



## Review article

# Improving bioenergy production in anaerobic digestion systems utilising chicken manure via pyrolysed biochar additives: A review

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## ABSTRACT

There is growing interest in the use of anaerobic digestion (AD) to treat organic waste resulting in volume reduction and stabilisation of the waste together with the production of renewable energy in the form of methane. Currently, livestock manure represents the largest organic waste stream in most countries, causing various negative environmental impacts. However, livestock manure can be used as a readily available feedstock for AD, reducing its environmental impact while simultaneously generating bioenergy. However, the AD of certain livestock manures such as chicken manure is not without constraints due to the high protein nature of the waste. These constraints are typically high digester pH, unfavourably low C:N ratio as well as the build-up of ammonia (NH<sub>3</sub>). Ammonia production will inevitably lead to NH<sub>3</sub> inhibition, which can irreversibly terminate AD and methane production. To mitigate the NH<sub>3</sub> stress that accompanies the use of chicken manure as a feedstock, various methods have been previously employed such as in situ NH<sub>3</sub> stripping, bentonite addition, Se supplementation, Fe<sup>2+</sup> and Ni<sup>2+</sup> supplementation, co-digestion, water extraction and biochar addition. Pyrolysed biochar addition represents a new, innovative, and promising method due to its current role in the circular economy. This review provides an in-depth analysis into the current uses and knowledge of biochar for the purpose of NH<sub>3</sub> stress mitigation. In addition, the review describes and compares factors that can potentially improve the efficacy of biochar in averting NH<sub>3</sub>-build up and suggests possible future studies.

## 1. Introduction

Anaerobic digestion (AD) refers to the natural biodegradation of organic matter using microorganisms in anoxic conditions [10]. Common waste streams which can be used as a feedstock for AD include livestock manure, lignocellulosic agricultural waste (bagasse, straws), food waste, garden waste and winery waste [29]. These organic wastes can be utilised to generate electricity and produce other useful digestate products [34]. Additionally, the use of AD to treat organic waste contributes to GHG savings; 1 tonne of organic waste treated by AD can save up to 143 kg of CO<sub>2</sub>-e [29]. On the other hand, other organic waste disposal methods such as landfill, incineration and composting all generate GHG emissions to the tune of 350 kg CO<sub>2</sub>-e, 1396.45 kg of CO<sub>2</sub>-e and 171.52 kg CO<sub>2</sub>-e, respectively [20]. Therefore, the diversion of organic waste into AD will lead to a reduction in GHG emissions coupled to bioenergy production.

Anaerobic digestion has attracted considerable interest in recent years. The use of chicken manure as a feedstock for AD is of particular importance for many countries as livestock manure often represents one of the largest organic waste streams. In Australia, livestock manure accounted for 34 % of all organic waste generated in 2017; an estimated 10.2 Mt of manure [29,34]. By 2019 this value had increased to 15 Mt [35]. Globally an estimated 20,708 Mt of chicken manure is produced annually [19]. While the high production of chicken manure makes it a cause for environmental concern, potentially it provides a readily available feedstock for AD to generate bioenergy. Potentially, the use of 20,708 Mt of chicken manure in AD can produce up to  $40 \times 10^{14}$  KJ of energy [19].

Common constraints associated with AD of livestock manure include high digester pH, low C:N ratios and the build-up of ammonia (NH<sub>3</sub>) within digesters. These constraints become amplified when chicken manure is mono digested in AD; chicken manure contains a higher

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percentage of N compared to other manures. Of the 3 constraints, the build-up of  $\text{NH}_3$ , which typically leads to inhibition of AD, can irreversibly halt the process and consequently the production of biogas. The build-up of  $\text{NH}_3$  is a major problem associated with AD systems utilising chicken manure, preventing its broad utilisation for bioenergy production. Table 1 highlights the difference in N composition between chicken manure, cow manure and swine manure from various agricultural surveys of different countries. In Australia, chicken manure typically contains 2.3 and 1.8 times more N than cow manure and swine manure, respectively (Table 1). In Ohio, U.S.A., a comparison of dry manures pack with bedding showed chicken manure having 6.5 and 7.88 times more N than cow manure and swine manure, respectively (Table 1). A survey carried out in Manitoba, Canada found that liquid chicken manure contained 5.1 and 4.2 times more ammonium ( $\text{NH}_4^+$ ) than liquid cow and swine manure, respectively (Table 1). Lastly, the Department for Environment Food and Rural Affairs (DEFRA) in the UK reported that chicken manure possessed 3.2 and 2.7 times more N than cow and swine manure, respectively (Table 1).

Biochar is a low-cost additive with many beneficial properties that can be effective even at low concentrations. However, the role of biochar in alleviating  $\text{NH}_3$  stress and improving AD is not well understood. This review aims to highlight how biochar functions as an effective additive in mitigating  $\text{NH}_3$  stress as well as improving the performance of AD systems; this will be performed through analysis of recent and relevant studies. In addition, the review will highlight the current knowledge gaps regarding the use of chicken manure in AD systems and suggest future studies. These findings will be beneficial in developing biochar as an economically viable additive to mitigate  $\text{NH}_3$  stress in the AD of chicken manure. With growing global interest in biomass to bioenergy production in the form of methane, a better understanding of biochar and its role in  $\text{NH}_3$ -stressed AD systems has been determined to be vital to increase the conversion efficiency of poultry manure to biomethane. In 2018, the International Energy Agency reported a global biomethane production of around 35 million tonnes of oil equivalent (Mtoe), which is only around 5 % of the global biomethane production potential and target of 730 Mtoe [7].

### 1.1. Anaerobic digestion of high-protein chicken manure

The biological conversion of a typical organic waste feedstock into biogas consists of 4 main stages; hydrolysis, acidogenesis, acetogenesis and methanogenesis [48]. During hydrolysis, bacteria break down complex organic matter into monomers or oligomers such as amino acids, sugar, glycerol and long-chain fatty acids [39,48]. Monomers are then converted into volatile fatty acids (VFA), organic acids and acid alcohols by fermentative bacteria during the second stage. Ammonia and hydrogen sulfide ( $\text{H}_2\text{S}$ ) are sometimes released during the process [48]. Thirdly, VFA are transformed into acetic acid ( $\text{CH}_3\text{COOH}$ ), carbon dioxide ( $\text{CO}_2$ ) and hydrogen ( $\text{H}_2$ ) by acetogenic bacteria via anaerobic oxidation [39,48]. Acetate ( $\text{CH}_3\text{COO}^-$ ) can also be produced from  $\text{H}_2$  and  $\text{CO}_2$  by homoacetogens,  $\text{H}_2$ -oxidising acetogenic bacteria [39]. In the

**Table 1**

The difference in nitrogen composition between chicken manure, cow manure and swine manure.

Country	Manure type and Nitrogen composition (%)			Reference
	Chicken	Cow	Swine	
Australia	3.4	1.5	1.9	Griffiths [14]
Ohio, United States of America	2.6	0.4	0.33	Ohio State University [30]
Canada	0.72	0.14	0.17	Manitoba Agriculture Food and Rural Development [27]
United Kingdom	1.9	0.6	0.7	DEFRA [9]

last stage, acetotrophic and hydrogenotrophic methanogens convert  $\text{CH}_3\text{COO}^-$  and  $\text{H}_2$  into a mixture of  $\text{CO}_2$  and methane ( $\text{CH}_4$ ) [39]. The digestate at the end of the process is of high agricultural value and can be used in soil applications. These stages are summarised in Fig. 1.

When chicken manure is used as a feedstock, the process becomes altered, as shown in Fig. 1. Undigested protein and uric acid represent the two main abundant sources of N in chicken manure and upon hydrolysis, will yield high levels of amino acids (Fig. 1) [38]. Consequently, acidogenesis of the high levels of amino acids will result in the build-up and eventual accumulation of  $\text{NH}_3$  [38]. The high concentration of  $\text{NH}_3$  will inevitably lead to the inhibition of methanogenesis due to changes in pH as well as several inhibitory effects on methanogens, resulting in low or no  $\text{CH}_4$  production [38]. The digestate at the end of the process is highly toxic to plants due to elevated concentration of  $\text{NH}_3$  and cannot be applied to soil.

