure 1). The remained decomposable carbon contributes to the biogas production (Munne et al., 2014). In high ammonia nitrogen system, VFAs can be easily accumulated, making the digestion system more fragile (Zheng et al., 2021). Biochar can provide high pH buffering capacity to AD system, leading to strong resistance to high ammonia nitrogen and VFAs (Wei et al., 2020; Indren et al., 2020b). Xu et al. (2018) reported that biochar also has a certain adsorption effect on VFAs due to its porosity. Biochar could adsorb ammonia nitrogen to relieve the ammonia inhibition because of the presence of polar functional groups and porous structure (Masebinu et al., 2019). The porous structure of biochar is beneficial to the growth of microorganisms, contributing to the improvement of digestion efficiency (Indren et al., 2020a). In addition, porosity and conductivity of biochar will improve DIET and help electron transfer (Wei et al., 2020). Biochar addition can increase the methane content in biogas to more than 90% (Wei et al., 2019). This could be explained from two aspects. On the one hand, the direct adsorption of CO_2 by biochar increases the absolute methane content (Wei et al., 2020).

On the other hand, biochar could promote the interaction between hydrogenophilic methanogens and SAOB and then accelerate the conversion of CO_2 to methane (Shen et al., 2015). The key properties of biochar that may affect biogas production is summarized and illustrated in Figure 4.

Besides the positive effect, some researchers also reported that biochar could affect digestion performance negatively (Wei et al., 2020; Mumme et al., 2014; Rasapoor et al., 2020). According to the chemical equilibrium of ammonia nitrogen, the high alkalinity and pH of biochar can promote the conversion of NH_4^+ to NH_3, which is unfavorable to AD system because NH_3 is more toxic than NH_4^+ to the digestion system (Wei et al., 2020). Therefore, the effect of biochar on alleviating ammonia inhibition is related to the TAN concentration of the digestion system and also properties of biochar. Mumme et al. (2014) found that when the TAN concentration was in the range of 3.1-6.1 g L^{-1}, biochar had no effect on alleviating ammonia inhibition. When TAN was 2.1 g L^{-1}, biochar alleviated ammonia inhibition significantly. Rasapoor et al. (2020) reported that biochar only accelerated the process of AD, but did not change the content of methane. Similarly, Chen et al. (2021) found in the AD of chicken manure that when the biochar addition exceeded a certain amount, the volumetric biogas production rate of the reactor decreased (Indren et al., 2020b).

5. ***Mechanisms of biochar in relieving ammonia inhibition***

As shown in Figure 3, there are mainly four mechanisms of biochar in relieving ammonia inhibition based on literature review, namely, 1) adsorption of ammonia nitrogen and pH buffering, 2) acceleration of the DIET pathway, 3) immobilization of microorganisms, and 4) provision of nutrients. These were discussed in detail as follows.

5.1.1 *Adsorption of ammonia nitrogen*

As shown in Figure 4, there are four mechanisms for ammonia nitrogen adsorption including chemical adsorption (electrostatic attraction, ion exchange, and complexation) and physical adsorption (Masebinu et al., 2019; Fagbohungbe et al., 2016). Biochar surfaces are normally negatively charged because of the presence and dissociation of oxygen-containing functional groups (OCFGs) such as carboxyl, lactone, phenol, carbonyl, lactol, anhydride, pyrone, ether, chromene and quinone (Tomczyk et al., 2020; Yan et al., 2021; Qiu et al., 2019). Electrostatic attraction, ion exchange and complexation are related to the number of OCFGs (Masebinu et al. ,2019; Qambrani et al., 2017; Ahmad et al., 2014). Compared with complexation and electrostatic attraction, the ion exchange plays a more significant role in chemical adsorption (Vu et al., 2018). All the four adsorption pathways are affected by biochar characteristics (functional groups type and number, porosity, and specific surface area) and digestion conditions such as pH and cation concentration.

5.1.2 *Functional groups*

Functional groups mainly affect the chemical adsorption. Figure 5a showed the typical functional groups on the surface of a biochar sample detected by FTIR (Fourier Transform infrared spectroscopy) (Tang et al., 2019; Zhang et al., 2020; Xue et al., 2019). Hydroxyl, carboxylic, and amino are main functional groups contributing to ammonia nitrogen absorption. In general, the ratio of H/C, O/C, and N/C (based number of moles) can represent the number of hydroxyls, carboxylic, and amino, respectively. At same times, the ratio of H/C and O/C are the indication of aromatization degree and the number of OCFGs (Tan et al., 2017; Ahmed et al., 2016a). The cationic exchange capacity (CEC) is positively related to the number of OCFGs of biochar. Ion exchange happens because of the potential metal exchange between NH_4^+ and alkali metals (such as K^+, Mg^{2+}, Ca^{2+} and Na^+), which are available on the biochar surface (Masebinu et al., 2019). The formation and number of OCFGs have a closed relationship with the pyrolysis temperature. During the biochar production process, dehydration and dehydrogenation increase with more OCFGs formed with the increase of pyrolysis temperature (Tang et al., 2019). However, the OCFGs gradually disappear with a further increase of the pyrolysis temperature (Figure 5b). Among these functional groups, the order of stability is amine and amides < polysaccharides or phosphodiesters < $-CH_3$, -OH, and -NH groups < carbonyl, carboxyl and aromatic ring (Figure 5b). The decrease of functional groups leads to the decrease of polarity, which has a negative relationship with chemical adsorption (Ahmad et al., 2014). Therefore, chemical attraction capacity is sensitive to the change of pyrolytic temperature of producing biochar (Ahmed et al., 2016a; Yin et al., 2017)

5.1.3 Specific surface area and porosity

The specific surface area and porosity are positively correlated with the ability of physical adsorption (mainly intraparticle diffusion and surface site absorption) to ammonia nitrogen. The specific surface area varies widely from 2.32 to 766.00 $m^2\ g^{-1}$ depending on the pyrolysis condition and type of raw material (Shen et al., 2020). The specific surface area mainly affects the capacity of surface site absorption. According to the pore size (diameter), pores in biochar is classified into macropores ($50\text{-}1.0*10^6$ nm), mesopores (2-50 nm), and micropores (0.1-50 nm) (Weber et al., 2018) with micro- and meso-pores being dominant in the adsorption process. The about eighty percentage of the porosity is contributed by the micropores (Weber et al., 2018). The porosity affects the physical adsorption of ammonia nitrogen by influencing the intraparticle diffusion.

Porosity and specific surface area can obviously be affected by pyrolysis temperature. As shown in Figure 2a and Figure 2d, the porosity and specific surface area of biochar increased significantly along with the increase of pyrolysis temperature (Weber et al., 2018).

5.1.4 Biochar addition ratio

The average adsorption capacity of biochar for ammonia nitrogen is about 50 mg g^{-1}. As shown in Table 1, the addition of biochar is positive for digestion system when the addition amount of biochar in high ammonia nitrogen system is 2-40 g L^{-1}. Excessive biochar addition may damage the digestion system in two ways. First, if the ammonia nitrogen concentration in the digestion system is low (< 2 g L^{-1}), the addition of a large amount of biochar could suppress the microbial growth and metabolism because ammonia nitrogen provides a nitrogen source for microbial growth and metabolism. In addition, biochar has high pH (6.8-11.3) (Table 1). Excessive biochar leads to an increase in the pH of the digestion system, which sometimes is extremely detrimental to microorganisms. Therefore, biochar addition ratio needs to be optimized when it is used as an additive in the digestion system to enhance biogas production and alleviate ammonia nitrogen.

5.1.5 pH of digestion system

The surface negative charge (SNC) is positively correlated with the surface polarity of biochar, which determines the ability of chemical adsorption (Tian et al., 2020; Rasapoo et al., 2020). pH and OCFGs have a close relationship with SNC (Tan et al., 2020). pH influences charge on the surface of biochar by affecting the protonation and deprotonation of OCFGs. Among these OCFGs, hydroxyl and carboxyl have decisive effect on the SNC. In addition, the number of hydroxyl group is higher than that of carboxyl.

The pH of the digestion system affects the adsorption performance of biochar on ammonium nitrogen, mainly by chemical adsorption, by affecting the form of ammonia nitrogen and the surface charge of biochar. The pH of AD is often in the range of 7-9 with the nitrogen-rich substrates. Biochar is usually alkaline due to the production of carbonate and phosphate during pyrolysis process. In addition, wood vinegar is produced during biochar production process, which causes the pH of biochar is above 7 (Zhang et al., 2019b). At the same times, the pH of biochar increases with the increase of pyrolysis temperature (Table 2). For instance, the pH value of rice straw biochar could reach 11.2 when the temperature is 750 °C (Yan et al., 2021). Therefore, adding biochar into AD often leads to a higher pH of the system and therefore excessive loading of biochar can negatively affect the performance of AD. On the other side, pH affects the transformation of ammonia nitrogen. For instance, NH_4^+ can be transformed to NH_3 as the pH increases (Zheng et al., 2021). Biochar adsorbs NH_3 only by physical adsorption, which is less efficient than the adsorption of NH_4^+. As a result, the ability of biochar to adsorb ammonia nitrogen decreases as the pH increases (Du et al., 2005; Yang et al., 2018).

As shown in Figure 6, the point of zero charge (pH_{pzc}) of the biochar is also critical parameters affecting the adsorption ability of the biochar to ammonia nitrogen. The pH_{pzc} is the pH of the digestion system under which there is no charge on the surface of biochar. In general, the pH_{pzc} is in the range of 2-8 (Song et al., 2018). At $pH_{pzc,}$ the adsorption ability of biochar to NH_4^+ through the electrostatic attraction pathway is weak (Shi et al., 2013). When the pH is smaller than pH_{pzc}, the positively charged NH_4^+ is repelled by the biochar with positive charge. Simultaneously, the positive charge and the amount of H^+ on the surface of biochar decrease as the pH of the digestion system increases (pH < pH_{pzc}) so that the adsorption capacity of the biochar for ammonia nitrogen increases. The H^+ will compete with NH_4^+ for the functional groups presented on the biochar surface, leading to a reduced adsorption efficiency. The surface of biochar is mainly negatively charged when the pH of the digestion system is higher than pH_{pzc}. The lower the pH_{pzc} is, the more negative charges on the surface. Therefore, the ability of biochar to adsorb ammonia nitrogen through electrostatic attraction, ion exchange and complexation is improved with biochar addition.

