The challenges of anaerobic digestion and the role of biochar in optimizing anaerobic digestion

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Abstract

Biochar, like most other adsorbents, is a carbonaceous material, which is formed from the combustion of plant materials, in low-zero oxygen conditions and results in a material, which has the capacity to sorb chemicals onto its surfaces. Currently, research is being carried out to investigate the relevance of biochar in improving the soil ecosystem, digestate quality and most recently the anaerobic digestion process. Anaerobic digestion (AD) of organic substrates provides both a sustainable source of energy and a digestate with the potential to enhance plant growth and soil health. In order to ensure that these benefits are realised, the anaerobic digestion system must be optimised for process stability and high nutrient retention capacity in the digestate produced. Substrate-induced inhibition is a major issue, which can disrupt the stable functioning of the AD system reducing microbial breakdown of the organic waste and formation of methane, which in turn reduces energy output. Likewise, the spreading of digestate on land can often result in nutrient loss, surface runoff and leaching. This review will examine substrate inhibition and their impact on anaerobic digestion, nutrient leaching and their environmental implications, the properties and functionality of biochar material in counteracting these challenges.

Keywords: biochar; inhibition; nutrient leaching; digestate; anaerobic digestion

1. Introduction

The number of anaerobic digestion (AD) systems has increased rapidly because of various factors including financial incentives for renewable energy facilities, governmental policies on climate change, landfill and an increasing energy need (Zglobisz et al., 2010; Klavon et al., 2013). Currently, in Europe and Asia, there are over 30 million large and small-scale anaerobic digesters for both commercial and domestic applications (Chen et al., 2010; De Baere, 2010; Donoso-Bravo et al., 2011; Ferrer et al., 2011). AD is the stepwise breakdown of an organic substrate by a consortium of mutually dependent groups of microorganisms (Fig 1). If the correct conditions are maintained, the AD process will be stable with high energy recovery (Dechrugsa et al., 2013). However, the technology still faces two major challenges: (i) operational instability and (ii) the quality of the digestate produced (Holm-Nielsen et al., 2009; Appels et al., 2011).

Organic substrate selection plays an important role in the stability of an AD system as some feedstocks can have inhibitory effects on AD processes. Substrate-induced inhibition (SII) in AD can occur when the constituent fraction(s) or metabolic intermediate product(s) from organic substrates inhibit microbial activity. These forms of inhibition have been reported for organic substrates containing high amounts of protein, lipids, limonene, furans, metals, pesticides, antibiotics and other organic compounds (El-Gohary et al., 1986; Palmqvist & Hahn-Hagerdal, 2000; Lallai et al., 2002; Wilkins et al., 2007; Alvarez et al., 2010; Sousa et al., 2013; Yangin-Gomec & Ozturk, 2013). SII is either through the direct addition of inhibitory compounds, such as limonene, or indirectly through the production of inhibitory intermediates, such as ammonium and hydrogen sulphide from protein (Table 1). Microbial adaptation to potential inhibitors and co-digestion with two or more substrates are commonly used

50   to reduce inhibition (El-Mashad & Zhang, 2010; Zhang & Jahng, 2012). During

51   microbial adaptation, the inhibitor can be transformed into metabolites with a similar

52   or lower level of toxicity while the application of co-digestion reduces the

53   concentration of the inhibitor by increasing the ratio of the co-substrate (Athanasoulia

54   et al., 2014). In most cases, AD operators prefer co-digestion of two or more

55   substrates in order to reduce possible inhibition that might result from the treatment of

56   individual feed-stocks (Cheng & Zhong, 2014). However, an alternative approach to

57   reducing inhibition in AD is to remove or reduce the mobility/bioavailability of the

58   inhibitors without affecting with the AD process.

59

60   Another major concern with AD is how to retain the nutritive value of the

61   digestate before and after application to land (Mihoubi, 2004; Mangwandi et al.,

62   2013). In most cases, digestate has a high moisture content and in an attempt to reduce

63   this, phase separating equipment is utilised. According to Vaneeckhaute et al. (2013),

64   43% of the total nitrogen (N) and 25% of the total phosphorus (P) will be lost if the

65   liquid fraction of pig slurry digestate is separated. Further nutrient and metal losses

66   can occur during and after the spreading of the digestate on farmland via transfer to

67   the surrounding watercourses or to the atmosphere. The volatilization of ammonium,

68   leading to ammonia emission, and the leaching of heavy metal as diffuse pollution, are

69   examples of losses that have a negative impact on the environment and crops

70   (Svoboda et al., 2013; Page et al., 2014). Nutrient recovery from digestate has been

71   considered as an option to reduce the nutrient loss from the digestate. However, this

72   approach might reduce the economic value of the digestate (Verstraete et al., 2009;

73   Batstone et al.,2015).

74   A better approach may be to focus on increasing the nutrient retention capacity of

75   the digestate material. There is a growing interest in the use of biochar in AD to both

76   increase the recovery rate of the process during SII and decrease the nutrient loss

77   before and after land application (Mumme et al., 2014; Dicke et al., 2015; Cai et al.,

78   2016; Lü et al., 2016; Sunyoto et al., 2016). This will potentially increase the

79   operation of mono-substrate AD, which is often used by single substrate onsite AD

80   operators, increase nutrient availability during digestate application to land and reduce

81   the environmental implications of diffuse pollution and nutrient leaching. This review

82   examines substrate-induced inhibition and its impact on anaerobic digestion, nutrient

83   leaching and its environmental implications, and the properties and functionality of

84   biochar material in counteracting these challenges.