### 1.2. Comparison of Low-solid anaerobic digestion (LSAD) and High-solid anaerobic digestion (HSAD) for chicken manure

The high total solids (TS) content of chicken manure makes it a desirable substrate for biogas production. Chicken manure typically possesses a TS content of at least 25 % [3]. These authors showed that the use of high-solid AD of chicken manure (i.e., a TS content between 10 % and 20 %) is more cost-effective than low-solid AD (TS content between 6 % and 10 %). Additional economic advantages associated with high-solid AD include higher loading capacity of waste material, higher volumetric efficiency and biogas production as well as reduced operational costs from heating large volumes of water involved with wet systems [23]. However, unmediated HSAD of chicken manure will inevitably result in low hydrolysis rates, low mass transfer efficiency and the accumulation of  $\text{NH}_3$  and subsequent  $\text{NH}_3$  inhibition [23].

There are also differences in digester performance of chicken manure between low-solid and high-solid AD systems. A recent study by Bi et al. [3] highlighted the differences in digester performance of chicken manure under different TS contents (5 %, 7.5 %, 10 %, 15 % and 20 %). The study found that methane yield was highest at 5 % TS content (low-solid AD, 0.36 L/g-VS) and lowest at 20 % TS content (high-solid AD, 0.02 L/g-VS). Increasing the TS content from 5 % to 20 % resulted in an 18-fold reduction in methane yield. This was due to a 3.7-fold increase in total ammoniacal nitrogen (TAN) in high-solid AD system.

## 2. Mechanism of ammonia ( $\text{NH}_3$ ) inhibition

In aqueous environments,  $\text{NH}_3$  exists in 2 forms: ionised ammonium nitrogen ( $\text{NH}_4^+$ ) and unionised free ammonia nitrogen (FAN/ $\text{NH}_3$ ) [18]. Together, they make up the total ammoniacal nitrogen (TAN). In recent literature, it has been reported that mesophilic AD of chicken manure was inhibited at 4.5 g/L and 0.7 g/L for TAN and FAN, respectively [1]. Ammonia inhibition is mainly caused by  $\text{NH}_3$ . Unionised  $\text{NH}_3$  is more toxic than its ionised form due to its uncharged nature and solubility in lipids; this allows for easy diffusion across biological cell membranes. The current knowledge of the chemical interaction between  $\text{NH}_3$  and methanogens (Stage 4 in Fig. 2) that lead to  $\text{NH}_3$  inhibition is outlined below.

Ammonia can diffuse freely through the cell membrane; this helps to maintain intracellular and extracellular equilibrium concentrations of  $\text{NH}_3$  [18]. Within the cell membrane,  $\text{NH}_3$  reacts with  $\text{H}^+$  entering the cell through the proton pump to form ionised  $\text{NH}_4^+$ , absorbing protons in the process. Ionised ammonium nitrogen cannot diffuse through the cell membrane freely like  $\text{NH}_3$  [18]. Therefore, the concentration of  $\text{NH}_4^+$  within a methanogen cell is dependent on 2 factors: the extracellular concentration of  $\text{NH}_3$  and the intracellular pH of the cell (concentration of  $\text{H}^+$ ). This mechanism of  $\text{NH}_3$  diffusion and  $\text{NH}_4^+$  formation inside a methanogen cell implies that high extracellular concentrations of  $\text{NH}_3$  would ultimately result in high accumulation of intracellular  $\text{NH}_4^+$  within these cells. On a cellular level,  $\text{NH}_3$  can cause imbalances in

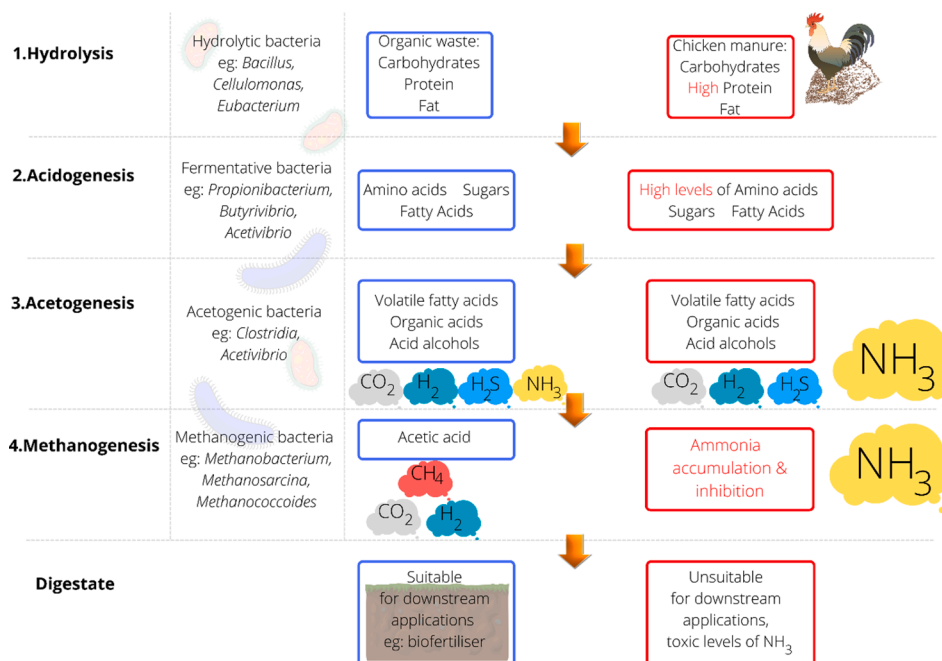


Fig. 1. The 4 stages of anaerobic digestion of a typical organic waste feedstock compared to chicken manure and the fate of their respective digestates.

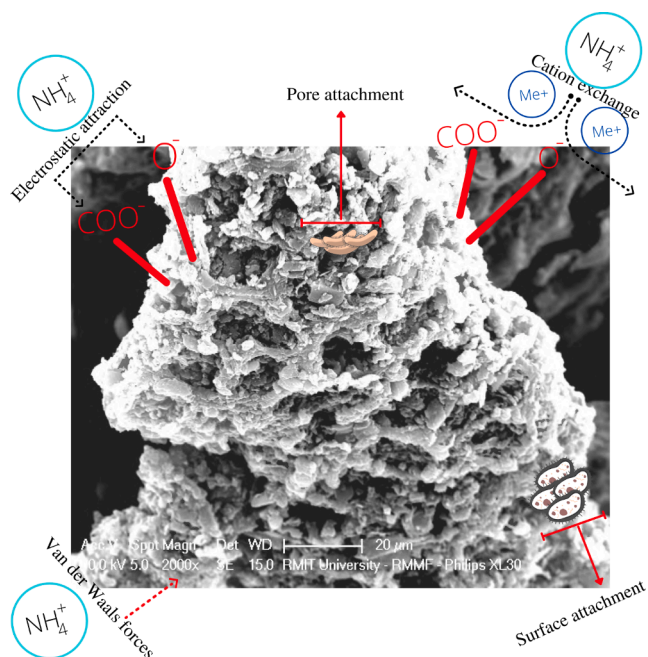


Fig. 2. Surface adsorption mechanisms between biochar particle and ammonium ions. ( $\text{NH}_4^+$  = ammonium ions,  $\text{O}^-$  &  $\text{COO}^-$  = functional groups present on biochar,  $\text{Me}^+$  = metal ion such as  $\text{Na}^+$ ), microbial sheltering between biochar surface and pores and methanogens.

intracellular pH, elevated maintenance energy requirements and depletion of intracellular  $\text{K}^+$  [37]. Accumulation of intracellular  $\text{NH}_4^+$ , coupled with the inability of  $\text{NH}_4^+$  to diffuse freely across cell membrane would result in an increase in the number of protons within the methanogen cells. This would in turn result in pH imbalance. Additionally, more energy must be expended by the cell for the potassium pump to balance the increase in protons by pumping intracellular  $\text{K}^+$  out of the cell, resulting in their depletion. Furthermore, when exposed to high concentrations of  $\text{NH}_3$ , the potassium pump may fail to keep up

with the rapid build-up of intracellular  $\text{NH}_4^+$ , resulting in failure to maintain intracellular pH and ultimately, cytotoxicity [18].