5.1.6 Temperature of digestion system

Based on digestion temperature, AD can be divided into psychrophilic (15-25℃), mesophilic (35-45℃) and thermophilic (55-65℃) digestion. High temperature benefits the degradation of nitrogen-rich substrates, resulting in high ammonia nitrogen (Cai et al., 2021c). It is generally believed that the adsorption of ammonia nitrogen by biochar is an exothermic reaction, suggesting that the ability of biochar to adsorb ammonia nitrogen decreases with the increase of digestion temperature. Therefore, the application of biochar is still challenging in the thermophilic anaerobic digestion of nitrogen-rich substrates.

5.1.7 Biochar modification

Biochar can be modified to enhance the adsorption performance by increasing functional groups and specific surface area and increasing the adsorption site. mainly including acid, alkali, and magnetic modification (Chen et al., 2021; Wang et al., 2019; Li et al., 2020; Qin et al., 2017). Some other modified methods such as carbonaceous materials, organic solvents have obvious disadvantages (mainly potential pollution and high cost), therefore, we don't discuss these methods in this review. The effect of the modified biochar on the performance of anaerobic digestion with high TAN concentration were summarized and listed in Table 2.

It is evident from Table 2 that acid (hydrochloric acid, nitric acid, sulfuric acid, and phosphoric acid) modification can increase the number of acidic functional groups (3.54-7.38 times) (Qiu et al., 2019). In addition, acid washing removes some of minerals, opening up pores and thus leading to high specific surface area (Wang et al., 2019). These changes will cause higher adsorption efficiency of biochar to ammonia nitrogen. In addition, acid modification can help formation of new functional groups with high adsorption capacity. For instance, after biochar modification using 0.2 mol L^{-1} H_2SO_4, the amount of carboxyl group decreased while the amount of the lactone group increased due to the dehydration effect of carboxyl and hydroxyl (Chen et al., 2021; Wang et al., 2014; Ahmed et al., 2016b). Due to the newly formed lactone groups, the ability of biochar to adsorb ammonia nitrogen through chemical adsorption (mainly electrostatic adsorption and complexation) increased by 1.6 times. In addition, the increase of acidic oxidizing groups can increase the hydrophilicity and cation exchange capacity of biochar (Wahab et al., 2012). Interestingly, acid modification also can increase aromaticity of biochar (Shi et al., 2013), which are beneficial for ammonia nitrogen adsorption. The acid-modified biochar can also reduce the pH_{pzc} of the biochar, which makes it have stronger adsorption capacity in the digestion system with neutral pH.

Alkali such as KOH and NaOH is also often used to modify biochar to increase specific surface area and functional groups (Wang et al., 2019). The increase in specific surface area might be due to the corrosiveness of strong alkalis, which can make the surface of biochar rougher. However, there is no related report on the mechanism of alkali affecting the number of functional groups. KOH has stronger alkaline than NaOH. In order to improve the adsorption effect, the concentration of NaOH and KOH should be higher than 3 M and 2 M, respectively. The modification effect of alkali also depends on the type of biochar. For instance, after NaOH modification, the specific surface area and total pore number of corncob wastes biochar increase. Finally, the capacity of biochar to adsorb ammonia nitrogen increased by 42% (Vu et al., 2018). However, Fan et al. (2010) found that NaOH modification only has slight effect on the surface area of bamboo biochar. It is worth noting that these cations in these alkalis will compete adsorption sites with NH_4^+, which will lead the decrease of absorption for NH_4^+ (Yang et al., 2018; Zheng et al., 2020). Therefore, the alkali concentration used for modification should not be too high. Most of biochar is alkaline and will be more alkaline after modification using alkali. Therefore, when applying strong alkali to modify biochar, special attention needs to be paid to the potential negative impact of pH on the digestion system.

Another modification method of biochar is magnetization using iron salt. After being magnetized, biochar is easier to be recycled. The iron oxide attached to the surface of the biochar can increase the specific surface area, and the Fe-O functional group provides new active sites, thereby increasing the adsorption capacity (Wang et al., 2021a). For instance, Qin et al. (2017) reported that the surface area of biochar rises 20 times after modification using $FeCl_3$ solution, which leads to 25% increase of methanogenic archaea. In addition, the magnetized biochar surface may have stronger electrical conductivity, which can enhance the DIET pathway (Qin et al., 2017).

Although they can improve the quality of biochar, they might have some negative effect on environment (potential secondary pollution), especially for chemical modified methods. Some researchers are dedicated to developing new modification methods.

Recently, Huang et al. (2021) reported that gas-modified biochar can significantly reduce the pore size of biochar and increase the specific surface area. Gas modification may mainly change the physical adsorption capacity of biochar for ammonia nitrogen. However, the performance of this modified biochar to adsorb ammonia nitrogen in an actual high ammonia nitrogen digestion system still needs to be determined.

5.2 Direct interspecies electron transfer

In AD system, methane is usually produced through the IHT (interspecies electron transfer) pathway (Martins et al., 2018) or direct interspecies electron transfer (DIET). DIET is more efficient and stable than IHT (Yang et al., 2017) since the velocity of electron transfer of DIET is several times than that of IHT (Viggi et al., 2014). Generally, the connection of DIET among different microorganisms are biological electrical connections such as conductive pili and e-transport protein (Park et al., 2018). It is reported that the DIET pathway could be enhanced by supplementing some conductive materials such as biochar. Biochar has certain conductivity due to its graphite structure, particularly when it is produced at high pyrolysis temperature (Martins et al., 2018). Biochar has been found to act as an electron carrier to favor DIET, thereby accelerating the production of methane (Wang et al., 2017; Yan et al., 2021). For instance, Chen et al. (2014) found that the DIET between *Geobacter metallireducens*, *Geobacter sulfurreducens* and *Methanosarcina barkeri* is through biochar instead of biological electrical connections. Pan et al. (2019) also reported that the interaction between bacteria and archaea linked by DIET to produce methane has high energy efficiency and such interaction can be enhanced with biochar addition. Syntrophic acetic acid oxidizing bacteria (SAOB) is the most common bacteria involved in DIET. Westerholm et al. (2012) reported that supplementation of biochar in the high ammonia nitrogen system resulted in a 9-fold increase in the abundance of *Syntrophaceticus schinkii*, and an increase in the proportion of the *Methanothermobacter thermautotrophicus*. However, if only supplemented *Methanothermobacter thermautotrophicus*, the abundance of *Syntrophaceticus schinkii* did not increase. This suggests that biochar provides a bridge for the DIET between *Syntrophaceticus schinkii* and *Methanothermobacter thermautotrophicus*, resulting in the rapid recovery of the digestion performance of ammonia inhibited system. Besides SAOB, *Geobacter* species is also a type of bacteria that can cooperate with archaea through DIET. *Geobacter* species involve the degradation of ethanol, propionate and butyrate. For example, Zhao et al. (2016) found that *Geobacter* and *Methanosaeta* or *Methanosarcina* can degrade propionic acid and butyric acid into methane through the DIET pathway. Wang et al. 2021 reported that rice straw biochar can improve the DIET pathway between *Geobacter* and *Methanosaeta* and *Methanosarcina*. Biochar also provides a suitable living environment for these microorganisms who participated in the DIET pathway to ensure their function. For example, Wang et al. (2018) found that biochar can simultaneously increase the abundance of Anaerolineaceae and *Methanosaeta*. Under different TAN concentrations, the degree of ammonia inhibition in the digestion system is different. As Table 3 shows, many methanogenic archaea can participate in the DIET pathway mediated by biochar such as *Methanosarcina*, *Methanosaeta* and *Methanospirillum* (Pan et al., 2019; Indren et al., 2020b). This allows biochar to be used at different TAN concentrations to mediate the DIET pathway. Figure 7 clearly shows the succession mechanism of DIET pathway mediated by biochar under different TAN concentration. The TAN and FAN concentrations together affect the community composition of methanogenic archaea.

Based on this specific community composition, biochar plays its role in promoting the DIET pathway.

Biochar's conductivity is the main factor affecting the efficiency of DEIT. The phenolic hydroxyl group is the main electron-donating group, and the quinone, carbonyl and carboxyl groups are the main electron-accepting groups. Therefore, the type and number of OCFGs on the surface of biochar can impact on the conductivity of biochar. If the number of OCFGs is used as the only indicator to compare the conductivity of different biochars, the opposite conclusion may be drawn (Shen et al., 2020; Xu et al., 2018; Indren et al. (2020a).

5.3 Immobilized microorganisms

Biochar can increases the absolute number and relative abundance of related microorganisms, and then enhances the ability of the digestion system to resist ammonia nitrogen inhibition. The enrichment capacity of biochar for microorganisms depends on the parent material of biochar, the number and types of pores. In general, the size of bacteria and archaea is in the range of 400-2000 and 100-15000 nm, respectively. Therefore, the mesopores (2-50 nm), and micropores (0.1-50 nm) are too small for microorganisms. Therefore, macropores is the most important for microbial colonization. Biochar provides a suitable micro-environment for microorganisms to survive, and increases the resistance of microorganisms to stress environments. In many previous studies, microorganisms and their DNA were found in the pores of biochar (Mumme et al., 2014; Indren et al., 2020a; Fagbohungbe et al., 2016). In addition, the difference in the number of macropores directly leads to the difference in the ability of microorganisms to colonize due to the different types of biochar (Indren et al., 2020a). The interaction between biochar and microorganisms has been reported in some literatures. Some studies have proved that biochar could promote the colonization of hydrogenophilic methanogens and versatile methanogen, thereby increasing the resistance of the digestion system to ammonia inhibition (Yan et al., 2021; Indren et al., 2021). In contrast, Shen et al. (2020) and Zhang et al. (2019b) revealed that biochar can only promote the growth of acetoclastic methanogens, but has little growth stimulating effect on hydrogenotrophic methanogens. These results illustrate that the immobilized effect of biochar on methanogenic archaea is not specific (Wei et al., 2020).