85

86   **2.   The Challenges with anaerobic digestion of organic susbtrate**

87   AD is the breakdown of complex organic material under anoxic conditions by a

88   consortia of microorganisms via a multistep process (Fig 1) (Chen et al., 2008). The

89   microorganisms that drive AD are divided into two groups: (i) acid producers

90   (acidogens and acetogens) and (ii) methane producers (methanogens). These two

91   groups of microorganisms differ physiologically and have different growth rates and

92   sensitivities to operational conditions (Ruiz & Flotats, 2014). The inability to maintain

93   a population balance between these two groups of microorganisms often results in AD

94   process failure. If conditions such as temperature, hydrogen partial pressure, pH and

95   organic loading rate are favourable for both microbial populations, the AD process

96   should be stable (Rudolfs & Amberg, 1952).

97   In addition to the controls exerted by the operating conditions, the stability of

98   the AD system can also be disrupted if metabolic intermediates of a substrate are

99   inhibitory to microbial activity (Palmqvist & Hahn-Hagerdal, 2000; Wilkins et al.,

100   2007; Sousa et al., 2013; Yangin-Gomec & Ozturk, 2013). This form of instability is

101   substrate-induced and is called substrate-induced inhibition (SII). According to Ruiz

102   and Flotats (2014), a chemical or metabolite can be termed inhibitory when it causes a

103   shift in microbial population or inhibits microbial activity. There is a wide variety of

104   biodegradable organic materials that have been classified as inhibitory to microbial

105   growth, particularly at higher concentrations (Fig 2 and Table 1). SII can be classified

106   into two categories, direct and indirect sources of inhibition. Direct inhibitors are

107   those that are supplied directly from substrates in the feedstock whilst indirect

108   inhibitors are metabolic intermediates produced during the AD process (Fig 2). The

109   following sections (2.1 and 2.2) describe the types of direct and indirect inhibitors

110   commonly associated with AD and the mechanisms by which inhibition occurs.

111

112   2.1.   Direct inhibition

113   As mentioned earlier, direct inhibition in AD results from a constituent of the organic

114   substrate; this implies that the compound is readily available to the microbial cells,

115   thus increasing the risk of AD process failure. The indirect inhibitors are not released

116   until after hydrolysis-acidogenesis and thus they do not pose an immediate threat to

117   the AD process. An example of direct inhibitors include limonene from citrus peel,

118   furans hydrolysate from the chemical pre-treatment of lignocellulose materials, azo-

119   dye from textile production, antibiotics and pesticides. Limonene occurs naturally in

120   citrus peel and reports show that the compound can inhibit the AD process at

121   concentrations of 65-88 g l^{-1} (Mizuki et al., 1990). Even after the extraction of

122   limonene prior to AD, studies have shown that inhibition of the AD process occurred,

123   particularly when the organic loading rate (OLR) was increased from 3.67-5.10 gVS l^{-}

124 ^{1} d^{-1} (Martin et al., 2010; Wikandari et al., 2015). In addition, the co-digestion of

125 orange peel and sewage sludge (70:30) resulted in a methane yield of 0.165 l gVS$^-$

126 $^1_{added}$ and the accumulation of volatile fatty acids when the OLR was above 1.6 gVS l^{-1}

127 d^{-1} (Serrano et al., 2014). Likewise, furans (furfural, hydroxymethylfurfural (5-HMF))

128 are produced during the dehydration of pentose- and hexose-sugars locked within the

129 lignin structure (Barakat et al., 2012). These are metabolites from the hydrolysis of

130 lignin but because they are not produced because of the microbial interaction, they are

131 considered to be directly inhibitory. There are indications that the furans are not

132 inhibitory and can be utilised for methane production at a concentration of less than 25

133 mM (Rivard & Grohmann, 1991; Belay et al., 1997). According to Barakat et al.

134 (2012), the 5-HMF is more inhibitory than the furfural compound because, after

135 incubation of 1 g l^{-1} of the compounds with 2 g l^{-1} of xylose separately, methane

136 values of 533 and 583 ml/g were recorded, respectively. Similarly, Monlau et al.

137 (2013) observed that the AD process was severely inhibited at 5-HMF concentration,

138 which was above 6 g l^{-1}. Other direct inhibitors are antibiotics and pesticides, which

139 are present in industrial and pharmaceutical wastewater (Lin, 1990; Ji et al., 2013).

140 Antibiotics such as amoxicillin (0.16 g l^{-1}), trihydrate (0.06 g l^{-1}), oxytetracycline

141 (0.12 g l^{-1}) and thiamphenicol (0.08 g l^{-1}) have been used to treat pigs and reports

142 show partial inhibition to AD (Lallai et al., 2002). Ji et al. (2013) showed acute

143 toxicity of four antibiotics in the order amoxicillin (0.39 g l^{-1}), lincomycin (0.43 g l^{-1}),

144 kanamycin (0.51 g l^{-1}) and ciprofloxacin (0.56 g l^{-1}). A noticeable trend common to all

145 direct inhibitors is the similarities in the mechanisms of inhibition. These compounds

146 inhibit the growth of microbial cells as follows: (i) diffusing through the cell

147 membrane; (ii) increasing the surface area of the cell membrane, and (iii) causing

148 leakage of the contents of the microbial cell (Sikkema et al., 1995; Griffin et al., 1999;

149 Fisher & Phillips, 2008).

150

151 2.2. Indirect inhibition

152 Indirect inhibition is displayed when metabolic intermediates are produced at high

153 concentrations during the AD thereby inhibiting microbial activity. They have been

154 reported to suppress microbial activity and reduce methane production. An examples

155 of indirect SII, their effects and counteracting measures. Metabolic intermediate

156 products are generally produced during the AD process and they depend on the

157 constituent of the substrate (Figure 1). Metabolic products such as acetic acid,

158 hydrogen and carbon dioxide are essential to the AD process and are used to produce

159 methane (Madsen et al., 2011). However, intermediates such as long chain fatty acid,

160 ammonia (NH_3) and ammonium (NH_4^+) are examples of indirect inhibitors.