### 3. Mitigating ammonia ( $\text{NH}_3$ ) inhibition

Various methods to overcome  $\text{NH}_3$  inhibition have been explored in AD set-ups utilising chicken manure as a feedstock. These methods include *in situ*  $\text{NH}_3$  stripping which involves the use of biogas recirculation to strip  $\text{NH}_3$  from the substrate and simultaneously recover  $\text{NH}_3$  using a phosphate or sulfate-containing receiver [1]. The use of bentonite has also been previously employed to promote the adsorption of  $\text{NH}_4^+$  in  $\text{NH}_3$  stressed AD of chicken manure [24]. In addition, Se supplementation or  $\text{Fe}^{2+}$  and  $\text{Ni}^{2+}$  supplementation have utilised the addition of these trace elements to enhance the microbial communities and stimulate methanogenesis even in  $\text{NH}_3$  stressed environments [28,2]. These essential trace elements promote more efficient syntrophic  $\text{CH}_3\text{CO}^-$  oxidation (SAO) at high TAN levels, by improving the effectiveness of an important SAO redox enzyme known as formate dehydrogenase (FDH). Paranhos et al. [33] employed the co-digestion of chicken manure with lignocellulosic biomass to counteract  $\text{NH}_3$  stress by providing a more favourable C/N ratio. Similarly, Böjti et al. [4] performed water extraction on chicken manure as a pre-treatment for the removal of toxic N-compounds; the C/N ratio was greatly improved. pH adjustment represents another effective method of alleviating  $\text{NH}_3$  stress; acid solution is added to reduce pH and FAN concentration [6]. Changes in pH can affect the equilibrium between  $\text{NH}_3$  and  $\text{NH}_4^+$ . Generally, a lower, more acidic pH will result in an increased concentration of non-toxic  $\text{NH}_4^+$  and reduce the concentration of toxic  $\text{NH}_3$ ; the higher the pH, the higher the concentration of toxic  $\text{NH}_3$  [8]. Lastly, Pan et al. [31] utilised the various physicochemical properties of biochar to mitigate  $\text{NH}_3$  stress in the AD of chicken manure. Table 2 highlights the approaches and their proposed mode or modes of mitigation including  $\text{NH}_3$  reduction, microbial enhancement and C/N ratio adjustment. Table 2 also compares the effect on TAN/FAN concentration or N content on methane yields as well as the methanogenic population as a result of these different treatments.

From Table 2, the use of *in-situ*  $\text{NH}_3$  stripping, and bentonite addition were reported to be successful in reducing TAN concentration by 20 % and 18 %, respectively;  $\text{CH}_4$  production also improved by 34 % and 33

**Table 2**

Approaches taken for the mitigation of ammonia (NH<sub>3</sub>) inhibition and their associated effects on Total Ammoniacal Nitrogen (TAN/Free Ammonia Nitrogen (FAN) concentrations, nitrogen (N) content, methane (CH<sub>4</sub>) yield and the methanogenic bacterial population.

Method	Mode of mitigation	Effect on TAN/FAN concentrations or N content	Effect on CH <sub>4</sub> yield	Effect on methanogenic population	Reference
<i>In situ</i> NH <sub>3</sub> stripping	NH <sub>3</sub> reduction	TAN concentration decreased by 20 %	CH <sub>4</sub> yield increased by 34 %	<ul style="list-style-type: none"> <li>Relative abundance of <i>Methanosarcina</i> sp. increased by 10 %</li> <li>Relative abundances of hydrogenotrophic methanogens decreased by 10 %</li> </ul>	Bi et al. [1]
Bentonite addition	NH <sub>3</sub> reduction	<ul style="list-style-type: none"> <li>TAN reduction of 18 % using 400 °C bentonite</li> <li>FAN reduction of 40 % using 500 °C bentonite</li> </ul>	Highest cumulative CH <sub>4</sub> yield increase of 33 % using 400 °C bentonite	Not reported	Ma et al. [24]
Se supplementation	Microbial enhancement	No effect	CH <sub>4</sub> yield increased by 50 %	Estimated 48 % increase in relative abundance of <i>Methanoculleus bourgensis</i>	Molaey et al. [28]
Fe <sup>2+</sup> and Ni <sup>2+</sup> supplementation	Microbial enhancement	No effect	<ul style="list-style-type: none"> <li>CH<sub>4</sub> yield increased by 40 %</li> <li>Accumulated CH<sub>4</sub> increased by 30 %</li> </ul>	<ul style="list-style-type: none"> <li>Relative abundance of <i>Methanosarcina</i> sp. increased by 20 %</li> <li>Relative abundances of hydrogenotrophic methanogens decreased by 9 %</li> </ul>	Bi et al. [2]
Co-digestion with lignocellulosic biomass	C/N ratio adjustment	<ul style="list-style-type: none"> <li>TAN concentrations did not exceed 2 g/L</li> <li>No inhibitory effects observed</li> </ul>	Highest increase of 26 % in CH <sub>4</sub> yield when using corn cob	Not reported	Paranhos et al. [34]
Water extraction	C/N ratio adjustment	<ul style="list-style-type: none"> <li>C/N ratio improved from 7.5 to 19.8</li> <li>N content decreased by 59 %</li> </ul>	CH <sub>4</sub> yield increased by 27 %	Not reported	Böjti et al. [4]
pH adjustment	NH <sub>3</sub> reduction	pH below 7.5 can relieve NH <sub>3</sub> inhibition	Reducing pH from 8.5 to 8 produced an 80 % increase in CH <sub>4</sub> yield	Not reported	Cai et al. [6]
Kiwi-fruitwood biochar	<ul style="list-style-type: none"> <li>NH<sub>3</sub> reduction</li> <li>Microbial enhancement</li> </ul>	<ul style="list-style-type: none"> <li>Increase in dissolved inorganic carbon</li> <li>NH<sub>3</sub> inhibition was delayed for 15 days under high-organic loading</li> </ul>	CH <sub>4</sub> production improved by up to 36 %	<ul style="list-style-type: none"> <li>Relative abundance of <i>Methanosaeta</i> higher in biochar treatments than controls by 5 %</li> <li>Relative abundance of <i>Methanospirillum</i> higher in biochar treatments than controls by 46 %</li> </ul>	Pan et al. [32]

%). However, the bentonite study did not investigate changes to the methanogenic population. The *in situ* NH<sub>3</sub> stripping study included the effects on the methanogenic population, reporting a 10 % increase in the relative abundance of *Methanosarcina* sp. and a 10 % decrease in the relative abundance of hydrogenotrophic methanogens. Similarly, Se and Fe<sup>2+</sup>/Ni<sup>2+</sup> supplementations were successful in improving CH<sub>4</sub> yields by 50 % and 40 %, respectively (Table 2). These methods also promoted positive changes to the methanogenic populations (Table 2). However, trace elements supplementation did not affect the concentration of TAN or FAN. Co-digestion with lignocellulosic biomass produced a significant reduction in TAN, reducing concentrations to below 2 g/L, preventing NH<sub>3</sub> inhibition, resulting in a 27 % increase in CH<sub>4</sub> yield (Table 2). However, the study did not include an investigation into the methanogenic population. Similarly, water extraction improved CH<sub>4</sub> yields by 27 %, increasing the C/N ratio from 7.5 to 19.8, and decreasing N-content by 59 % (Table 2). pH adjustment, reducing the pH from 8.5 to 8 resulted in an 80 % increase in CH<sub>4</sub> yield; reducing the pH to below 7.5 was also shown to relieve NH<sub>3</sub> inhibition [6] (Table 2). Finally, the use of biochar was observed to delay NH<sub>3</sub> inhibition by 15 days and improve the C/N ratio by increasing the concentration of dissolved inorganic carbon (Table 2). Methane production was also improved by 36 % and positive changes were observed in the methanogenic population. The use of biochar increased the relative abundance of *Methanosaeta* and *Methanospirillum* by 5 % and 46 %, respectively compared to the controls. *Methanosaeta* is intolerant of high TAN concentration; the increase in the relative abundance is indicative of the ability of biochar to mitigate NH<sub>3</sub> stress. In addition, both *Methanosaeta* and *Methanospirillum* can directly accept electrons. This coupled with the improvement in CH<sub>4</sub> production when compared to the control treatment, suggested that biochar was able to facilitate Direct Interspecies Electron Transfer (DIET); this is further discussed below.