The absolute TAN and FAN concentration are the decisive parameters for the succession of methanogenic archaea (Capson-Tojo et al., 2020). This means that which methanogenic archaea is immobilized in surface of biochar mainly depends on the concentration of ammonia nitrogen. Interestingly, some researchers have a different view. They believe that biochar itself can promote the succession of microorganisms. For instance, Giwa et al. (2019) reported that *Methanothrix* (strict hydrogenophilic methanogen) is more resistant to ammonia nitrogen than *Methanosarcina*, resulting in *Methanothrix* and *Methanosarcina* dominates in biochar-added and control reactors, respectively, when the TAN concentration is greater than 2.45 g L^{-1}. Similarly, Ma et al. (2019) reported that biochar can promote the succession of *Methanosaeta* to *Methanosarcina*, which lead the increase of capacity of resisting ammonia nitrogen inhibition. In their study, although the digestion system was inhibited by ammonia nitrogen, the original ammonia nitrogen concentration,before the addition of biochar, was generally 2-5 g L^{-1} (inhibited steady-state). The adsorption capacity of biochar for ammonia nitrogen has a sufficiently large impact on the ammonia nitrogen concentration of digestion system. This may be an indirect mechanism about that biochar affects the structure of the archaeal community. Unfortunately, the direct mechanism of biochar to promote the succession of methanogenic archaea remains unclear. The immobilization effect of biochar may be related to the cell morphology of the archaea when multiple archaea with the same methanogenesis pathway exist. It still requires further research to explore these unknown. Besides archaea, the adsorption and immobilization effect of biochar on bacteria is also often reported (Indren et al., 2020b). For example, Wei et al. (2020) reported that the *Rhodobacter sp*., which was responsible for hydrolysis, dominates the biochar-added reactor, and the abundances of *Paludibacter sp*. and *Proteinclasticum sp*., which can produce VFAs and hydrogen respectively, increased by 39.4% and 46.25, respectively (Wang et al., 2017). In addition, biochar also has a certain activation effect on *Epsilonproteobacteria*, which has function of denitrification (Pan et al., 2019).

5.4 Provision of nutrients

Although there is no direct relationship between trace elements and the adsorption ability, trace elements have been proved by many articles that they can alleviate ammonia inhibition by improving microbial activity, especially methanogenic archaea (Molaey et al., 2018b; Molaey et al., 2018c). Biochar contains abundant macro elements (C, H, O, K, Na, and Ca) and trace elements (Fe, Co, Ni, Mn, Mo, Se and Zn) (Wambugu et al., 2019; Indren et al., 2020a; Sanchez et al., 2021). The elemental composition of biochar is directly related to the parent material used to produce biochar. Indren et al. (2020a) compared the composition of trace elements in wood pellet, wheat straw and sheep manure biochar and found that Fe, Mn, and Zn content in sheep manure biochar is the most abundant. Wambugu et al. (2019) tested the elemental composition in the leachate of the biochar and found that the potassium content is greater than 1g kg^{-1}, while the Fe, Co, Ni, and Mn content are less than 10 mg kg^{-1}. Compared with wood and straw biochar, sludge and livestock manure biochar contain higher ash content. For instance, the ash content of sludge biochar is 40-70%, while the ash content of coconut shell biochar is only 2-4%, which means that there are more mineral elements in the sludge (Zhang et al., 2019b). Sugiarto et al., 2021 extract the biochar's leachate using citric acid and find that the leachate rich in Fe and can obviously enhance digestion performance due to the increase of *Clostridia* and *Methanosaeta*.

In general, macronutrients are sufficient in digestion systems, while the deficiency of trace elements is often reported (Molaey et al., 2018a; Bhatnagar et al., 2020). The deficiency of trace elements will lead to the accumulation of volatile fatty acids (Cai et al., 2017). Supplementation of trace elements is often used as an important strategy to alleviate ammonia inhibition (Cai et al., 2021b). Biochar have been proven to promote digestion performance due to the abundance of trace elements. For example, Sanchez et al. (2021) reported that the content of acetyl-CoA synthase and methyl coenzyme M in the biochar-added treatment was higher, which may be related to the presence of Fe, Co, Ni and Mn. Similarly, Yue et al. (2019) also found that the biochar can promote the growth of microorganisms due to the existence of trace element. Interestingly, Cai et al. (2018) found that the deficiency of trace elements in the digestion system is also related to the low bioavailability of trace elements. In digestion systems with high ammonia nitrogen, the pH is often greater than 8, which often leads to low bioavailability of trace elements. The bioavailability of trace elements (Fe, Co, Ni) can be enhanced by biochar, thereby increasing the abundance of corresponding enzyme genes and enzyme activity (Qi et al., 2021). Generally, chemical ligands such as EDTA and EDDS are commonly used to regulate the bioavailability of trace elements (Cai et al., 2019). In fact, some bio-ligands such as SMPs and EPS can also regulate the bioavailability of trace elements. The concentrations of SMP and EPS both depend on the activity of microorganisms. Biochar increases the concentration of SMP and EPS by improving the activity of microorganisms, resulting in the bioavailability of trace elements is at an appropriate level (Qi et al., 2021).

6. ***Conclusions and prospectives***

6.1 Conclusions

Ammonia is a common toxic substance in AD system, and the addition of biochar could help mitigate this problem. Biochar can adsorb ammonia nitrogen by electrostatic attraction, ion exchange, complexation and physical adsorption due to the porous structure and the abundant OCFGs on the surface of biochar. The porous structure of biochar provides an ideal place for the colony and growth of microorganisms, enhancing the resistance of the digestion system to ammonia toxicity. Due to the conductivity property, biochar addition can promote DIET between bacteria and archaea. The DIET mediated by biochar is mostly between the hydrogenophilic methanogens and SAOB, which also benefits from the immobilization of microorganisms by biochar. As an alkaline additive, biochar can buffer pH of the AD with high ammonia nitrogen. Finally, biochar can provide abundant trace elements for the digestion system to increase the resistance of microorganisms to ammonia nitrogen. Simultaneously, biochar can increase the bioavailability of trace elements by increasing the concentration of SMP and EPS, thereby improving the ability of the digestion system to resist ammonia inhibition. The properties of biochar can be modified to improve its capability of adsorbing ammonia nitrogen.

6.2 Prospectives

1. The adsorption capacity of ammonia nitrogen by biochar is affected by pH of the

AD system. The AD system with high ammonia nitrogen usually has a pH value ranging from 7 to 8.5 and the addition of alkaline biochar would change the pH of the system and thus affect the subsequent adsorption capacity. It is therefore essential to study biochar's adsorption capacity of ammonia under different pH which will help engineer biochar and control operation conditions of AD to achieve the best performance.

2. The effect of biochar on the alleviating ammonia nitrogen depends on a number factors such as the properties of biochar, biochar addition ratio and the operation conditions of AD (temperature and pH) and TAN concentration Therefore, for a given substrate, the use of biochar as an additive to remove ammonia nitrogen needs to be examined and optimized individually. The properties of biochar can be tuned by controlling the pyrolysis conditions such as temperature but biochar modification can also be deployed to improve the adsorption efficiency. However, the existing modifications such as acid, alkali, and oxidant modification still face a number of challenges such as high cost and potential environmental risks to the digestion system. It is still in great need of the development of safe, efficient and practical modification methods.

3. The average adsorption capacity of biochar is less than 50 mg g^{-1}, and sometimes the adsorption capacity may not be the main mechanism for biochar to relieve ammonia inhibition. Therefore, a deep understanding of working mechanisms of biochar in relieving ammonia inhibition is still needed, particularly in the high ammonia nitrogen concentration.

4. Versatile methanogen (*Methanosarcina*) and hydrogenotrophic methanogen

(mainly *Methanobacterium*, *Methanoculleus*, *Methanothermobacter*) are the main archaea existing in the high ammonia nitrogen digestion system. It has been reported that the beneficial effect of biochar in AD with high ammonia nitrogen is caused by promoting the DIET pathway. However, hydrogenotrophic pathway is the main methane-producing way and therefore, it is important to reveal how biochar promotes the growth of versatile methanogen, hydrogenotrophic methanogen and SAOBs and their interactions.

Acknowledgements

This study was supported by the National Key Research and Development Program of China (Grant number: 2019YFC0408700) and CSCDAAD (National Scholarship Council and German Academic Exchange Center).

References

1. Ahmad, M., Rajapaksha, A.U., Lim, J.E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S.S., Ok, Y.S., 2014. Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere 99, 19–33.
2. Ahmed, M.B., Zhou, J.L., Ngo, H.H., Guo, W., 2016a. Insight into biochar properties and its cost analysis. Biomass Bioenerg. 84, 76–86.
3. Ahmed, M.B., Zhou, J.L., Ngo, H.H., Guo, W., Chen, M.F., 2016b. Progress in the preparation and application of modified biochar for improved contaminant removal from water and wastewater. Bioresour. Technol. 214, 836–851.
4. Baek, G., Kim, J., Kim, J., Lee, C., 2018. Role and potential of direct interspecies electron transfer in anaerobic digestion. Energies. 11, 107.
5. Banks, C.J., Zhang, Y., Jiang, Y., Heaven, S., 2012. Trace element requirements for stable food waste digestion at elevated ammonia concentrations. Bioresour. Technol. 104, 127–135.
6. Barua, S., Dhar, B.R., 2017. Advances towards understanding and engineering direct interspecies electron transfer in anaerobic digestion. Bioresour. Technol. 244, 698–707.
7. Bhatnagar, N., Ryan, D., Murphy, R., Enright, A.M., 2020. Trace element supplementation and enzyme addition to enhance biogas production by anaerobic digestion of chicken litter. Energies. 13 (13), 3477.
8. Bonk, F., Popp, D., Weinrich, S., Strauber, H., Kleinsteuber, S., Harms, H., Centler, F., 2018. Ammonia inhibition of anaerobic volatile fatty acid degrading microbial communities. Front. Microbiol. 9, 2921.
9. Cai, Y., Hu, K., Zheng, Z., Zhang, Y., Guo, S., Zhao, X., Cui, Z., Wang, X., 2019. Effects of adding EDTA and Fe^{2+} on the performance of reactor and microbial community structure in two simulated phases of anaerobic digestion. Bioresour. Technol. 275, 183–191.
10. Cai, Y., Hua, B., Gao, L., Hu, Y., Yuan, X., Cui, Z., Zhu, W., Wang, X., 2017. Effects of adding trace elements on rice straw anaerobic mono-digestion: focus on changes in microbial communities using high-throughput sequencing. Bioresour. Technol. 239, 454–463.
11. Cai, Y., Janke, L., Zheng, Z., Stinner, W., Wang, X., Pröter, J., Schäfer, F., 2021c. Exploring the combined effect of total ammonia nitrogen, pH and temperature on anaerobic digestion of chicken manure using response surface methodology and two kinetic models. Bioresour. Technol. 125328. https://doi.org/10.1016/j.biortech.2021.125328.
12. Cai, Y., Janke, L., Zheng, Z., Wang, X., Proter, J., Schafer, F., 2021b. Enhancing anaerobic digestion of chicken manure leachate: Effects of trace elements supplementation on methane production. Bioresour. Technol. Rep. 14, 100662.