161 Researchers have shown that free ammonia is more toxic than ammonium nitrogen

162 because of its ability to penetrate the cell membrane (Gallert & Winter, 1997; Sung &

163 Liu, 2003). According to Zeshan et al. (2012), an increase in the C/N ratio of the

164 feedstock can minimise the possible effect of high protein feedstock because the

165 addition of carbon will reduce the concentration of nitrogen rich material and also

166 provide alternative metabolic routes thereby reducing the production of NH_4^+. They

167 recorded a 30% reduction in the NH_3 content of the digestate and 50-73% surplus

168 energy when the C/N ratio of the feedstock was increased to 32. Yangin-Gomec and

169 Ozturk (2013) achieved a 1.2 fold increase in the methane yield when maize silage

170 was co-digested with chicken and cattle manure to suppress ammonia toxicity. As

171 mentioned earlier, protein is essential for microbial growth but at a high concentration,

172 it will increase the possibility of ammonia toxicity. Ammonia is beneficial to the

173 growth of anaerobic bacteria as long as it does not exceed a certain concentration that

174 can be toxic to methangenic activity (Angelidaki and Ahring, 1994). Similarly, a

175 substrate high in lipid produces a higher concentration of long-chain fatty acids

176 (LCFAs) and glycerol during hydrolysis. LCFAs (e.g. oleate, stearate and palmitate)

177 can be converted into hydrogen and acetate through the β-oxidation pathway (Alves

178 et al., 2009). According to Sousa et al. (2013), methanogens can be inhibited by

179 LCFAs at concentrations between of 0.3 and 1 mM. Like LCFAs, the mechanisms of

180 suppression of microbial activity during indirect inhibition are similar (i) diffusing

181 through the cell membrane; (ii) inhibiting methane producing enzymes, and (iii)

182 causing proton imbalance and potassium deficiency (Rinzema et al., 1994; Gallert &

183 Winter, 1997; Chen et al., 2008; Rajagopal et al., 2013; Zonta et al., 2013).

184

185 2.3. Acclimation of microbial cells to inhibition

186 The mechanisms of direct and indirect inhibition are not similar; a general model

187 illustrating the various mechanisms of attack (cell membrane disorder, interference

188 with fermentative pathway and intracellular swelling/leakage) of the microbial cell is

189 represented in Figure 2. SII cannot be avoided during the operation of AD systems,

190 but to some extent the ability of microorganisms to adapt to unfavourable conditions

191 can alleviate the effects of SII. Acclimation is the adaptation of microbial populations

192 to changes in conditions and can be achieved in different ways: (i) synthesis of

193 specific enzymes which were absent prior to exposure to the inhibiting condition; (ii)

194 emergence of new metabolic capabilities/pathway, and (iii) modification of the

195 surface layer of the microbial cell membrane (Liebert et al., 1991; Ruiz & Flotats,

196 2014). An example of modification of the surface layer of a cell membrane was

197 observed during the exposure of microbial cells to a high dose of limonene; this

198   resulted in increases in the concentration of unsaturated fatty acids in the cell

199   membrane (Ruiz & Flotats, 2014). Another example has been reported where

200   methanogens were exposed to 2 g l^{-1} of ammonia and, following a subsequent increase

201   in the concentration of ammonia to 11 g l^{-1}, no inhibition was recorded (Koster &

202   Lettinga, 1988; Borja et al., 1996a). This implies that the microbial cells were able

203   adapt to the unfavourable conditions and further suggests that AD operators should

204   only inoculate their plant with inoculum from an active AD system using a similar

205   substrate. Quintero et al. (2012) showed that the hydrolysis of lignocellulose was more

206   efficient when the feedstock was inoculated with microflora from cattle rumens rather

207   than pig manure. Likewise, Van Velsen (1979) showed that the microbial community

208   in the pig manure inoculum acclimated to 2.4 g l^{-1} of NH_4^+ while the digested sewage

209   sludge acclimation rate was limited to 1.8 g l^{-1} of NH_4^+.

210

3.   Nutrient loss and environmental pollution

212   In order to keep up with the increasing demand for food production, soil fertility is

213   maintained by adding fertilizers (Qin et al., 2015). The spreading of anaerobic

214   digestate and compost material on farmland has increased and has become a method

215   of complimenting or replacing synthetic fertilizer usage. In addition, this is driven by

216   changes in agricultural practices and policies that focus on reducing climate change

217   and improving soil quality (Qin et al., 2015; Stoate, 2009; Riding et al., 2015).

218   Anaerobic digestate is rich in minerals, biomass, nitrogen, phosphorus and carbon

219   which are essential for maintaining the soil ecosystem and sustaining increased plant

220   growth (Montemurro et al., 2010; Tambone et al., 2010). In a study carried out by

221   Alburquerque et al. (2012), the effect of digestate on horticulture crop production

222   showed that the application of digestate provided a short term source of phosphorus

and nitrogen and the microbial biomass and enzyme activities were relatively higher

than the non-amended soil. Despite the benefits of utilizing digestate, the risk of

atmospheric and water pollution following the application of digestate to land are high

(Tiwary et al., 2015). This problem is particular to digestate because of the fast release

of nutrients, which is often beyond the utilization rate of the plants and soil

microorganisms, thus making leaching and nutrient loss unavoidable. Unlike the

digestate, the nutrient content of the inorganic fertilizer is slowly released into the

environment, thus reducing the possibility of leaching in relation to organic fertilizers

(Basso & Ritchie, 2005; Kim et al., 2014). Digestates with high concentrations of

inorganic N are of particular concern due to the high potential for volatilization of