#### 4. The role of biochar in anaerobic digestion systems: Current knowledge

Biochar or hydrochar is a recalcitrant, carbonaceous material derived from the thermochemical conversion of biomass such as agricultural by-products and forestry residues. The thermochemical conversion processes include wet methods such as hydrothermal carbonisation/liquefaction as well as dry methods such as gasification and pyrolysis. These processes produce biochar with varying characteristics. The literature reports the char produced from wet methods as hydrochar and from dry methods char as biochar [11]. The available literature reports that biochar produced from dry method, mainly pyrolysis, exhibits the ability to perform surface adsorption of NH<sub>4</sub><sup>+</sup>, mitigating the build-up of NH<sub>3</sub> and improving CH<sub>4</sub> production in AD systems using chicken manure as a feedstock. Far less is reported regarding the potential of biochars/hydrochars produced using other technologies. Hydrochar produced from hydrothermal carbonisation or liquefaction may also offer potential as a means of mitigating the build-up of NH<sub>3</sub> in AD. Given their lower production temperatures they are expected to retain O<sub>2</sub>-containing functional groups on their biochar surface. These functional groups are mainly responsible for the absorption of NH<sub>4</sub><sup>+</sup>. In contrast biochar produced from gasification may have reduced O<sub>2</sub>-containing functional groups and hence may have lower value in terms of the absorption of NH<sub>4</sub><sup>+</sup>. However, to the best of authors' knowledge, to date no literature has been published reporting the use of hydrochars and gasified biochar in AD of chicken manure. The following sections discuss the mechanisms underlying the observed beneficial impacts of the addition of pyrolysed biochar in terms of CH<sub>4</sub> production during AD.



#### 4.1. Surface adsorption and microbial sheltering mechanism of biochar

Biochar serves to mitigate the build-up and accumulation of TAN by providing surface functional groups and surfaces for the direct adsorption of  $\text{NH}_4^+$  as well as colonisation by microbes. Among the many beneficial properties that biochar possesses, their highly developed porous structure, negative surface charge and extensive surface area are particularly important in terms of mitigating ammonia stress. The adsorption of  $\text{NH}_4^+$  reduces its bioavailability to the methanogens while the colonisations of the pores further allow methanogens to be sheltered from ammonia present in the environment (Fig. 2).

There are 3 main surface adsorption mechanisms occurring between biochar particles and  $\text{NH}_4^+$  viz; electrostatic attraction, cation exchange and physical adsorption (Fig. 2). Firstly, hydroxyl ( $\text{OH}^-$ ) and carboxyl ( $-\text{COO}^-$ ) groups present on the surface of biochar particles can react with  $\text{NH}_4^+$  in solution via electrostatic attraction to promote surface adsorption of  $\text{NH}_4^+$  [45]. Secondly, existing metal elements on biochar such as sodium ( $\text{Na}^+$ ) can promote cation exchange between  $\text{NH}_4^+$  and the cationic species found on biochar, leading to the surface adsorption of  $\text{NH}_4^+$  [45] (Fig. 2). Lastly, the absorbent porous structure of biochar can promote direct physical adsorption of  $\text{NH}_4^+$  onto biochar surfaces via non-selective Van der Waals forces [15] (Fig. 2).

Electrostatic attraction and cation exchange are termed chemical adsorption mechanisms or chemisorption. The level of chemisorption of  $\text{NH}_4^+$  is directly affected by the availability, abundance and content of the functional groups present on the biochar surface; the more suitable functional groups available for adsorption, the higher the level of  $\text{NH}_4^+$  adsorption [15]. The physical adsorption capacity of  $\text{NH}_4^+$ , physisorption, is primarily dependent on the Brunauer–Emmett–Teller (BET) surface area of biochar.

Recent studies have investigated the efficacy of biochar to reduce TAN concentrations in AD systems utilising chicken manure. Table 3 summarises the key findings of these studies. Biochar characteristics such as biomass used, pyrolysis temperature and particle size are presented, along with biochar dosage used. In addition, the reduction of TAN concentration observed are reported as well as any correlation to biochar addition.

In general, a positive correlation was observed between biochar addition and reduction in TAN. For example, a 1 % biochar dosage by volume achieved up to 19.5 % reduction in TAN compared to the untreated control treatment Yu et al. [47]. Additionally, there appeared to be an increasing positive effect on TAN reduction when biochar dosage was increased, as highlighted by Ma et al. [25]. Increasing the biochar dosage by volume from 1.8 % to 5.2 % resulted in a 16 % increase in the reduction of TAN. Another study conducted by Pan et al. [31] concluded that a 5 % biochar dosage by volume can reduce TAN by up to 25 %. In addition, this study investigated the efficacy of 3 different types of biochar made from different materials: fruitwood, wheat straw and air-dried chicken manure, in the reduction of TAN. Fruitwood biochar achieved the highest level of TAN reduction, followed by wheat straw and lastly, air-dried chicken manure, at 25 %, 21.4 % and 13.4 %, respectively. Hence, it can be observed that the use of woody biochar can bring about a higher reduction in TAN concentration.

However, two other studies have reported contrasting results. Indren et al. [17] utilised 24.5 % biochar dosage by volume but could not achieve significant TAN reduction. However, the biochar utilised in this study were wood pellet biochar pyrolysed at 770 °C, 10–20 mm in length and 4–6 mm in diameter. When compared to the other studies that have yielded positive correlation, the biochar used by Indren et al. [17] was pyrolysed at 220 °C higher. This higher pyrolysis temperature could have resulted in the volatilisation of surface functional groups that were essential for TAN reductions; Zhao et al. [49] reported a reduction in  $\text{H}_2$  and  $\text{O}_2$  with increasing biochar pyrolysis temperature. Additionally, the biochar particles were much larger compared to those used in the other studies which were < 2 mm and hence, surface area for adsorption was greatly reduced. Further, Ma et al. [26] reported that a 5 % biochar

**Table 3**

Biochar characteristics, concentrations and the observed effects on Total Ammoniacal Nitrogen (TAN) concentration.

Biochar characteristics	Biochar dosage	TAN concentration reduction	Correlation between biochar addition and TAN concentration reduction	Reference
Fruitwood, 550 °C, 0.3–0.45 mm particle size	1.8 %, 2.5 %, 3.5 %, 4.5 %, 5.2 %	Up to 16 % reduction at the 5.2 % biochar dosage compared to 1.8 %	Positive correlation observed	Ma et al. [25]
Ricehusk, 550 °C, <0.425 mm particle size	1 %	19.5 % reduction compared to untreated control	Positive correlation observed	Yu et al. [47]
Fruitwood, 550 °C, <2 mm particle size	5 %	25 % reduction compared to control	Positive correlation observed	Pan et al. [31]
Wheat straw, 550 °C, <2 mm particle size	5 %	21.4 % reduction compared to control	Positive correlation observed	
Air-dried chicken manure, 550 °C, <2 mm particle size	5 %	13.4 % reduction compared to control	Positive correlation observed	
Wood pellet, 770 °C, 10–20 mm length, 4–6 mm diameter	24.5 %	No reduction	No correlation observed	Indren et al. [17]
Fruitwood, 550 °C, <2 mm particle size	5 %	Increase in TAN concentration	Negative correlation observed	Ma et al. [26]

dosage resulted in an increase in TAN compared to the untreated control, however, a negative correlation was observed. This was attributed to the faster hydrolysis rate induced by biochar supplement.

#### 4.2. Biochar functionalisation for the purpose of ammonium removal

Functionalisation of biochar refers to the modification of biochar's surface chemistry to improve its adsorption efficiency. The surface chemistry of biochar dictates its ability to adsorb  $\text{NH}_4^+$  to a much higher degree than BET surface area and pore structure [42]. As such, the main goal of biochar functionalisation is to improve or increase the number of surface functional groups that can facilitate the adsorption of  $\text{NH}_4^+$ . Table 4 highlights the different methods of biochar functionalisation and their associated effects on  $\text{NH}_4^+$  removal.

Modification of biochar involves wet activation (referred to as activation in Table 4) of biochar with its respective functionalising agents. Activation is a cheap and simple method of loading a porous structure such as biochar, with metal/non-metal components [41]. This involves soaking the porous structure (solid) with the metal/non-metal component dissolved in a liquid solution [41]. For biochars activated with acid as shown in Table 4, washing of biochar with distilled water is required to prevent a pH imbalance. Biochars were also washed to remove potentially toxic compounds to limit any negative effects on the AD systems as well as the digestate. These compounds can include VOC, polycyclic aromatic hydrocarbon (PAH) and dioxins [50]. For example, corncob biochars were rinsed repeatedly using distilled water until the pH of the flushing liquid was around 7–8 [42]. Similarly, corn stalk and

**Table 4**The type of biochar, its functionalising agents and methods, the improved characteristics acquired through functionalisation and effects on  $\text{NH}_4^+$  adsorption capacity.