13. Cai, Y., Wang, J., Zhao, Y., Zhao, X., Zheng, Z., Wen, B., Cui, Z., Wang, X., 2018a. A new perspective of using sequential extraction: to predict the deficiency of trace elements during anaerobic digestion. Water Res. 140, 335–343.

14. Cai, Y., Zheng, Z., Wang, X., 2021a. Obstacles faced by methanogenic archaea originating from substrate-driven toxicants in anaerobic digestion. J. Hazard. Mater. 403, 123938.

15. Capson-Tojo, G., Moscoviz, R., Astals, S., Robles, A., Steyer, J.P., 2020. Unraveling the literature chaos around free ammonia inhibition in anaerobic digestion. Renew. Sustain. Energy Rev. 117, 109487.

16. Chen, S., Rotaru, A.E., Shrestha, P.M., Malvankar, N.S., Liu, F., Fan, W., Nevin, K.P., Lovley, D.R., 2014. Promoting interspecies electron transfer with biochar. Sci. Rep. 4, 5019.

17. Chen, M., Wang, F., Zhang, D.L., Yi, W.M., Liu, Y., 2021. Effects of acid modification on the structure and adsorption NH_4^+-N properties of biochar. Renew. Energ. 169, 1343–1350.

18. Chiappero, M., Norouzi, O., Hu, M., Demichelis, F., Berruti, F., Di Maria, F., Mašek, O., Fiore, S., 2020. Review of biochar role as additive in anaerobic digestion processes. Renew. Sust. Energ. Rev. 131, 110037.

19. Cho, K., Shin, S.G., Kim, W., Lee, J., Lee, C., Hwang, S., 2017. Microbial community shifts in a farm-scale anaerobic digester treating swine waste: Correlations between bacteria communities associated with hydrogenotrophic methanogens and environmental conditions. Sci. Total Environ. 601–602, 167–176.

20. Chuenchart, W., Logan, M., Leelayouthayotin, C., Visvanathan, C., 2020. Enhancement of food waste thermophilic anaerobic digestion through synergistic effect with chicken manure. Biomass and Bioenerg. 136, 105541.

21. Cui, Y., Mao, F., Zhang, J., He, Y., Tong, Y.W., Peng, Y., 2021. Biochar enhanced high-solid mesophilic anaerobic digestion of food waste: Cell viability and methanogenic pathways. Chemosphere. 272, 129863.

22. Du, Q., Liu, S.J., Cao, Z.H., Wang, Y.Q., 2005. Ammonia removal from aqueous solution using natural Chinese clinoptilolite. Sep. Purif. Technol. 44(3): 229–234.

23. Fagbohungbe, M.O., Herbert, B.M.J., Hurst, L., Ibeto, C.N., Li, H., Usmani, S.Q., Semple, K.Y., 2017. The challenges of anaerobic digestion and the role of biochar in optimizing anaerobic digestion. Waste Manage. 61, 236-249.

24. Fagbohungbe, M.O., Herbert, B.M.J., Hurst, L., Li, H., Usmani, S., Semple, K., 2016. Impact of biochar on the anaerobic digestion of citrus peel waste. Bioresour. Technol. 216, 142–149.

25. Fan, Y., Wang, B., Yuan, S., Wu, X., Chen, J., Wang, L., 2010. Adsorptive removal of chloramphenicol from wastewater by NaOH modified bamboo charcoal. Bioresour. Technol. 101, 7661–7664.

26. Huang, W.H., Lee, D.J., Huang, C., 2021. Modification on biochars for applications: A research update. Bioresour. Technol. 319, 124100.

27. Indren, M., Birzer, C.H., Kidd, S.P., Hall, T., Medwell, P.R., 2020a. Effects of biochar parent material and microbial pre-loading in biochar amended high-solids anaerobic digestion. Bioresour. Technol. 298, 122457.

28. Indren, M., Birzer, C.H., Kidd, S.P., Hall, T., Medwell, P.R., 2021b. Effect of wood biochar dosage and re-use on high-solids anaerobic digestion of chicken litter. Biomass and Bioenerg. 144, 105872.

29. Indren, M., Birzer, C.H., Kidd, S.P., Medwell, P.R., 2020. Effect of total solids content on anaerobic digestion of poultry litter with biochar. J. Environ. Manage. 255, 109744.

30. Jang, H.M., Brady, J., Kan, E., 2021. Succession of microbial community in anaerobic digestion of dairy manure induced by manure-derived biochar. Environ. Eng. Res. 26(1), 200001.

31. Karlsson, A., Ejlertsson, J., 2012. Addition of HCl as a means to improve biogas production from protein-rich food industry waste. Biochem. Eng. J. 61, 43–48.

32. Kumar, M., Dutta, S., You, S., Luo, G., Zhang, S., Show, P.L., Sawarkar, A.D., Singh, L., Tsang, D.C.W., 2021. A critical review on biochar for enhancing biogas production from anaerobic digestion of food waste and sludge. Journal of Cleaner Production. 305, 127143.

33. Kwon, K., Kim, H., Kim, W., Lee, J., 2019. Efficient nitrogen removal of reject water generated from anaerobic digester treating sewage sludge and livestock manure by combining anammox and autotrophic sulfur denitrification processes. Water 11, 204. https://doi.org/10.3390/w11020204.

34. Li, H., Dong, X., da Silva, E.B., de Oliveira, L.M., Chen, Y., Ma, L.Q., 2017. Mechanisms of metal sorption by biochars: biochar characteristics and modifications. Chemosphere. 178, 466–478.

35. Li, X., Wang, C., Zhang, J., Liu, J., Liu, B., Chen, G., 2020. Preparation and application of magnetic biochar in water treatment: A critical review. Science of the Total Environment. 711, 134847.

36. Liu, X.Y., Chen, G.X., Keller, A.A., Su, C.M, 2013. Effects of dominant material properties on the stability and transport of TiO_2 nanoparticles and carbon nanotubes in aquatic environments: from synthesis to fate. Environmental Science: Processes &Impacts, 15(1): 169–189.

37. Ma, J., Pan, J., Qiu, L., 2019. Biochar triggering multipath methanogenesis and subdued propionic acid accumulation during semi-continuous anaerobic digestion. Bioresource Technology. 293, 122026.

38. Martins, G., Salvador, A.F., Pereira, L., Alves, M.M., 2018. Methane production and conductive materials: a critical review. Environ. Sci. Technol. 52 (18), 10241–10253. https://doi.org/10.1021/acs.est.8b01913.s001.

39. Masebinu, S.O., Akinlabi, E.T., Muzenda, E., Aboyade, A.O., 2019. A review of biochar properties and their roles in mitigating challenges with anaerobic digestion. Renew. Sustain. Energy Rev. 103, 291–307.

40. Molaey, R., Bayrakdar, A., Çalli, B., 2018b. Long-term influence of trace element deficiency on anaerobic mono-digestion of chicken manure. J. Environ. Manage. 223, 743–748.

41. Molaey, R., Bayrakdar, A., Surmeli, R.O., Calli, B., 2018c. Anaerobic digestion of chicken manure: Mitigating process inhibition at high ammonia concentrations by selenium supplementation. Biomass and Bioenerg. 108, 439–446.

42. Molaey, R., Bayrakdar, A., Sürmeli, R.O., Çalli, B., 2018a. Influence of trace element supplementation on anaerobic digestion of chicken manure: linking process stability to methanogenic population dynamics. J. Clean. Prod. 181, 794–800.

43. Munne, J., Srocke, F., Heeg, K., Werner, M., 2014. Use of biochars in anaerobic digestion. Bioresour. Technol. 164, 189–197.

44. Park, J.H., Kang, H.J., Park, K.H., Park, H.D., 2018. Direct interspecies electron transfer via conductive materials: A perspective for anaerobic digestion applications. Bioresour. Technol. 254, 300-311.

45. Pan, J., Ma, J., Zhai, L., Liu, H., 2019. Enhanced methane production and syntrophic connection between microorganisms during semi-continuous anaerobic digestion of chicken manure by adding biochar. J. Clean. Prod. 240, 118178.

46. Pandey, D., Daverey, A., Arunachalam, K., 2020. Biochar: Production, properties and emerging role as a support for enzyme immobilization. J. Clean. Prod. 255, 120267.

47. Poirier, S., Desmond-Le, Q.E., Madigou, C., Bouchez, T., Chapleur, O., 2016. Anaerobic digestion of biowaste under extreme ammonia concentration: identification of key microbial phylotypes. Bioresour. Technol. Rep. 207, 92–101.

48. Qambrani, N.A., Rahman, M.M., Won, S., Shim, S., Ra, C., 2017. Biochar properties and ecofriendly applications for climate change mitigation, waste management, and wastewater treatment: a review. Renew. Sustain. Energy Rev. 79, 255-273.

49. Qi, Q., Sun, C., Zhang, J., He, Y., Tong, Y.T., 2021. Internal enhancement mechanism of biochar with graphene structure in anaerobic digestion: The bioavailability of trace elements and potential direct interspecies electron transfer. Chem. Eng. J. 406, 126833.

50. Qin, Y., Wang, H., Li, X., Cheng, J.J., Wu, W., 2017. Improving methane yield from organic fraction of municipal solid waste (OFMSW) with magnetic rice-straw biochar. Bioresour. Technol. 245, 1058–1066.

51. Qiu, L., Deng, Y., Wang, F., Davaritouchaee, M., Yao, Y. 2019. A review on biochar-mediated anaerobic digestion with enhanced methane recovery. Renew. Sustain. Energy Rev. 115, 109373.