NH_3 (Fernandes et al., 2012). Reports have shown that N losses are also significant

during the processing of digestate with up to 85% of the NH_4^+ content emitted as NH_3

gas (ApSimon et al., 1987; Rehl and Müller, 2011). NH_3 is recognised as a major

contributor to nitrous oxide (N_2O) production, a biological process carried out by

ammonia-oxidizing bacteria (Law et al., 2013). The N_2O is formed as an intermediate

product between nitrification and de-nitrification. The microorganisms first convert

NH_3 into hydroxylamine (NH_2OH), then into nitrite (NO_2^-) and finally into N_2O. N_2O

is an important atmospheric gas but at high concentrations it contributes to the

formation of acid rain and thinning of the ozone layer (Badr & Probert, 1993). Tiwary

et al. (2015) reported that the emission of NH_3 may be reduced by 85% if the digestate

is introduced into the subsoil but the emission of N_2O is inevitable and it was found to

be 2% higher than the other assays because of the contribution of the subsurface

denitrifying microorganisms. Another route for nutrient loss from digestate applied to

soil is diffuse pollution. Nutrient leaching from the digestate can result in the transfer

of N and P to water bodies causing eutrophication (Anthonisen et al., 1976; Soaresa et

248   al., 2011). Eutrophication itself is a process whereby an ecosystem is transformed

249   through nutrient enrichment from an external source (Conley et al., 2009). Following

250   the increase in nutrients, the growth of certain organisms such as algae, photosynthetic

251   and heterotrophic bacteria increases, thus raising demand for resources which were

252   present during the influx of the external enrichment resources (O'Sullivan, 1995).

253   Accelerated eutrophication of aquatic ecosystems owing to nitrogen and phosphorus

254   enrichment has been reported to have a negative impact on the aquatic life. Firstly,

255   light penetration into the littoral zone is limited thus inhibiting the growth of plant and

256   predators that depend on light for survival; dissolved inorganic carbon is depleted and

257   the alkalinity of the water increases (Lansing et al., 2008). Secondly, after depletion of

258   the nutrients, the algal boom dies and microbial decomposition of the algal biomass

259   depletes the dissolved oxygen, thus creating an anoxic or dead zone (Nagamani &

260   Ramasamy, 1999). In addition, the proliferation of pathogens such as *Ribeiroia*

261   *ondatrae,* which infects birds, snails and amphibian lava causing limb deformation has

262   also been reported in the literature (Johnson et al., 2007). Apart from nutrients,

263   digestate may also contain metals, particularly heavy metals (Ni, Zn, Cu, Pb, Cr, Cd,

264   and Hg) in varying concentrations (Demirel et al., 2013). Digested sewage sludge is

265   an example of feedstock with high heavy metal concentrations; this places a limitation

266   on its land application (Wang et al., 2005). In Guangzhou, China, the concentrations

267   of heavy metals in wet sludge samples were 4567±143, 81.2±2.8, 148±6, 121±4,

268   785±32 and 5.99±0.18 mg·kg^{-1} DM for Cu, Pb, Ni, Cr, Zn and Cd, respectively (Liu

269   & Sun, 2013). Comparing these values with the PAS 110 upper limit standards, which

270   were set at 200, 200, 50, 100, 400 and 1.5 mg·kg^{-1} $_{DM}$, only the concentrations of Pb

271   and Zn were below the standard thresholds. German sewage sludge recorded 202, 5,

272   131, 349, 53 and 1446 mg kg^{-1} DM for Pb, Cd, Cr, Cu, Ni, Zn and only copper and

273   nickel were below the standard thresholds (Benckiser & Simarmata, 1994). Amongst

274   the prevalent heavy metals in sewage sludge, Cr, Ni, Cd and Pb have been considered

275   as the most toxic elements in the environment (Lei et al., 2010). When applied to

276   farmland, high levels of these metals in soil can lead to phytotoxicity, which

277   ultimately ends up in the human diet through crop uptake (Islam et al., 2014). The

278   ingestion of heavy metals is associated with health risks and reports show that

279   countries like Bangladesh have high levels of Pb and As in their cereals and pulses

280   (Islam et al., 2014). However, in developed countries, such as the UK, PAS 110 sets a

281   threshold standard for heavy metal concentration in digestate and for operators who

282   cannot meet this standard the digestate resource cannot be spread on farmland.

283

284   **4. Optimizing the AD process: the use of adsorbent**

285   As mentioned earlier, inhibition in AD has been counteracted with numerous

286   approaches ranging from the acclimation of bacterial cells, adopting thermophilic

287   operating conditions and reducing the concentration of the inhibitors either by dilution

288   or co-digestion with other substrates (Table 1). These approaches do not remove the

289   inhibitor from the process, which can result in accumulation of the inhibitor and the

290   eventual destabilization of the AD system. It is beneficial to look for methods that

291   remove, reduce the mobility or bioavailability the inhibitor within the digestion

292   process (Chen et al., 2008). An example of a technique that can be used to remove

293   potential inhibitors is the steam distillation of citrus peel to remove limonene prior to

294   AD (Martin et al., 2010). Air stripping and chemical precipitation have also been used

295   to remove NH_3 and toxic heavy metals, respectively (Chen et al., 2008). There is the

296   possibility that carbonaceous sorbents could also be used to remove contaminants or

297   toxic compounds. This approach is currently employed by industries involved in food,

beverage and textile production and by water companies (Borja et al., 1996b; Palatsi

et al., 2012). The use of adsorbents such as bentonite, activated carbon and zeolites in

AD has been investigated and the removal of inhibitors has been observed (Angelidaki

& Ahring, 1992; Milan et al., 2003; Bertin et al., 2004; Mumme et al., 2014).