Biochar type	Functionalising agent	Functionalisation method	Improved characteristics from control (unmodified) to functionalised (modified)	Effect on adsorption capacity	References
Corn cob biochar	$\text{HNO}_3$	Activation of corn cob biochar using $\text{HNO}_3$ in 1:7 ratio (weight to volume) for 8 h	<ul style="list-style-type: none"> <li>Carboxylic functional groups increased from 0.62 <math>\text{mmol g}^{-1}</math> to 1.37 <math>\text{mmol g}^{-1}</math></li> <li>Lactonic functional groups increased from 1.48 <math>\text{mmol g}^{-1}</math> to 2.75 <math>\text{mmol g}^{-1}</math></li> <li>Acid functional groups increased from 2.58 <math>\text{mmol g}^{-1}</math> to 4.30 <math>\text{mmol g}^{-1}</math></li> </ul>	$\text{NH}_4^+$ adsorption increased from 3.5 $\text{mg g}^{-1}$ (control, unmodified) to 8.6 $\text{mg g}^{-1}$	Vu et al. [42]
Corn cob biochar	$\text{HNO}_3$ , NaOH	<ul style="list-style-type: none"> <li>Activation of corn cob biochar using <math>\text{HNO}_3</math> in 1:7 (weight to volume) ratio for 8 h</li> <li>Subsequent activation with NaOH in 1:20 (weight to volume) ratio for 24 h</li> </ul>	<ul style="list-style-type: none"> <li>Carboxylic functional groups increased from 0.62 <math>\text{mmol g}^{-1}</math> to 0.87 <math>\text{mmol g}^{-1}</math></li> <li>Lactonic functional groups increased from 1.48 <math>\text{mmol g}^{-1}</math> to 1.86 <math>\text{mmol g}^{-1}</math></li> <li>Acid functional groups increased from 2.58 <math>\text{mmol g}^{-1}</math> to 3.47 <math>\text{mmol g}^{-1}</math></li> </ul>	$\text{NH}_4^+$ adsorption increased from 3.5 $\text{mg g}^{-1}$ (control, unmodified) to 11.67 $\text{mg g}^{-1}$	
Corn stalk biochar	$\text{H}_2\text{SO}_4$	Activation of corn stalk biochar with $\text{H}_2\text{SO}_4$ followed by shaking at 200 rpm, 60 °C, 24 h	<ul style="list-style-type: none"> <li>O % composition increased from 15.92 % to 16.26 %</li> <li>O/C ratio increased from 0.20 to 0.21</li> <li>H/C ratio increased from 0.04 to 0.05</li> <li>Acid containing oxygen functional groups increased from 3.45 <math>\text{mmol g}^{-1}</math> to 12.3 <math>\text{mmol g}^{-1}</math></li> </ul>	$\text{NH}_4^+$ adsorption increased by 1.59 times as compared to unmodified control	Yu et al. [47]
Rice husk biochar	$\text{H}_2\text{SO}_4$	Activation of rice husk biochar using $\text{H}_2\text{SO}_4$ followed by shaking at 200 rpm, 60 °C, 24 h	<ul style="list-style-type: none"> <li>O % composition increased from 5.03 % to 10.44 %</li> <li>O/C ratio increased from 0.05 to 0.12</li> <li>H/C ratio increased from 0.03 to 0.04</li> <li>Acid containing oxygen functional groups increased from 1.6 <math>\text{mmol g}^{-1}</math> to 12.1 <math>\text{mmol g}^{-1}</math></li> </ul>	$\text{NH}_4^+$ adsorption amount increased by 1.31 times as compared to unmodified control	
Soybean straw biochar	Mg-Al	<ul style="list-style-type: none"> <li>Impregnation of soybean straw and agents in a 1:7 ratio (weight to volume)</li> <li>Pyrolysis of impregnated soybean straw at 500 °C for 2 h</li> </ul>	<ul style="list-style-type: none"> <li>More metallic oxides and oxygen functional groups found on Mg-Al biochar than unmodified biochar</li> <li>Mg % composition increased from 1.54 % to 10.81 %</li> <li>Al % composition increased from 0.11 % to 11.12 %</li> <li>O % composition increased from 9.59 % to 28.12 %</li> <li>O/C ratio increased from 0.12 to 0.60</li> <li>H/C ratio improved by 1.97 times</li> <li>O/C ratio improved by 54.5 %</li> <li>Hydroxyl and carboxyl functional groups increased from 10.2 % to 30.1 %</li> <li><math>\text{Fe}^{3+}/\text{Fe}^{2+}</math> redox coupling functioned as electron shuttle to promote ammonium adsorption</li> </ul>	$\text{NH}_4^+$ adsorption amount increased from 0.52 $\text{mg g}^{-1}$ (control, unmodified) to 0.70 $\text{mg g}^{-1}$	Yin et al. [46]
Wheat straw biochar	$\text{FeCl}_3$	<ul style="list-style-type: none"> <li>Impregnation of wheat straw biochar and <math>\text{FeCl}_3</math> in a 1:10 (weight:volume) ratio</li> <li>Calcined in a muffle furnace at 400 °C, under <math>\text{N}_2</math>, 2 h</li> </ul>	<ul style="list-style-type: none"> <li><math>\text{Fe}^{3+}/\text{Fe}^{2+}</math> redox coupling functioned as electron shuttle to promote ammonium adsorption</li> </ul>	$\text{NH}_4^+$ adsorption amount increased by 17 % as compared to unmodified control	Wang et al. [43]
Wheat straw biochar	HCl, $\text{FeCl}_3$	<ul style="list-style-type: none"> <li>Impregnation of wheat straw biochar and HCl for 1 h</li> <li>Calcined in muffle furnace at 400 °C, under <math>\text{N}_2</math>, 2 h</li> <li>Followed by impregnation with <math>\text{FeCl}_3</math></li> </ul>	<ul style="list-style-type: none"> <li>H/C ratio improved by 2.59 times</li> <li>O/C ratio improved by 91.2 %</li> <li>Hydroxyl and carboxyl functional groups increased from 10.2 % to 40.7 %</li> <li><math>\text{Fe}^{3+}/\text{Fe}^{2+}</math> redox coupling functioned as electron shuttle to promote ammonium adsorption</li> </ul>	$\text{NH}_4^+$ adsorption amount increased by 14 % as compared to unmodified control	

rice husk biochars were washed several times with distilled water until a pH of 7 was reached [47].

In the recent studies shown in Table 4, activation of biochar, regardless of the type of agent used, led to an increase in O<sub>2</sub>-containing functional groups such as COO<sup>-</sup>, OH<sup>-</sup> and lactones (C<sub>10</sub>H<sub>15</sub>NO<sub>4</sub>). This increase in O<sub>2</sub>-containing functional groups as well as metal oxides led to an increase in biochar's  $\text{NH}_4^+$  adsorption capacity (Table 4). Ammonium adsorption increased up to 3.33 times compared to unmodified controls in corn cob biochar functionalised with  $\text{HNO}_3$  and NaOH (Table 4). In particular, the O/C ratio of functionalised biochar compared to their respective unmodified controls improved up to 91.2 %; this is indicative of an increasing affinity for  $\text{NH}_4^+$  [43]. The soybean straw-biochar described in Table 4 was functionalised via impregnation with Mg-Al [46], referred to as impregnation. Functional groups containing metal oxides were found on the biochar surface (Table 4). These groups can further facilitate cation exchange with  $\text{NH}_4^+$  as discussed in

Fig. 3. Lastly, for wheat straw biochar impregnated with  $\text{FeCl}_3$ , an electron shuttle was established by  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox coupling, promoting enhanced binding between  $\text{NH}_4^+$  and biochar particles [43]. Modified biochars are organised in increasing functionality in Table 4, from biochars containing more oxygen functional groups, to biochar containing more O-functional groups and metal oxides, to biochar containing more O-functional groups and electron shuttles.