52. Rasapoor, M., Young, B., Asadov, A., Brar, R., Sarmah, A.K., Zhuang, W.Q., Baroutian, S., 2020. Effects of biochar and activated carbon on biogas generation: A thermogravimetric and chemical analysis approach. Energ. Convers. Manage. 203, 112221.

53. Sanchez, E., Herrmann, C., Maja, W., Borja, R., 2021. Effect of organic loading rate on the anaerobic digestion of swine waste with biochar addition. Environ. Sci. Pollut. Res. https://doi.org/10.1007/s11356-021-13428-1.

54. Shen, Y., Linville, J.L., Urgun-Demirtas, M., Schoene, R.P., Snyder, S.W., 2015. Producing pipeline-quality biomethane via anaerobic digestion of sludge amended with corn stover biochar with in-situ CO_2 removal. Appl. Energ. 158, 300–309.

55. Shen, R., Jing, Y., Feng, J., Luo, J., Yu, J., Zhao, L., 2020. Performance of enhanced anaerobic digestion with different pyrolysis biochars and microbial communities. Bioresour. Technol. 296, 122354.

56. Shen, Y., Linville, J.L., Ignacio-de Leon, P.A.A., Schoene, R.P., Urgun-Demirtas, M., 2016. Towards a sustainable paradigm of waste-to-energy process: Enhanced anaerobic digestion of sludge with woody biochar. J. Clean. Prod. 135, 1054–1064.

57. Shi, M., Wang, Z., Zheng, Z., 2013. Effect of Na^+ impregnated activated carbon on the adsorption of NH_4^+-N from aqueous solution. J. Environ. Sci. 25 (8), 1501–1510.

58. Song, T., Lai, X., Wang, Z., Fang, M., Yang, D., Ju, X., Li, J., Zhang, G., 2018. Adsorption of ammonium nitrogen by biochars produced from different biomasses. Journal of Agro-Environment Science. 37(3), 576–584.

59. Su, H.J., Liu, L., Wang, S.J., Wang, Q.F., Jiang, Y.X., Hou, X.C., Tan, T.W., 2015. Semicontinuous anaerobic digestion for biogas production: influence of ammonium acetate supplement and structure of the microbial community. Biotechnol. Biofuels 8.

60. Sun, W., Gu, J., Wang, X., Qian, X., Tuo, X., 2018. Impacts of biochar on the environmental risk of antibiotic resistance genes and mobile genetic elements during AD of cattle farm wastewater. Bioresour. Technol. 256, 342–349.

61. Sugiarto, Y., Sunyoto, N.M.S., Zhu, M.M., Jones, I., Zhang, D.K. 2021. Effect of biochar addition on microbial community and methane production during anaerobic digestion of food wastes: The role of minerals in biochar. Bioresour. Technol. 323, 124585.

62. Tan, Z., Lin, C.S.K., Ji, X., 2017. Rainey TJ. Returning biochar to fields: a review. Appl Soil Ecol. 116, 1–11.

63. Tan, Z., Yuan, S., Hong, M., Zhang, L., Huang, Q., 2020. Mechanism of negative surface charge formation on biochar and its effect on the fixation of soil Cd. J. Hazard. Mater. 384, 121370.

64. Tang, Y., Alam, M.S., Konhauser, K.O., Alessi, D.S., Xu, S., Tian, W., Liu, Y., 2019. Influence of pyrolysis temperature on production of digested sludge biochar and its application for ammonium removal from municipal wastewater. J. Clean. Prod. 209, 927–936.

65. Tomczyk, A., Sokołowska, Z., Boguta, P., 2020. Biochar physicochemical properties: pyrolysis temperature and feedstock kind effects. Rev Environ Sci Biotechnol. 19, 191–215.

66. Viggi, C.C., Rossetti, S., Fazi, S., Paiano, P., Majone, M., Aulenta, F., 2014. Magnetite particles triggering a faster and more robust syntrophic pathway of methanogenic propionate degradation. Environ Sci Technol. 48, 7536–7543.

67. Vu, M.T., Chao, H.-P., Van Trinh, T., Le, T.T., Lin, C.-C., Tran, H.N., 2018. Removal of ammonium from groundwater using Noah-treated activated carbon derived from corncob wastes: batch and column experiments. J. Clean. Prod. 180, 560–570.

68. Wahab, M.A., Boubakri, B., Jellali, S., Jedidi, N., 2012. Characterization of ammonium retention processes onto cactus leaves fibers using FTIR, EDX and SEM analysis, J. Hazard Mater. 241-242, 101-109.

69. Wambugu, C.W., Rene, E.R., Vossenberg, J.V.D., Dupont, C., Hullebusch, E.D.V., 2019. Role of Biochar in Anaerobic Digestion Based Biorefinery for Food Waste. Front. Energy Res. 7, 14.

70. Wang, D., Ai, J., Shen, F., Yang, G., Zhang, Y., Deng, S., Zhang, J., Zeng, Y., Song, C., 2017. Improving anaerobic digestion of easy-acidification substrates by promoting buffering capacity using biochar derived from vermicompost. Bioresour. Technol. 227, 286–96.

71. Wang, W., Lee, D.J., 2021c. Direct interspecies electron transfer mechanism in enhanced methanogenesis: A mini-review. Bioresour. Technol. 330, 124980.

72. Wang, C., Liu, Y., Wang, C., Xing, B., Zhu, S., Huang, J., Xu, X., Zhu, L., 2021a. Biochar facilitates rapid restoration of methanogenesis by enhancing direct interspecies electron transfer after high organic loading shock. Bioresour. Technol. 320, 124360.

73. Wang, T., Li, G., Yang, K., Zhang, X., Wang, K., Cai, J., Zheng, J., 2021b. Enhanced ammonium removal on biochar from a new forestry waste by ultrasonic activation: Characteristics, mechanisms and evaluation. Sci. Total Environ. 778, 146295.

74. Wang, L., Liu, X., Zhang, L., Li, M., Zhang, H., 2014. Effect of lignite semi-coke by acid solution treatment on its performance for elemental mercury removal in the flu, China Environ. Sci. 34 (12), 3056-3061.

75. Wang, G., Qian, L., Xin, G., Wang, X.C., 2018. Synergetic promotion of syntrophic methane production from anaerobic digestion of complex organic wastes by biochar: Performance and associated mechanisms. Bioresour. Technol. 250, 812.

76. Wang, F., Sang, Q., Deng, Y., Zhao, Y., Yang, Y., Chen, Y., Ma, J., 2021. Synthesis of Magnetic Iron Modifying Biochar for Ammonia Nitrogen Removal from Water. Environ. Sci. 42(4), 1914-1922.

77. Wang, Y., Wang, D., Liu, Y., Wang, Q., Chen, F., Yang, Q., Li, X.M., 2017. Triclocarban enhances short-chain fatty acids production from anaerobic fermentation of waste activated sludge. Water Res. 127, 150–161.

78. Wang, J., Wang, S., 2019. Preparation, modification and environmental application of biochar: A review. J. Clean. Prod. 227, 1002–1022.

79. Weber, K., Quicker, P., 2018. Properties of biochar. Fuel. 217, 240–261.

80. Wei, W., Guo, W., Ngo, H.H., Mannina, G., Wang, D., Chen, X., Liu, Y., Peng, L., Ni, B.-J. 2020. Enhanced high-quality biomethane production from anaerobic digestion of primary sludge by corn stover biochar. Bioresour. Technol, 123159.

81. Westerholm, M., Levén, L., Schnürer, A. 2012. Bioaugmentation of syntrophic acetate-oxidizing culture in biogas reactors exposed to increasing levels of ammonia. Appl. Environ. Microbiol., 78(21), 7619–7625.

82. Xu, J., Mustafa, A.M., Lin, H., Choe, U.Y., Sheng, K., 2018. Effect of hydrochar on anaerobic digestion of dead pig carcass after hydrothermal pretreatment. Waste Management. 78, 849–856.

83. Xue, S., Zhang, X., Ngo, H.H., Guo, W., Wen, H., Li, C., Zhang, Y., Ma, C., 2019. Food waste based biochars for ammonia nitrogen removal from aqueous solutions. Bioresource Technology. 292, 121927.

84. Yan, M., Fotidis, I.A., Tian, H., Khoshnevisan, B., Treu, L., Tsapekos, P., Angelidaki, I., 2019. Acclimatization contributes to stable anaerobic digestion of organic fraction of

municipal solid waste under extreme ammonia levels: focusing on microbial community dynamics. Bioresour. Technol. 286, 121376.

85. Yan, M., Zhu, X., Treu, L., Ravenni, G., Campanaro, S., Goonesekera, E.M., Ferrigno, R., Jacobsen, C.S., Zervas, A., Angelidaki, I., Fotidis, I.A., 2021. Comprehensive evaluation of different strategies to recover methanogenic performance in ammonia-stressed reactors. Bioresour. Technol. doi: https://doi.org/10.1016/j.biortech.2021.125329.

86. Yang, S., Chen, Z., Wen, Q., 2021b. Impacts of biochar on anaerobic digestion of swine manure: Methanogenesis and antibiotic resistance genes dissemination. Bioresour. Technol. 324, 124679.

87. Yang, H.I., Lou, K., Rajapaksha, A.U., Ok, Y.S., Anyia, A.O., Chang, S.X., 2018. Adsorption of ammonium in aqueous solutions by pine sawdust and wheat straw biochars. Environ. Sci. Pollut. Res. 25 (26), 25638–25647.

88. Yang, Z., Wang, W., He, Y., Zhang, R., Liu, G., 2018. Effect of ammonia on methane production, methanogenesis pathway, microbial community and reactor performance under mesophilic and thermophilic conditions. Renew. Energ. 125, 915–925.

89. Yang, Y., Zhang, Y., Li, Z., Zhao, Z., Quan, X., Zhao, Z., 2017. Adding granular activated carbon into anaerobic sludge digestion to promote methane production and sludge decomposition. J. Clean. Prod. 149. 1101–1108.

90. Yang, P., Peng, Y., Tan, H., Liu, H., Wu, D., Wang, X., Li, L., Peng, X., 2021a. Foaming mechanisms and control strategies during the anaerobic digestion of organic waste: A critical review. Sci. Total Environ. 779, 146531.