Adsorbents are chemically inert materials with adhesive properties that cause the

accumulation of atoms, ions or molecules on their surface. This is a surface based

interaction between a solid and a fluid; the rate of sorption depends on the adsorbent

(the material used as the adsorbing phase) and the adsorbate (the material being

adsorbed). There are different types of adsorbent with a variety of applications; some

are synthetic whilst others are made from agricultural residues or modified plant and

animal material (Angelidaki & Ahring, 1992; Milan et al., 2003; Bertin et al., 2004;

Mumme et al., 2014). Biochar is an example of adsorbent made from agricultural

residues and because it relatively cheaper to adsorbents like activated carbon, zeolite,

and its application is gradually increasing. The subsequent subheading will be

focusing on different adsorption mechanisms of the biochar material.

4.1.   Mechanisms of biochar adsorption

Adsorption is a dynamic process where the adsorbate associates with the surface of

the adsorbent until an equilibrium state is achieved. The process of adsorption can be

achieved by (i) adsorbate settling on the surface of the adsorbent (physical

adsorption), (ii) adsorbate forming layers on the surface of the adsorbent (surface

precipitation and complexation), (iii) condensation of the adsorbate into the pores of

the adsorbent (pore filling), hydrogen bonding, electrostatic attraction, ion exchange

and hydrophobic effect (Pignatello, 2011). This process occurs in stages: the clean

zone (no adsorption), the mass transfer zone (adsorption in progress) and the

323 exhausted zone (equilibrium), (De Ridder, 2012). Furthermore, the saturated and clean

324 zones will increase and decrease respectively but the mass transfer zone will remain

325 unchanged unless the concentration of the adsorbate is increased. When the material is

326 passed through the adsorbent, it associates with the first section of the adsorbent

327 before moving to another section. This trend continues until the adsorbent is nearly

328 saturated; the near saturation point is called the breakthrough point (Moreno-Castilla,

329 2004).

330 Figure 3 shows the mechanisms of adsorption of organic and metal adsorbates.

331 For metals adsorption largely occurs through electrostatic attraction, ion-exchange and

332 precipitation onto the surface of the adsorbent. For organic molecules, important

333 mechanisms are hydrophobic interactions and hydrogen bonding (Figure 3). Another

334 mode of adsorption that is common for organic compounds is the van de Waals force

335 of attraction. This form of adsorption is induced by the surface chemistry of the

336 biochar. Brennan et al. (2001) showed evidence of different functional groups such as

337 nitro, chloro, hydroxyl, amine, carbonyl, and carboxylic on the surface of biochar.

338 This form of sorption can be described as the electron donor-acceptor mechanism

339 (Mattson et al., 1969). The uneven distribution of electrons between the adsorbent

340 functional group and the organic compound creates an electron donor-acceptor

341 relationship. However, for complex organic compounds with substituent groups

342 (nitro- and chloro-) the electron density of the interaction between the compound and

343 the adsorbent is greatly reduced and this increases the electrostatic interaction between

344 them (Cozzi et al., 1993). This is because the substituent group in the compound is a

345 stronger electron acceptor (Dubinin, 1960; Liu et al., 2010).

346

347 4.2.   Controls on biochar adsorption processes

348   The factors that influence the performance of adsorbent during adsorption have been

349   extensively reported in literature. These parameters include the contact time, operating

350   temperature, adsorbent and adsorbate dosage, particle size and pore distribution,

351   surface chemistry and pH (Li et al., 2014; Hadi et al., 2015; Yargicoglu et al., 2015).

352

353   *4.2.1. Structure and pore size*

354   Adsorbent materials contain pores of various sizes, which have been categorised into

355   micropores mesopores and macropores. Based on the size of the various pores, the

356   sorption rate of the adsorbate is expected to increase in this order: macropores >

357   mesopores > micropores, although this also depends on the size of the adsorbate

358   (Zabaniotou et al., 2008). Biochar material has been reported to have an abundance of

359   micropores, which have a high capacity for adsorbate and water uptake (Zabaniotou et

360   al., 2008). As mentioned earlier, the size of the adsorbate also has some effect on the

361   rate of sorption (Duku et al., 2011). For example, if the size of the adsorbate is

362   relatively large or there are fewer sites for diffusion, this might be affected by steric

363   hinderance (Liu et al., 2010). Further, large adsorbate size can cause exclusion or

364   blockage of smaller sorption sites (Duku et al., 2011). Studies have shown that smaller

365   particle sizes reduce the mass transfer limitation and increase the van der Waal or

366   electrostatic force for penetration of the adsorbate inside the adsorbent (Daifullah &

367   Girgis, 1998).

368

369   *4.2.2. Surface chemistry and pH*

370   The functional groups on the surface of the biochar will influence the adsorption rate.

371   For instance, biochars derived from sewage sludge and poultry manure have higher

372   amounts of nitrogen and sulphur functional groups than woody biomass materials

373 (Koutcheiko et al., 2007). Brennan et al. (2001) reported the presence of different

374 functional groups on the surface and pores of biochar, including hydroxyl, amine and

375 carboxylic groups. The surface chemistry of a carbonaceous sorbent can change,

376 particularly when it is immersed in water; these changes are attributed to the chemical

377 characteristics of the adsorbent (functional groups or ionic compound present in

378 water) and the pH of the solution (Moreno-Castilla, 2004). As illustrated in Figure 4,

379 at higher pHs, phenolic and carboxylic groups release protons and obtain a negative

380 charge, while at low pH basic functional group, such as amine, take up a proton and

381 obtain a positive charge (Schwarzenbach et al., 2005). This implies that the adsorption

382 behaviour of asorbent is a function of the pH of the medium. Changes in the pH can

383 have significant impacts on the ability of a material to adsorb certain compounds. For

384 example, soluble mercury species can be easily adsorbed at higher pHs, whereas

385 lowering the pH increases the solubility of mercuric ions (Eligwe et al., 1999).