Yin et al. [46] concluded that BET surface area was not the most crucial factor for the adsorption of  $\text{NH}_4^+$ ; the physisorption (Van der Waals forces of attraction) of  $\text{NH}_4^+$  to biochar surfaces contributes little to its overall adsorption capacity. Instead, adsorption capacity was more dependent on chemisorption (electrostatic attractions and cation exchanges). As such, functional groups present on the surface of biochar play a more crucial role in the overall  $\text{NH}_4$  adsorption capacity of biochar.

The  $\text{NH}_4^+$  adsorption capacity of biochar was also observed to be

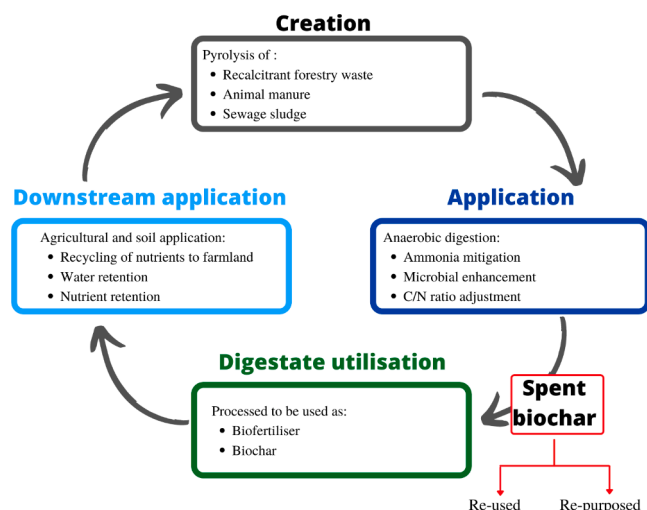


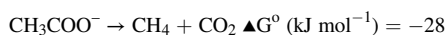
Fig. 3. Biochar as part of the circular economy.

poor at low pH ( $\text{pH} < 7$ ). This was attributed to the highly protonated surface functional groups on the biochar surface, producing a higher proportion of positively charged biochar particles. The presence of positively charged biochar particles greatly hinders  $\text{NH}_4^+$  adsorption due to electrostatic repulsion between  $\text{NH}_4^+$  and biochar particles. At a more optimal pH range (pH of 7 to 9), the presence of negatively charged biochar particles greatly promotes  $\text{NH}_4^+$  chemisorption. Hence, pH and surface functional groups produced a synergistic effect in terms of the level of chemical interaction between biochar and  $\text{NH}_4^+$ ; the higher the pH, the higher the level of adsorption.

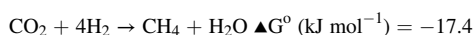
#### 4.3. Conductive material for Direct Interspecies electron Transfer (DIET)

During methanogenesis, approximately 70 % of the total  $\text{CH}_4$  is produced by acetoclastic methanogenesis (AM), where methanogens utilise acetate as a substrate, known as “acetate splitting” [39]. The remaining  $\text{CH}_4$  is produced by the reduction of  $\text{CO}_2$  using  $\text{H}^+$  as an electron donor; this is facilitated by hydrogenotrophic methanogens in a process known as “ $\text{CO}_2$  reduction” [39]. Typically, “acetate splitting” is more spontaneous compared to “ $\text{CO}_2$  reduction”; it has a more negative Gibbs Free Energy. The equations and corresponding Gibbs Free Energy values are given below:

Equation 1: Acetate splitting



Equation 2:  $\text{CO}_2$  reduction



However, under the conditions imposed by chicken manure feed-stock AD systems,  $\text{CH}_3\text{COO}^-$  splitting becomes less favourable; acetoclastic methanogenesis is strongly inhibited by  $\text{NH}_3$  stress [5]. However, the effect of  $\text{NH}_3$  stress on hydrogenotrophic methanogenesis is small [5]. As a result,  $\text{CH}_4$  production decreases, since 70 % of total  $\text{CH}_4$  is produced via acetate splitting.

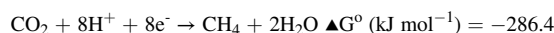
Direct Interspecies Electron Transfer (DIET) has been widely employed to improve the effectiveness of AD systems under ammonia stress; conjugating DIET and AD leads to an increase in biogas yield by increasing the conversion efficiency of macromolecules into organic acids and into  $\text{CH}_4$ . During methanogenesis, DIET has been found to occur between *Geobacter* and certain methanogens such as the *Methanosaeta* species, to facilitate the bio-transformation of  $\text{CO}_2$  to  $\text{CH}_4$  via the  $\text{CO}_2$  reduction pathway;  $\text{H}_2$  would otherwise be required for the reduction of  $\text{CO}_2$  [12]. Other methanogenic species capable of engaging in DIET includes *Methanosarcina* and *Methanospirillum* [32]. Direct

Interspecies Electron Transfer is a process where electrons flow directly from one cell to another without the need for a reducing agent such as  $\text{H}_2$  [12]. This flow of electrons between the species is primarily dependent on the stability and durability of the contact between the cells [12]. This contact can be either direct cell to cell contact, or indirect contact mediated by a conductive material.

Biochar can be utilised as a conductive material to facilitate DIET for the improvement of methanogenesis in  $\text{NH}_3$  stressed AD systems. As a conductive material, biochar can provide high surface area, reactivity and specificity and increases the number of active sites for *Geobacter* species and *Methanosaeta* species; biochar strengthens the indirect contact required for interspecies electron transfer [12].

An electron donor, or an exoelectrogen such as those from the *Geobacter* sp. oxidises organic matter into  $\text{CO}_2$  while extracellularly releasing electrons into the conductive material, such as biochar. The electrons are transmitted from the donor through biochar to electron acceptors, such as methanogens from the *Methanosaeta* species. The methanogen then utilises the transported electrons to reduce  $\text{CO}_2$  to  $\text{CH}_4$  without the need for an electron carrier such as  $\text{H}_2$ . The conversion of  $\text{CO}_2$  to  $\text{CH}_4$  via DIET, facilitated by biochar is more spontaneous than the conventional pathway using  $\text{H}_2$  (see Equation 2). This is further confirmed by the Gibbs Free Energy value of this modified  $\text{CO}_2$  reduction pathway shown in Equation 3 below:

Equation 3: DIET mediated  $\text{CO}_2$  reduction



The current knowledge of DIET in AD systems utilising chicken manure is summarised in Table 5. The table highlights the recent use of biochar to facilitate DIET in anaerobic digestion of chicken manure from various studies. In these studies, the composition of methanogens, either attached to biochar or present in the final digestate, was investigated, as well as any reduction in lag-time and improvement in methane yield as a result of DIET compared to control treatments.

In a recent study by Indren et al. [17], *Methanosaeta* species was reported to be the dominant methanogen found on all biochar surfaces at all different dosages, accounting for 46 % to 52 % of methanogens (Table 5). *Methanosaeta* species have been known to engage in DIET with *Geobacter*; this was further confirmed by a reduction in lag time and increase in daily methane yield observed compared to the control. The highest lag time reduction of 33.5 % was observed when wood pellet biochar was utilised at 59 g/L dosage (Table 5). The highest increase in methane yield of 30.1 % was observed using either wood pellet biochar or re-used wood pellet biochar at 34 g/L and 59 g/L dosage, respectively (Table 5). The high concentration of *Methanosaeta* species on biochar surfaces in this study suggested that *Methanosaeta* can utilise biochar to form microbial attachment to engage in DIET and improve digester performance. However, *Methanosaeta* species was more dominant in wood pellet biochar compared to re-used biochar at all dosage levels; inactive microorganisms attached to the re-used biochar surface can deter new attachments by active methanogens. As such, the use of re-used biochar is not as effective as pristine biochar in maximising the potential of DIET due to a lower degree of methanogenic attachment.

The methanogenic composition of the final digestate can also be analysed to understand the degree of DIET during the digestion process. In another study performed by Ma et al. [26], *Methanosarcina* made up 89 % of the methanogenic population when a 5 % biochar dosage was used (Table 5). While no significant difference was observed for the lag-time,  $\text{CH}_4$  production increased by 12 % (Table 5). This was attributed to DIET between *Methanosarcina* and organic acids oxidising bacteria, allowing *Methanosarcina* to reduce propionate directly to  $\text{CH}_4$ . Pan et al. [32] conducted a similar experiment using a 5 % biochar dosage applied to 3 different organic loading rates: low, medium and high; 0.63 g vS  $\text{L}^{-1}$  day, 3.13 g vS  $\text{L}^{-1}$  day and 6.25 g vS  $\text{L}^{-1}$  day, respectively (Table 5). While the increase in organic loading rate was expected to cause an increase in digester instability and lower  $\text{CH}_4$  production, DIET

**Table 5**

The dominant methanogens on the surfaces of different biochar types, at different dosages or present in the final digestate, and the observed effects on lag-time reduction and methane yield from various studies involving chicken manure.