91. Yin, Q., Zhang, B., Wang, R., Zhao, Z., 2017. Biochar as an adsorbent for inorganic nitrogen and phosphorus removal from water: a review. Environ Sci Pollut Res. 24, 26297–26309.

92. Yu, X., Zhou, S., 2009. Effect of surface modification on adsorption properties of activated carbon, Chin. Chem. (1), 24–25.

93. Yuan, H., Zhu, N., 2016. Progress in inhibition mechanisms and process control of intermediates and by-products in sewage sludge anaerobic digestion. Renew. Sust. Energ. Rev. 58, 429–438.

94. Zhao, Z., Zhang, Y., Yu, Q., Dang, Y., Li, Y., 2016. Quan, X. Communities Stimulated with Ethanol to Perform Direct Interspecies Electron Transfer for Syntrophic Metabolism of Propionate and Butyrate. Water Res. 102, 475–484.

95. Zhang, M., Li, J., Wang, Y., Yang, C., 2019b. Impacts of different biochar types on the anaerobic digestion of sewage sludge. RSC Adv. 9 (72), 42375–42386.

96. Zhang, T., Wu, X., Shaheen, S.M., Zhao, Q., Liu, X., Rinklebe, J., Ren, H., 2020. Ammonium nitrogen recovery from digestate by hydrothermal pretreatment followed by activated hydrochar sorption. Chem. Eng. J. 379, 122254.

97. Zhang, Z., Zhu, Z., Shen, B., Liu, L., 2019a. Insights into biochar and hydrochar production and applications: A review. Energy. 171, 581-598.

98. Zheng, Z., Cai, Y., Zhang, Y., Zhao, Y., Gao, Y., Cui, Z., Hu, Y., Wang, X., 2021. The effects of C/N (10–25) on the relationship of substrates, metabolites, and

microorganisms in “inhibited steady-state” of anaerobic digestion. Water Res. 188, 116466.

99. Zheng, X., Shi, T., Song, W., Xu, L., Dong, J., 2020. Biochar of distillers’ grains anaerobic digestion residue: Influence of pyrolysis conditions on its characteristics and ammonium adsorptive optimization. Waste Manage. Res. 38(1), 86–97.

100. Zhou, J., Zhang, Y., Khoshnevisan, B., Duan, N., 2021. Meta-analysis of anaerobic co-digestion of livestock manure in last decade: Identification of synergistic effect and optimization synergy range. Appl. Energy. 282, 116128.

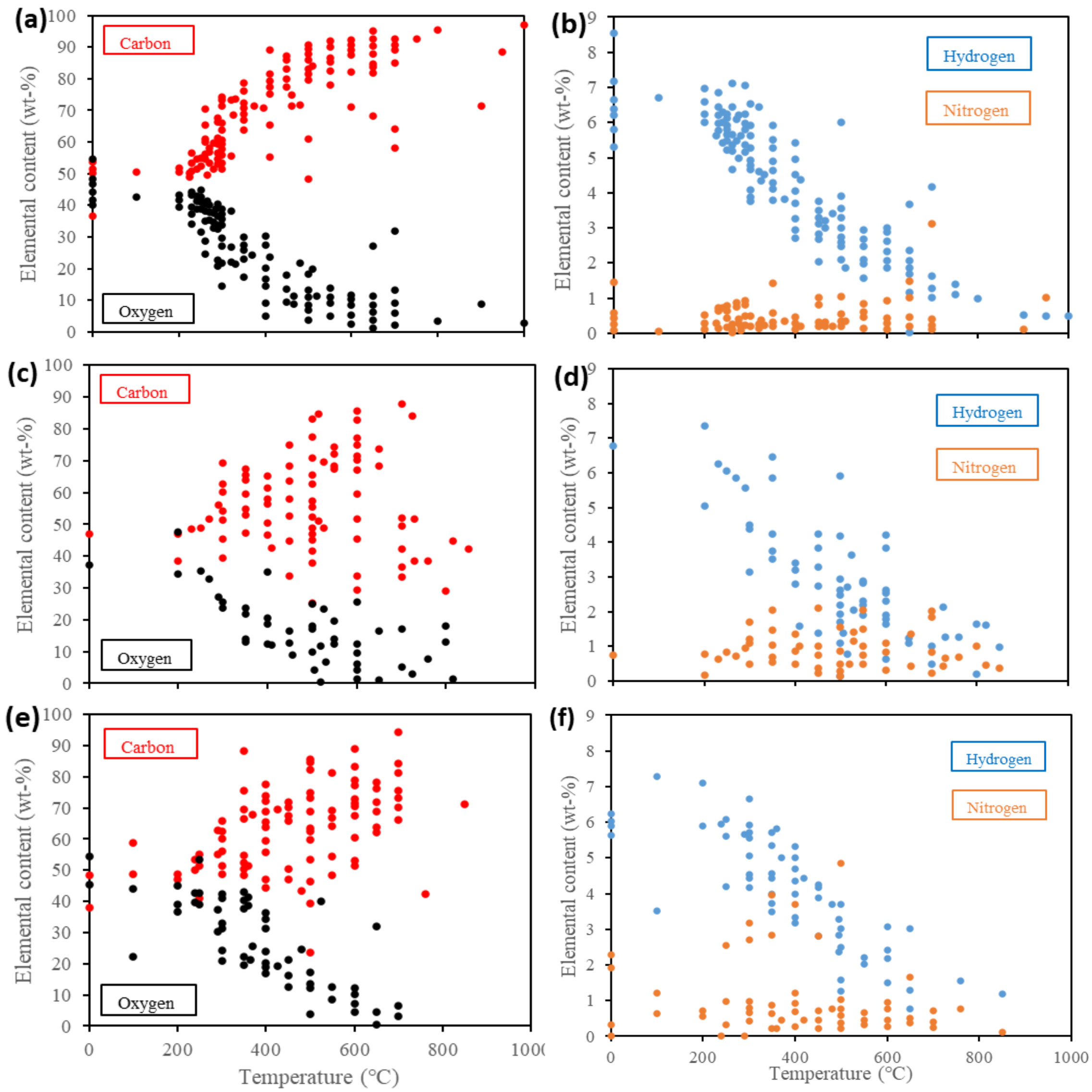

Figure 1. The effect of pyrolysis temperature on the contents of carbon, nitrogen, hydrogen and oxygen of wood biochar (a-b), straw biochar (c-d) and grass biochar (e-

f) (The data were obtained from Zhang et al., 2019; Weber et al., 2018; Xu et al., 2018).

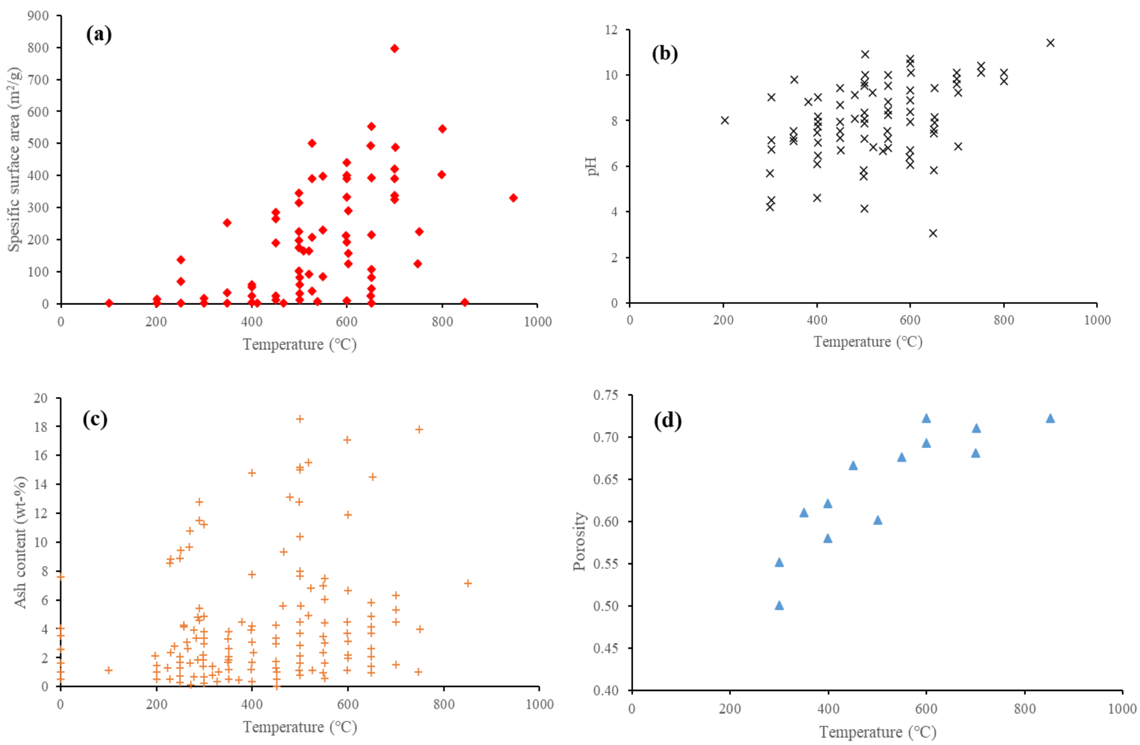

Figure 2. The effect of pyrolysis temperature on specific surface area (a), pH-value (b), ash content (c), and porosity (d) of wood biochar (The data were obtained from Pan et al., 2019; Weber et al., 2018).