386 Changes in pH may also result in reductions in the electrostatic force between the

387 adsorbate ions and the adsorbent (Rao et al., 2009).

388

389

390

391 *4.2.3. Hydrophobicity*

392 The presence and number of O- and N-containing functional groups determine the

393 hydrophobic nature of biochars. Biochars with less O- and N-containing functional

394 groups are typically less hydrophobic (Moreno-Castilla, 2004). Hydrophobic

395 interactions are believed to contribute to the sorption of insoluble adsorbates (Moreno-

396 Castilla, 2004). In aqueous solutions, the adsorbate with the least solubility has the

397 tendency to be adsorbed and retained in the pore of the adsorbent. According to Li et

398 al. (2003), removal of adsorbates, such as 2-propanol, is higher with β-zeolite than

399 dealuminated β-zeolite because the latter is less hydrophobic. Equally, Li et al.

400 (2002) showed that hydrophobic activated carbon is more effective in the removal of

401 relatively polar methyl tertiary-butyl ether (MTBE) and relatively nonpolar

402 trichloroethene (TCE). The hydrophilic adsorbents are less effective because of the

403 sorption of water, which in turn reduces the available sites for the adsorbate-adsorbent

404 interaction (Li et al., 2002).

405

406 4.3.   Mechanisms of desorption or regeneration

407 Adsorbents are useful for separation applications, especially in the purification of

408 wastewater and gaseous compounds. However, the progressive accumulation of

409 adsorbate on the surface of the adsorbent will reduce its sorption capacity until the

410 breakthrough point and finally equilibrium (Salvador et al., 2015). However, the

411 regeneration of the adsorbent gives it an economical advantage over other separation

412 methods and numerous regeneration methods have been developed (Lu et al., 2011;

413 Martin & Ng, 1987; Salvador et al., 2015). Regeneration pathways involve the

414 removal of the adsorbate from the adsorbent. These have been demonstrated using

415 chemical reagents, water, hot gases, ozone, superficial fluid, electric current and

416 microorganisms (Salvador et al., 2015).

417   In AD the application of water in regeneration is not efficient because water is not

418 a good solvent of organic material and in the process of regeneration the water is

419 polluted with the contaminant. Chemical regeneration employs the use of reagents

420 such as NaOH to remove contaminants, or to change the pH of the adsorbent so that

421 non-reactive chemicals like aniline and dye can be desorbed (Leng & Pinto, 1996).

422 However, chemical agents are expensive and the chances of environmental pollution

423   are often high. Supercritical fluid regeneration employs a combination of pressurised

424   CO_2 and water at 125-250 bar to desorb benzene, naphthalene and phenol from

425   activated carbon (Chihara et al., 1997; Tan & Liou, 1989). However, this approach is

426   energy intensive. Another approach called ozone (O_3) regeneration employs the O_3 in

427   direct oxidation of the contaminant. The hydroxyl and oxygen radicals are very

428   reactive and able to oxidize the contaminant. There are indications of moderate

429   efficiency of 80-90% when O_3 is used because some of the oxidative product might

430   block the pore sites (Valdés et al., 2002). Unlike the other regeneration methods

431   mentioned earlier, the biological approach is the most economical and

432   environmentally friendly because it employs the activities of microorganisms in the

433   regeneration of the adsorbent. For instance, the biological activated carbon added to

434   activate sludge in wastewater treatment improves the simultaneous sorption and

435   biological degradation of the contaminant under aerated conditions (Xiaojian et al.,

436   1991). Another approach to the microbial regeneration of an adsorbent is the

437   inoculation of an exhausted adsorbent with microorganisms. This approach has been

438   reported to be less effective because of the eventual blockage of the pore entrance by

439   colonies of microorganisms. (Hutchinson & Robinson, 1990; Toh et al., 2013).

440   Perhaps the application of water solvent as a backwash can be used to supplement the

441   microbial regeneration of exhausted adsorbent. Considering that the level of

442   contamination from SII is relatively lower and less recalcitrant when compared to

443   wastewater industries, biological regeneration could be easily achieved but this needs

444   to be optimized with solvent backwash.

445

446   **5.   The role of biochar in anaerobic digestion**

447   5.1.   Biochar

448   Biochar is a soil additive produced from the thermal degradation of organic material

449   in the presence of little or no amount of oxygen, a process known as pyrolysis

450   (Shafizadeh, 1982). During pyrolysis the volatilization of the organic matter increases,

451   the pore sizes enlarge and the structure of the biomass is rearranged Lua et al. (2004).

452   Factors such as biomass retention time, the properties of the biomass and the

453   operational parameters can influence the final structure of the biochar (Lua & Guo,

454   2000). Novakov (1984) describes biochar (or black carbon) as "combustion produced

455   black particulate carbon having graphitic microstructure". Biochar is a carbonaceous,

456   porous and carbon stable material but it is distinctly different because it is produced at

457   a lower temperature ($< 700\ ^{0}C$) without any form of activation (Schulz & Glaser,

458   2012). This makes the surface area of the biochar less efficient than that of the

459   activated carbon but in terms of production cost, biochar is cheaper (Lehmann &

460   Joseph, 2012). Biochar material is attracting attention as a means of improving plant

461   growth and cleaning contaminated water and land (Tan et al., 2015). Apart from the

462   direct benefits of plant growth and the cleaning-up of polluted ecosystems, biochar

463   can serve as carbon storage, thus contributing to the mitigation of climate change

464   (Montanarella & Lugato, 2013). Biochar material is stable and like other carbon

465   capture technologies it can ensure long-term storage of carbon and reduced CO_2

466   emission (Woolf et al., 2010). The use of biochar as an adsorbent in AD has not been

467   fully investigated as yet, but there is potential for it to have a positive impact both on

468   the operational stability of the AD process and the quality of the digestate produced

469   (Mumme et al., 2014). The continuous addition of biochar during AD can be

470   suggested to reduce SII and increase process stability in three ways: (i) through the

471   sorption of inhibitors, (ii) by increasing the buffering capacity of the system, and (iii)

472   through immobilization of bacterial cells. In addition, the application of biochar can

473   be extended to the improvement of digestate quality. The addition of biochar to

474   digestate can contribute to nutrient retention, increase the carbon to nitrogen ratio and

475   reduce nutrient leaching after land application of the digestate mixture (Figure 6).