Biochar type	Biochar dosages	Dominant methanogen family/genus	Lag-time	Improvement in CH <sub>4</sub> yield	Reference
Wood pellet, 770 °C	59 g/L	52 % <i>Methanosaeta</i>	33.5 % reduction	Daily yield increased by 23.1 %	Indren et al.
	34 g/L	52 % <i>Methanosaeta</i>	12.5 % reduction	Daily yield increased by 30.1 %	[17]
	8 g/L	52 % <i>Methanosaeta</i>	10.5 % reduction	Daily yield increased by 23.1 %	
Re-used wood pellet, 770 °C, digested for 90 days	59 g/L	47 % <i>Methanosaeta</i>	17.5 % reduction	Daily yield increased by 30.1 %	
	34 g/L	47 % <i>Methanosaeta</i>	29.5 % reduction	Daily yield increased by 15.4 %	
	8 g/L	46 % <i>Methanosaeta</i>	18.5 % reduction	Daily yield increased by 7.69 %	
Fruitwood, 550 °C	5 % of Total solids	89 % <i>Methanosarcina</i>	No significant difference	12 % increase in CH <sub>4</sub> production	Ma et al. [26]
Orchard wood, 550 °C	5 % of Total solids	88.5 % <i>Methanosarcina</i>	No significant difference	<ul style="list-style-type: none"> <li>• 33 % increase in CH<sub>4</sub> production under Low-OLR</li> <li>• 36 % increase in CH<sub>4</sub> production under Medium-OLR</li> <li>• 32 % increase in CH<sub>4</sub> production under High-OLR</li> </ul>	Pan et al. [32]
Wood pellet, 770 °C	1:1 ratio biochar to feedstock (dry mass)	89.6 % <i>Methanosaetaceae</i>	4 % reduction	Mean cumulative CH <sub>4</sub> yield increased by 32 %	Indren et al. [16]
Wood pellet, 770 °C, 30 days pre-loaded in LSAD		88.4 % <i>Methanosaetaceae</i>	12.7 % reduction	Mean cumulative CH <sub>4</sub> yield increased by 22 %	
Wood pellet, 770 °C, 90 days pre-loaded in HSAD		76.6 % <i>Methanosaetaceae</i>	33 % reduction	Mean cumulative CH <sub>4</sub> yield increased by 69 %	
Wheat straw, 680 °C		55.3 % <i>Methanosaetaceae</i>	57.3 % increase	No effect on CH <sub>4</sub> yield	
Sheep manure, 720 °C		87.2 % <i>Methanosaetaceae</i>	86 % increase	No effect on CH <sub>4</sub> yield	

LSAD: low solids anaerobic digestion (5% total solid content), HSAD: high solids anaerobic digestion (20% total solid content), Low-OLR: Low Organic loading rate, Medium-OLR: medium organic loading rate, High-OLR: High organic loading rate.

established between methanogens and fermentative bacteria using biochar improved CH<sub>4</sub> yield via promoting the most efficient metabolic pathway. This was reflected by the fact that the relative abundance of *Methanosarcina* found in the final digestate was 88.5 %; *Methanosarcina* can reduce propionate directly to CH<sub>4</sub> using DIET (Table 5). As a result, CH<sub>4</sub> production improved by 33 %, 36 % and 32 % for low, medium and high organic loading rate, respectively (Table 5). Similar with previous studies, no significant changes were observed in the lag-time.

A study performed by Indren et al. [16] investigated the efficacy of different types of biochar in establishing DIET and improving digester performance using a 1:1 ratio of biochar to feedstock (dry mass), comparing between wood pellet biochar, wheat straw biochar and sheep manure biochar. In addition, wood pellet biochar was divided into 3 categories: raw, pre-loaded with microorganisms under low solids AD (LSAD) for 30 days, or under high solids anaerobic digestion (HSAD) for 90 days. Among the 5 different biochar treatments, the use of pre-loaded HSAD biochar produced the highest reduction in lag-time (33 %) and the highest increase in mean cumulative CH<sub>4</sub> yield (69 %) (Table 5). This was attributed to DIET between *Methanosaetaceae* and propionate/isovalerate-oxidising bacteria; 76.6 % of methanogens found on this biochar was *Methanosaetaceae*. In comparison, the use of LSAD biochar produced a lower reduction in lag time of only 12.7 % while the use of raw wood pellet biochar produced the lowest reduction of 4 % (Table 5). Similarly, the improvement in cumulative CH<sub>4</sub> yield also decreased to 22 % when LSAD biochar was used, and to 32 % when raw wood pellet biochar was used (Table 5). Lag-time increased by 57.3 % and 87.2 % with the use of wheat straw biochar and sheep manure biochar respectively; no significant changes in CH<sub>4</sub> yield was observed (Table 5). Investigation into the level of total microbial attachment on the biochar revealed the reason for this increase in lag-time. The highest level of microbial attachment, 67 ng<sup>-1</sup>μL<sup>-1</sup>g<sup>-1</sup> biochar was observed for HSAD biochar, which corresponded to the best improvement in digester performance as a result of DIET. Low solids anaerobic digestion biochar had a lower level of attachment (22 ng<sup>-1</sup>μL<sup>-1</sup>g<sup>-1</sup> biochar) compared to raw wood pellet biochar, 31 ng<sup>-1</sup>μL<sup>-1</sup>g<sup>-1</sup> biochar [16]. This resulted in the slightly greater reduction in lag-time and improvement in CH<sub>4</sub> yield produced by raw wood-pellet biochar compared to LSAD biochar [16]. Sheep manure biochar showed the lowest degree of microbial attachment (14 ng<sup>-1</sup>μL<sup>-1</sup>g<sup>-1</sup> biochar), but with no significant improvement in

CH<sub>4</sub> yield [16]. While wheat-straw biochar showed the highest level of microbial attachment (79 ng<sup>-1</sup>μL<sup>-1</sup>g<sup>-1</sup> biochar), the low bulk density nature of wheat straw biochar reduced the volumetric efficiency and performance of the digester; working volume was increased by 130 % [16].

## 5. Biochar and the circular economy

While biochar functions and performs similarly to other methods of NH<sub>3</sub> mitigation, the role that biochar can play in creating a circular economy and closing many organic waste loops cannot be ignored. This section discusses the importance and advantages of using biochar as a preferred method of NH<sub>3</sub> mitigation, as well as highlighting recent studies that have investigated the potential of biochar to create circular economies.

Unlike *in situ* NH<sub>3</sub> stripping, bentonite addition, Se supplementation, Fe<sup>2+</sup> and Ni<sup>2+</sup> supplementation, co-digestion and water extraction, using biochar as a method of mitigation represents the first step in closing a waste loop as biochar is inherently a recalcitrant waste material. Biochar is a product from the pyrolysis of various biomass such as forestry residues, animal manure or sewage sludge; while there are other methods of creating biochar, pyrolysed biochar exhibits the highest suitability for utilisation in AD systems. When comparing pyrolysed biochar to other types of biochar, it is more economically viable and does not contain toxic by-products. For example, biochar produced via gasification yields on average 10 % of biochar from the biomass; this extremely low yield places gasified biochar production at an economic disadvantage [21]. While biochar produced by hydrothermal carbonisation can retain more surface functional groups and have much higher yields compared to those produced by pyrolysis, 70 % as compared to 50 %, hydrothermal carbonisation can incur extremely high operational costs [21]. The need for a continuous and recirculating large volume of water in industrial hydrothermal carbonisation makes it economically unviable [21]. Wet and dry torrefaction can produce biochar with higher heating values, energy densities and carbon content but with extremely low H/C and O/C atomic ratios, making them unsuitable for use as bioadsorbents due to the lower concentration of surface functional groups [13]. As a result, biochar produced by torrefaction are generally used as coal fuel [13].