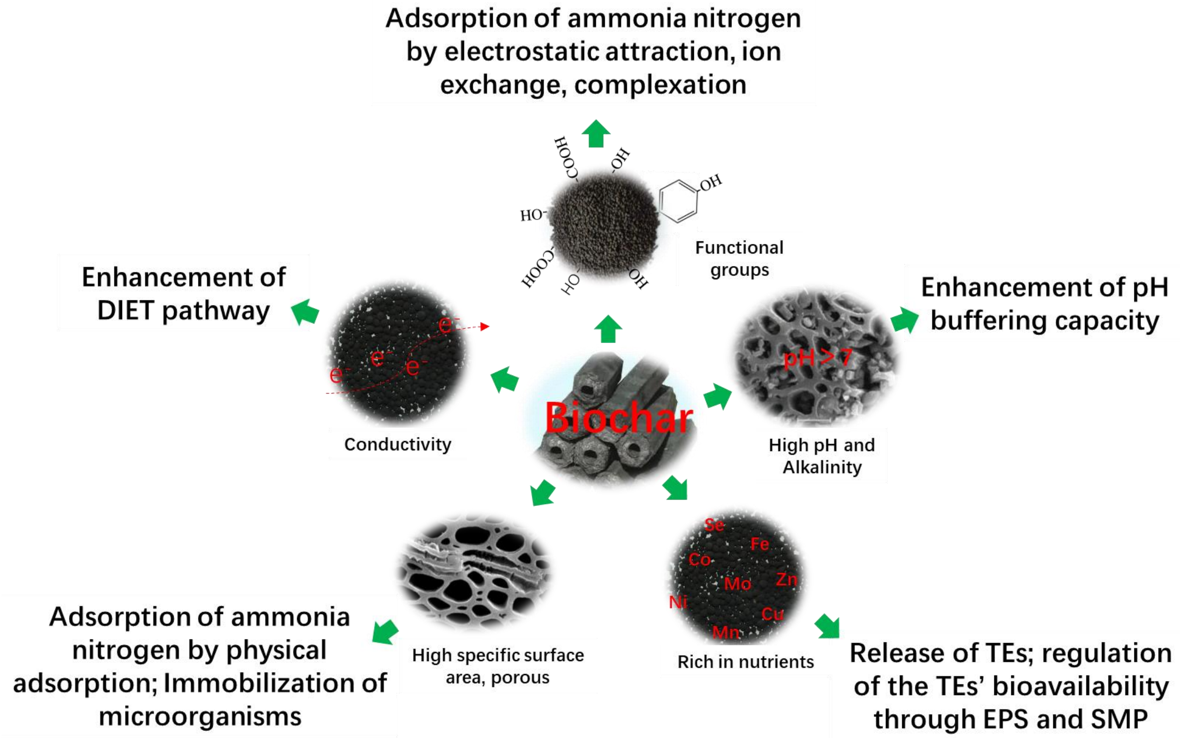

Figure 3. The characteristics and functions of biochar in high ammonia nitrogen AD

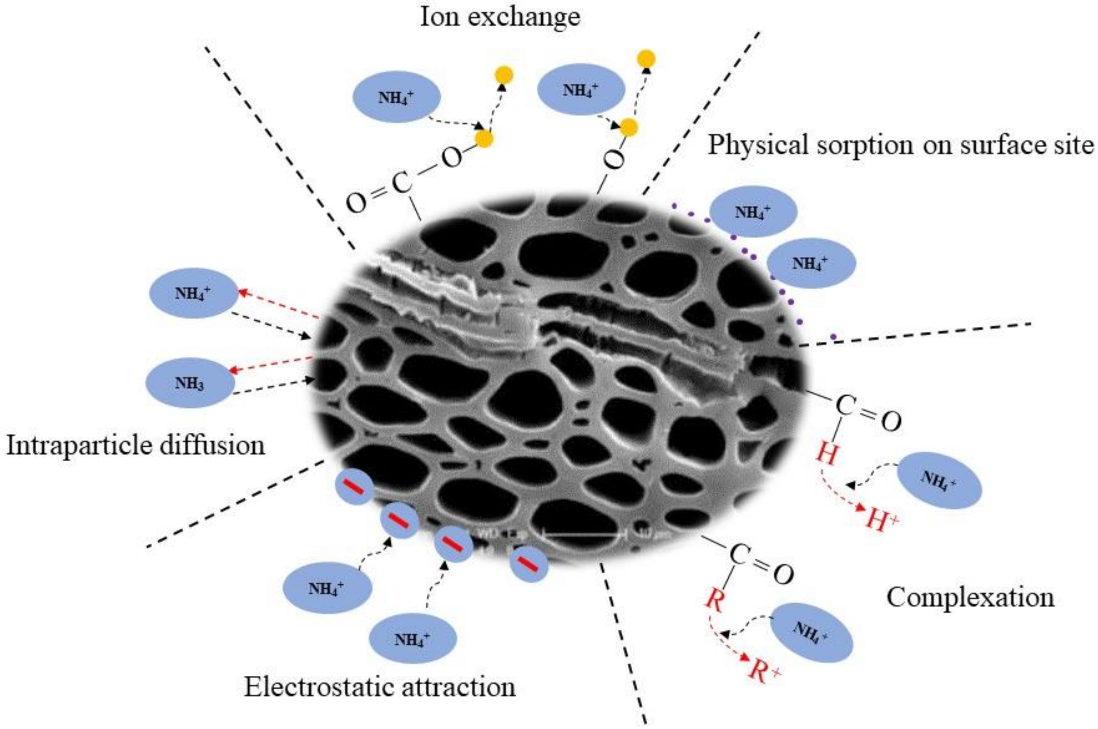

Figure 4. Mechanism of ammonia nitrogen adsorption on biochar (Chen et al., 2021; Wang et al., 2021b; Li et al., 2017).

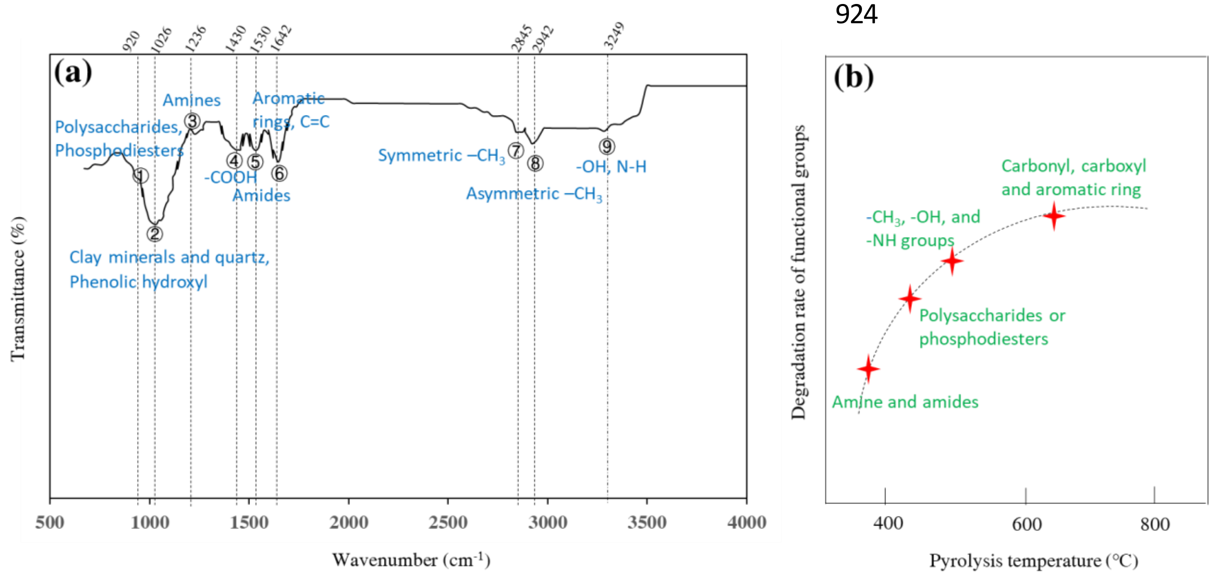

Figure 5. Typical functional groups on the surface of biochar that determine ammonia absorption (a); degradation rate of functional groups (b). Some information originates from Tang et al. (2019), Zhang et al. (2020) and (Xue et al., 2019)

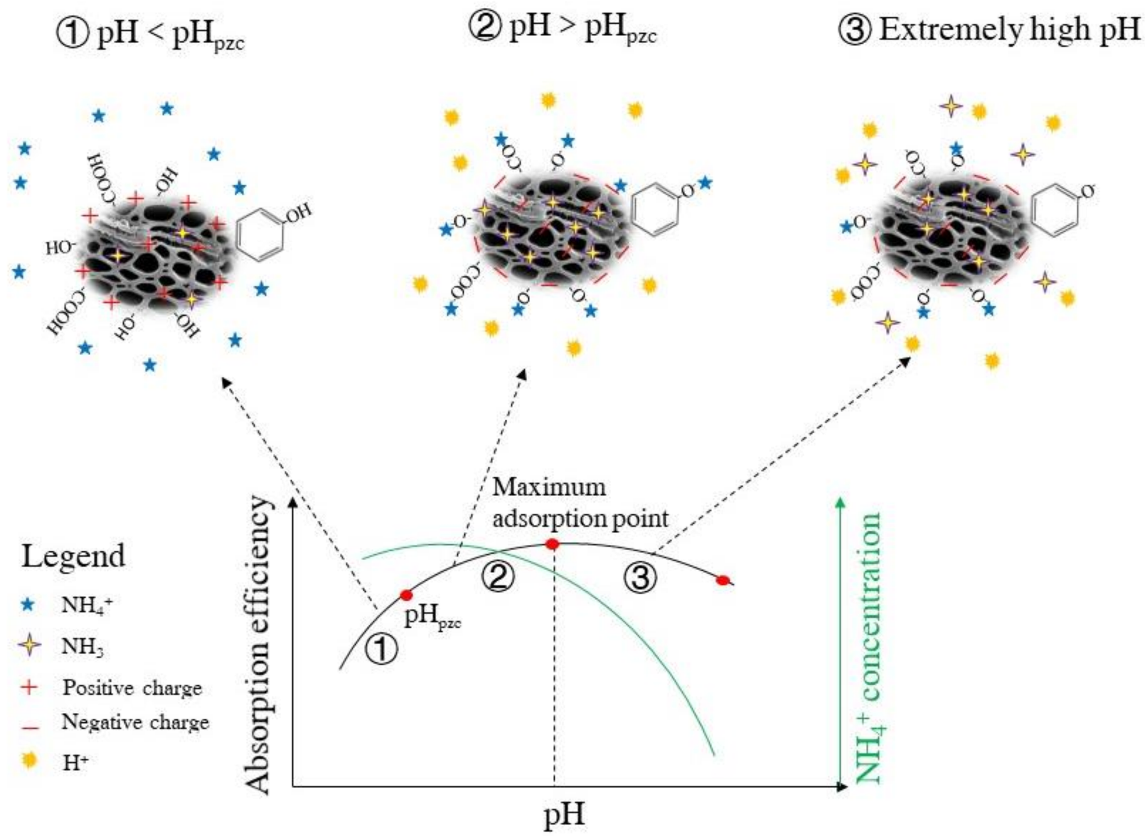

Figure 6. The relationship between the pH in the digestion system and the adsorption efficiency of ammonia nitrogen by biochar