476

477   5.2.   Adsorption of inhibitors

478   Inhibitors, such as LCFA, ammonia, limonene, heavy metals and phenols, are either

479   degraded or transformed into other metabolites and these metabolites can be as

480   inhibitory as their precursors (Duetz et al., 2003). There is the opportunity for

481   microbial acclimation to inhibitory compounds, but for most commercial operators

482   there are cost implications of waiting for the whole consortia of cells to acclimate. The

483   application of an adsorbent such as biochar creates an alternative route for removing

484   and reducing the effect of SII during AD. This is because there are indications that

485   biochar can sorb heavy metals and other organic compounds like pesticides, furfural

486   and limonene (Kılıç et al., 2013; Taha et al., 2014; Hale et al., 2015). According to

487   Komnitsas et al. (2015), 10 g l^{-1} biochar produced after pyrolysis at 550 ^{o}C was able to

488   remove 0.015 g l^{-1} of Cu and Pb with almost 100% removal efficiency. Likewise,

489   biochar has been shown to sorb organic compounds. For instance, in the amendment

490   of polycyclic aromatic hydrocarbons in sewage sludge, when compared to the

491   expensive activated carbon material, biochar does not have a greater effect with regard

492   to sorption (Oleszczuk et al., 2012). Taghizadeh-Toosi et al. (2012) showed that

493   biochar can adsorb NH_4^+ and remain stable in ambient air but on exposure to the soil

494   the NH_4^+ is made bioavailable for plant uptake. Lü et al. (2016) equally reported that

495   the application of biochar alleviate NH_4^+ inhibition during anaerobic digestion of 6 g l^{-}

496   ^{1}of glucose solution at an NH_4^+concentration of 7 g l^{-1}. In addition, a recent report by

497   Chen et al. (2015) showed that biochar can also be deployed to contaminated fields

because of its affinity for polycyclic aromatic hydrocarbons. The sorption capacity of

biochar with different organic and inorganic materials has been extensively reported

in the literature but with regard to most inhibitory compounds during AD it has not

been well documented (Mohan et al., 2014). This may be attributed to the uncertainty

surrounding the addition of biochar to AD systems. Adsorbents like biochar are not

selective during sorption; hence, there is the possibility that some of the nutrients or

useful metabolites will be adsorbed during the AD process (Mumme et al., 2014). This

may not pose a major issue as a proportion of the material trapped within the pores of

the adsorbent can be metabolised by the microorganisms attached to the adsorbent

surface. In order to avoid nutrient or metabolite fouling of the biochar pores, the

organic substrate can be pre-treated with the biochar before AD. However, this

approach might limit the benefits of applying biochar with regard to the removal of

only direct forms of SII.

5.3. Increasing buffering capacity

Alkalinity is a measure of the reactor's liquid capacity to neutralise acids, i.e. absorb

hydrogen ions without a significant pH change. Alkalinity is produced in AD through

the degradation of some feedstocks and alkalinity is lost through the production and

accumulation of VFAs. The accumulation of acid is an expected occurrence during

AD, but in the event of high organic overloading and microbial inhibition, the

accumulation of VFA can reduce the buffering capacity of the system (Chen et al.,

2008; Rétfalvi et al., 2011). Nonetheless, the buffering capacity of an AD process can

be increased or maintained by adding some alkali compounds or by controlling the

OLR (Ward et al., 2008). A biochar material can be alkaline depending on the

biomass source (Gul et al., 2015). Yuan et al. (2011) showed that the alkalinity of a

523   biochar increases with an increase in the pyrolysis operating temperature. The

524   application of biochar for the purpose of increasing the buffering capacity is not well

525   known, but this could be recognised as one of the benefits of adding biochar to the AD

526   process. For instance, most operators usually add lime to the AD system to combat

527   acidification. However, the continuous addition of alkaline biochar could increase the

528   buffering capacity of the system (Cao et al., 2012; Zhang et al., 2014). A study by Luo

529   et al. (2015), which compared biochar and non-biochar incubation using glucose as a

530   substrate, showed that the biochar containing incubation increased the methane yield

531   by 86.6% and reduced acidification. Likewise, Sunyoto et al. (2016) reported that the

532   application of biochar not only support microbial metabolism and growth but buffered

533   pH during bio-hydrogen production.

534

535   5.4.   Immobilization of microbial cell

536   Immobilization refers to the colonization of microbial cells on the surface of a solid

537   material. The conventional methods for the immobilization of microbial cells are the

538   use of entrapments such as gels, and physical adsorption to a solid surface, but this

539   approach is limiting because of poor mass transfer (Hori et al., 2015). The discovery

540   of naturally occurring immobilized cells called biofilms has received more attention

541   because it allows the colonization of microbial cells on polymerised surfaces (Cheng

542   et al., 2010). The immobilization of microbial communities in AD is important,

543   particularly for the methanogens because it facilitates electron transfer between

544   interspecies (Lü et al., 2014). One of the benefits of cell immobilization is to reduce

545   biomass washout, an occurrence that is common with wastewater treatment.

546   Anaerobic digesters such as fixed and fluidised beds have been designed with support

547   media to increase and retain the growth of microbial cells (Fernandez et al., 2007).