The effectiveness of pyrolysed biochar in  $\text{NH}_3$  stress mitigation is primarily dependent on its synthesis conditions: pyrolysis temperature, type of feedstock and functionalisation. Pyrolysis temperature should not exceed  $550^\circ\text{C}$  to avoid the volatilisation of O-containing functional groups required for adsorption (low percentage composition of O and H observed) (Fig. 2). The biomass used in pyrolysis is often the by-product from various industries and hence, the use of biochar in AD represents the utilisation of a waste product to treat another waste product; this is the first step to creating a circular economy and can only be achieved via the use of biochar. Additionally, the spent biochar from AD can be further re-used or re-purposed for other uses. The digestate obtained from AD with biochar can be processed into biofertiliser or pyrolysed to create new biochar. The biofertiliser or biochar created from the digestate carry high agricultural values and have the potential for various downstream applications. Fig. 3 summarises the proposed circular economy brought about with biochar in AD.

The application of biochar in AD does not represent the end-use of biochar as the spent biochar can be re-used in subsequent AD or re-purposed for other uses (Fig. 3). A recent study by Indren et al. [17] demonstrated the viability of using spent biochar for subsequent AD processes. The study found that the use of either new or spent biochar can shorten the retention time to allow for more batches of waste to be processed annually [17]. When compared to control treatments, the addition of new or spent biochar allowed the maximum annual volumetric efficiency to be obtained within 41 days instead of 57 days; this translated to 7 batches of AD per annum instead of 5 [17]. Another recent study by Lee et al. [22] looked into the re-purposing of spent biochar as an anaerobic digestate filter. The use of spent biochar as an anaerobic digestate filter was found to be effective in reducing the chemical oxygen demand (COD) and total suspended solids (TSS) to 14.5 % and 97 % below the maximum permissible limit, respectively; the digestate was legally approved for reuse as a biofertiliser [22]. Therefore, the use of biochar, when compared to the other methods, carries the distinct advantage of being recyclable as subsequent usage of biochar does not decrease its effectiveness and performance.

The digestate obtained from AD with biochar can also be processed to be used as a biofertiliser or pyrolysed to create new biochar (Fig. 3). Consequently, the biofertiliser or biochar obtained can be applied to agriculture to recycle nutrients to farmland or improve water and nutrient retention in the soil and closing waste loops (Fig. 3). The study by Plaimart et al. [36] highlighted the high agricultural value of biochar amended anaerobic digestate. The study revealed that biochar amended digestate can reduce nitrate leaching upon soil application by up to 80 % as compared to unamended digestate; this minimises groundwater pollution during heavy rainfall [36]. The reduction in nitrate leaching also translated into longer nutrient retention in the topsoil for plant growth [36]. In another recent study by Tayibi et al. [40], the benefits of using biochar obtained from the pyrolysis of AD digestate were investigated. The study concluded that the application of biochar obtained from the pyrolysis of an anaerobic digestate could improve the gravimetric water retention by up to 40 % [40]. In addition, when biochar was incorporated into the same digestate and applied to soil, similar results to those reported by Plaimart et al. [36] were obtained; nitrate ( $\text{NO}_3^-$ ) leaching was reduced by up to 91 % [40]. Finally, the use of biochar amended digestate in soil resulted in enhanced production of wheat, measured in aerial dry biomass, by up to 67.8 % as compared to soil alone [40].

As such, the use of biochar in AD not only serves as a method of  $\text{NH}_3$  mitigation, but also carries the advantage of being recyclable as well as many downstream applications such as agricultural or soil application. Therefore, the use of biochar in the AD of chicken manure is a novel approach as it promotes the circular re-utilisation of two different waste residues from different industries. To date, no studies have investigated the potential of anaerobic digestate from *in situ*  $\text{NH}_3$  stripping, bentonite addition, Se supplementation,  $\text{Fe}^{2+}$  and  $\text{Ni}^{2+}$  supplementation, co-digestion, and water extraction for downstream applications.

## 6. Summary of current knowledge

Pyrolysed biochar has been proposed to be a highly effective additive for the purpose of mitigating  $\text{NH}_3$  stress in AD systems utilising chicken manure. Pyrolysed biochar serves to balance the unfavourable C:N ratio that exists in these system as well as provide surfaces for the adsorption of  $\text{NH}_4^+$ . In addition, pyrolysed biochar can provide microbial sheltering, allowing methanogens to colonise its porous structure, protecting them from ammonia stress. Pyrolysed biochar has also been demonstrated to facilitate DIET between exoelectrogens such as *Geobacter* sp. and electron acceptors such as methanogens from the *Methanosaeta* species to produce  $\text{CH}_4$ . Finally, pyrolysed biochar is a promising candidate when compared to other methods of  $\text{NH}_3$  mitigation due to the important role it can play in many circular economy models.

To ensure effective  $\text{NH}_4^+$  chemisorption by surface functional groups, pyrolysed biochar must be further functionalised using agents similar to those listed in Table 3. The level of functionalisation will determine the type and abundance of surface functional groups; some biochar have been shown to possess redox coupling potential (Table 2). Moreover, functionalised pyrolysed biochar has been shown to perform  $\text{NH}_4^+$  chemisorption more effectively at pH 7–9; a pH below 7 will result in electrostatic repulsion between  $\text{NH}_4^+$  and biochar particles. This makes pyrolysed biochar extremely suitable for mitigating  $\text{NH}_3$  stress since AD systems utilising chicken manure will inevitably produce high digester pH. The degree of DIET is also influenced by the parent material used. Manure based biochar produced undesirable effects and was incapable of facilitating DIET. Woody biochar, especially if pre-loaded with microorganisms under high solids AD, can enhance DIET and greatly improve digester performance. Non-woody biochar such as wheat straw biochar, while capable of facilitating DIET, is not suitable for use due to the low bulk density nature which can hamper digester performance.

### 6.1. Conclusion and future prospects

The review has shown that biochar pyrolysed at temperatures not exceeding  $550^\circ\text{C}$  has been effective in mitigating  $\text{NH}_3$  stress arising from chicken manure AD systems; pyrolysed fruitwood and wheat straw biochars produced at  $550^\circ\text{C}$  achieved 25 % and 21.4 % TAN reduction as compared to non-functionalised control, respectively. Pyrolysis temperatures greater than  $550^\circ\text{C}$  resulted in the undesirable volatilisation of surface O-functional groups and undermined the TAN surface adsorption capacity of biochar. Pyrolysed biochar can also be functionalised to maximise their  $\text{NH}_4^+$  chemisorption capacity to better mitigate  $\text{NH}_3$  stress using a variety of functionalising methods and agents. A functionalisation study involving the activation of corncob biochar with  $\text{HNO}_3$  and  $\text{NaOH}$  resulted in a 333 % increase in  $\text{NH}_4^+$  adsorption. In addition, pre-loading the biochar with methanogenic bacteria such as *Methanosaetaceae* under HSAD can maximise its DIET facilitating potential resulting in a 29 % reduction in lag time and a 69 % increase in mean cumulative  $\text{CH}_4$  yield. While there are other methods of  $\text{NH}_3$  alleviation, the utilisation of biochar can create circular economies to close existing organic waste loops. Furthermore, biochar carries the distinct advantage of being a recyclable additive, allowing it to be reused or repurposed for other uses; this further increases the overall cost-effectiveness of biochar. Currently, spent biochar has been utilised as additives for subsequent AD processes, anaerobic digestate filter or as a biofertiliser.

Future studies on  $\text{NH}_3$  stress mitigation in AD systems utilising chicken manure should explore the use of other types of biochar made from dry torrefaction, hydrothermal carbonisation (wet torrefaction), gasification and hydrothermal processing. Currently, this presents a research gap as most AD studies involving chicken manure mainly utilised pyrolysed biochars. The current knowledge on the effects of the different types of biochar within  $\text{NH}_3$  stressed, chicken manure AD systems need to be further explored. Xu et al. [44] recently reported that

biochar produced from hydrothermal carbonisation enhanced digester performance due to its more abundant surface functional groups. Filling this current knowledge gap will facilitate better utilisation of chicken manure as a feedstock. In addition, three important findings should also be addressed in all future studies: the degree of colonisation by methanogens on biochar surfaces, the level of  $\text{NH}_4^+$  chemisorption by surface functional groups and  $\text{CH}_4$  production. These findings will help to clarify whether biochar is an effective additive for the purpose of  $\text{NH}_3$  stress mitigation while simultaneously improving  $\text{CH}_4$  production via DIET.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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