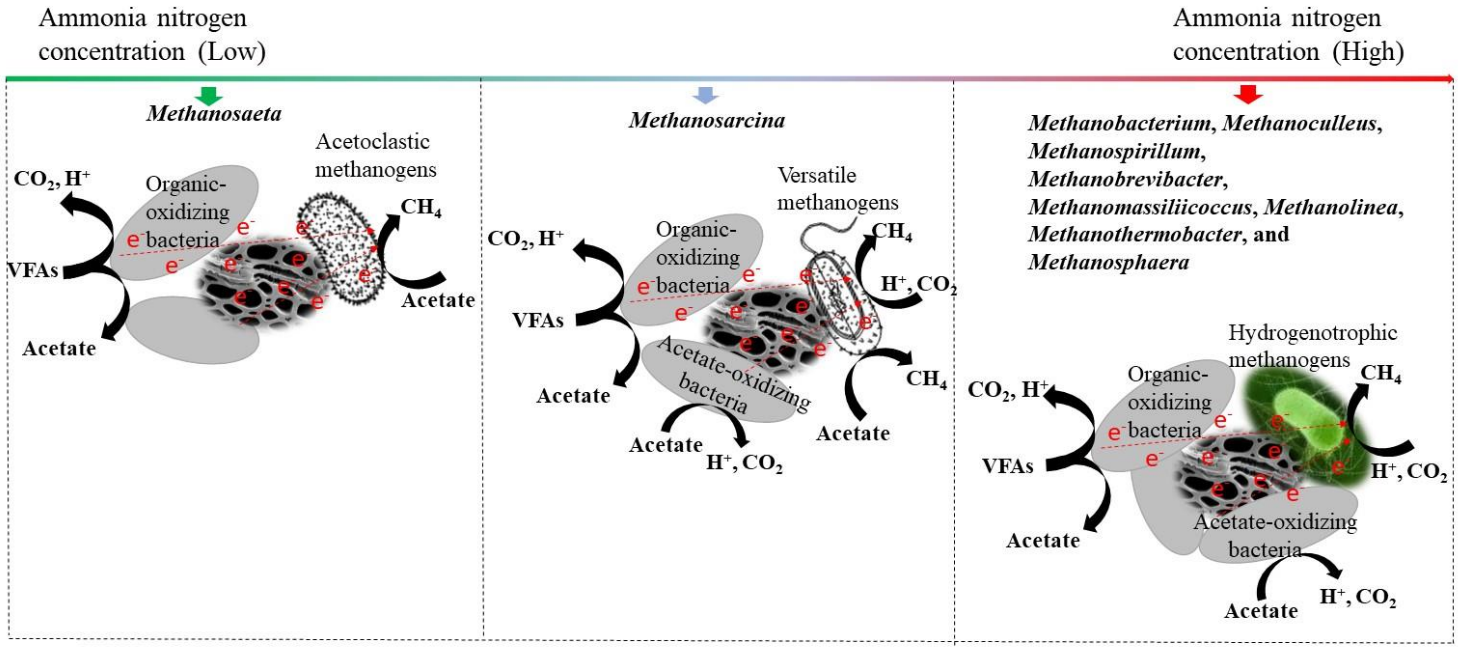

Figure 7. The succession mechanism of DIET pathway mediated by biochar under different ammonia nitrogen concentrations (Baek et al., 2018; Wang et al., 2021c).

Table 1. Effect of biochar on the performance of AD with high ammonia nitrogen

Biochar type	pyrolysis conditions	Average pore size (nm)	Ash content (wt%)	pH	Specific surface area of biochar (m^2 g^{-1})	TAN concentration of digestion system (g L^{-1})	Addition ratio of biochar (g L^{-1})	TAN removal (mg g^{-1})	Performance	Reference
Straw biochar	750 °C	-	55.20	11.24	12.00	4	4	6.65	Methane yield was improved 35%. The number of *Methanosarcina thermophila* increase.	Yan et al., 2021
Corn stover biochar	600 °C	5.9	-	10.1	302.6	0.62	-	-	Methane content and yield increased by 28.9% and 17.8%, respectively.	Wei et al., 2020
Woody biochar	1100 °C	-	9.40	10.08	766.00	4	4	41.94	Methane yield was improved 24%. DIET was enhanced.	Yan et al., 2021
Woody biochar	500-600 °C	0.3-0.45	16.92	9.26	209	0.99-16	-	-	Biochar reduced the TAN concentration and increased the methane yield (32-36%) and enhanced tolerance of *MST* to ammonia nitrogen. It also enhanced DIET between bacteria and methanogens. .	Pan et al., 2019
Paper sludge and wheat husks (1:2 (v/v))	500 °C	-	-	-	-	2.1-6.6	20	2.4-6.8	Methane yield was improved 32%. When the TAN is below 2.1g/L, biochar can alleviate ammonia inhibition.	Mumme et al., 2014
Wheat straw digestate	230 °C	-	-	-	-	2.1-6.6	20	3.0-8.2	No noticeable effect was observed	Mumme et al., 2014
Coconut shell biochar	-	< 2	-	-	774.48	-	5-40[a]	-	The methane yield was improved 13%. Biochar	Shen et al., 2020

									enhanced the growth of acetoclastic methanogens.	
Rice straw biochar	600 °C	21.5	5.19	6.83	65.18	0.9-3.5	2-15	150-650	Biogas production was increased by 78.3% when the dose of biochar was 15g/L.	Cheng et al., 2020
Corn straw biochar	400-600 °C	-	17.1-20.8	8.2-8.3	29.8-56.6	4.28	8	55.0-98.8	Methane yield increased by 57.5-87.1%. The stability and buffering capacity increased.	Zhang et al., 2019
Coconut shell biochar	400-600 °C	-	2.5-3.6	9.3-9.7	16.1-26.3	4.28	8	76.3-98.8	Methane yield increased by 32.8-42.2%. The stability and buffering capacity increased.	Zhang et al., 2019
Sewage sludge biochar	400-600 °C	-	42.2-67.3	8.7-11.1	2.32-12.7	4.28	8	91.3-110	Methane yield increased by 22.4-49.1%. The stability and buffering capacity increased.	Zhang et al., 2019
Rice straw biochar	160-260 °C	13.0	-	7.3	19.4	2.08	2-10	25	Biochar enhances the intensity of functional groups and the immobilization of microorganism, which strengthens the conversion of organic acids to biogas.	Xu et al., 2018

Note: a, the dose of biochar was calculated based on 1 kg=1 L

Table 2. The effect of biochar modification on its capacity for removing ammonia nitrogen in AD systems.

Biochar type	Biochar production condition	Modification method	Effect of modification on biochar characteristics	Effect of modified biochar on ammonia removal	Reference
Corn stalk and rice hull	Pyrolysis at 450-550 °C	H_2SO_4 (0.2 M): Biochar = 1:50. The mixture shaken at 200 r min^{-1} at 60 °C for 24 h	Decreasing carboxyl group and increasing the lactone group, which means that the number of acidic OCFGs rise. At the same times, new substituents form.	Chemical adsorption (mainly electrostatic adsorption and complexation) of modified biochar to NH_4^+-N was enhanced.	Chen et al., 2021
-	-	HNO_3 (5.0 M): Biochar =1:50. HCl: Biochar =1:50.	Enhancing the available functional groups and improving the quality of biochar's structure (homogenous).	Capacity of adsorbing ammonia nitrogen was enhanced.	Shi et al., 2013
Corncob wastes	Pyrolysis at 400 °C, 90 min	NaOH (0.3 M): Biochar =1:20 (v/w)	Total pore and specific surface area of modified biochar increase.	Adsorption capacity of biochar for ammonia nitrogen increased by 42% compare with raw biochar.	Vu et al., 2018
Rice straw	Pyrolysis at 500 °C for 2 h in N_2 environment	Rice straw: $FeCl_3$ solution = 1:8 for 2 h.	Specific surface area and active sites increase after magnetization.	Total amount of methane archaea increased by 25% and methane production greatly increased.	Qin et al., 2017
Sludge	Pyrolysis at 500 °C for 1 h in N_2 environment	1 g biochar mixed with 0.90 g $NH_4Fe(SO_4)_2{\cdot}12H_2O$ and 0.39 g $(NH_4)_2Fe(SO4)_2{\cdot}6H_2O$	The active sites increase after magnetization.	Adsorption capacity of modified biochar for ammonia nitrogen reached 17. 52 mg·g^{-1}.	Wang et al., 2021a

Table 3: Related microorganisms (mainly bacteria and archaea) participated DIET with biochar in AD systems.

Substrate	Biochar type	TAN concentration and pH	Related electrotrophic methanogen	Related electron donating bacteria	Reference
Pig manure	Rice husk	TAN: 4.14-12.24; pH: 6.77-8.02	*Methanothrix*	*Defluviitoga*, *Thermovirga* and *Cloacibacillus*	Yang et al., 2021b
Glucose; H_2/CO_2	Straw and spruce Woodchip	pH: 6.25-7.25	*Methanothermobacter thermautotrophicus sp.3*	*S. schinkii sp.28*	Yan et al., 2021
Food waste	Waste wood	-	*Syntrophomonas*	*Methanosarcina*	Cui et al., 2021
Ethanol	Wood chips	-	*Pseudomonas*	*Methanosaeta*	Qi et al., 2021
Dairy manure	Dairy manure	-	*Clostridium, Syntrophomonas and Syntrophus*	*Methanobacterium, Methanolinea and Methanomassiliicoccus*	Jang et al., 2021
Synthetic wastewater,	Rice straw	-	*Bacteroidetes*, *Smithella*, *Desulfovibrio* and *Geobacter*	*Methanosaeta*, *Methanosarcina*	Wang et al., 2021
Waste activated sludge	Sewage sludge	pH=7.1	*Syntrophomonas*, and *Peptococcaceae*	*Methanosaeta*, *Methanobacterium*	Wu et al., 2019