548 Another advantage of using an immobilized cell is the acclimation rate of the

549 microbial cell during SII (Chen et al., 2008; Montalvo et al., 2012). Sawayama et al.

550 (2004) compared dispersed and immobilised cells, and observed that the biomass and

551 methane production rate of the immobilised cells were higher even at an ammonium

552 concentration of less than 6 gl^{-1}. Furthermore, immobilization of microbial cells has

553 also been reported to reduce the distance between syntrophic bacteria and

554 methanogens (Zhao et al., 2015). It has been reported that a distance of less than 1 μm

555 is essential for the oxidation of volatile fatty acids and hydrogen production (Stams,

556 1994; Schink, 1997). Cell immobilization is often achieved when a bacterial cell is

557 able to attach or grow on a support material. Support materials such as zeolite, clay,

558 activated carbon and other plastic materials have been used to support microbial

559 attachment and growth (Borja et al., 1993; Sawayama et al., 2004; Chauhan & Ogram,

560 2005; Bertin et al., 2010). The macropores aid the attachment of bacterial cells (Laine

561 et al., 1991). Although, the application of biochar for cell immobilization is not as

562 extensive as most other adsorbents, there is an indication that the macropores enhance

563 the attachment of bacterial cells (Watanabe & Tanaka, 1999). Luo et al. (2015)

564 observed the colonization of *Methanosarina* on biochar material during the AD of

565 glucose solution and when compared to the non-biochar study, methane production

566 was higher by 86.6%. There are several reports that shows that the addition of biochar

567 increases microbial metabolism and growth, because the material provides favourable

568 support (Cai et al., 2016; Lü et al., 2016; Sunyoto et al., 2016).

569

570 5.5.   *Nutrient retention*

571 The management of digestate is attracting attention currently because it contains

572 useful amounts of micronutrients, ammonium, phosphate, metal and organic material,

573 hence making it a good soil conditioner (Sapp et al., 2015). Using a circular economic

574 approach where food waste is returned to land as a resource reduces the dependency

575 on inorganic fertilizer, improves the soil ecosystem and provides an alternative source

576 of phosphorous, which is currently limited (Hendrix, 2012; Zeshan & Visvanathan,

577 2014). Depending on the characteristics of the organic substrate and the stability of the

578 AD process, the nutrient content of the digestate will vary. However, as mentioned

579 earlier, a major problem with spreading digestate on land is leaching as this causes

580 diffuse pollution to watercourses or the emission of residual CH_4 and NH_3 gas into the

581 environment (Menardo et al., 2011). In order to reduce diffuse pollution resulting

582 from digestate application to land, the C/N ratio of the digestate must be adjusted and

583 the season of application must be considered (Zeshan & Visvanathan, 2014).

584 However, these approaches are not solely effective because of the slow rate of

585 microbial processes in soil thus extending the chances for nutrient loss from applied

586 digestate via leaching or changes in the soil conditions (Alburquerque et al., 2012).

587 The addition of biochar during or after AD can potentially improve nutrient retention

588 and reduce leaching of digestate nutrient.

589   Studies examining the interactions between biochar and digestate have shown

590 that the addition of biochar to digestate before land application increases the retention

591 period of the nutrients for plant and bacterial uptake (Marchetti & Castelli, 2013;

592 Eykelbosh et al., 2014). Biochar material was found to allow the sorption of organic

593 matter and inorganic nutrients (Lehmann & Joseph, 2012). The surface of biochar is

594 complex with pores containing metallic and organic compounds; this property is

595 essential in the sorption behaviour of biochar. Research has shown that biochar can

596 adsorb organic substrates, phosphate, nitrate, nitrite, ammonium, metals and carbon

597 dioxide (Bagreev et al., 2001). According to Koukouzas et al. (2007) some biochar

material may contain metal oxides (MgO, CrO, CaO and Fe_2O_3) on its surface or

pores and this induces the adsorption of NH_4^+, thus reducing leaching and diffuse

pollution (DeLuca et al., 2006). Le Leuch and Bandosz (2007) showed that the

sorption of ammonium by biochar immobilizes the ammonium concentration in soil

thus reducing the volatilization of ammonium to ammonia under alkaline conditions

and during temperature changes within the soil. DeLuca et al. (2006), observed that

ammonification reduction was higher in soil containing biochar and this would only

have been possible due to the slow release of the ammonium compound. The

advantage of this behaviour to the soil is that it immobilizes organic nitrogen within

the pores and reduces nutrient loss during leaching thus making nutrients readily

available over a longer term. An additional environmental benefit of nutrient sorption

by biochar is the potential to mitigate the microbial production of N_2O following

digestate application. Dicke et al. (2015) studied the effect of biochar material and

digestate on N_2O fluxes under field conditions and showed that the addition of biochar

reduced N_2O emissions, although the emission of N_2O was mostly influenced by

temperature and precipitation. It could be argued that the higher specific surface area

of the activated carbon is better than the biochar material thus making it a more

reliable resource for microbial cell immobilization and the sorption of contaminants

(Wang & Han, 2012). However, because biochar is cheaper to make there is no need

to recover the material after the AD process and this will increase the value of the

digestate.

6. Conclusions.

The application of biochar has the potential to improve AD process by counteracting

SII, improve digestate quality through nutrient retention, contributing to the buffering

623   capacity of the system and create a surface area for the colonization of microbial cell.

624   Comparatively, these functions can be achieved by another adsorbent like activated

625   carbon with higher efficiency. However, the production of biochar is cost effective

626   hence AD operators can afford to use the material without any need for recovery and

627   this will further encourage the spreading of biochar and digestate on land. Biochar was

628   not primarily designed for AD, hence future research in the interaction between

629   biochar and AD microbes, buffering capacity of biochar during AD and sorption

630   effect of biochar material on the AD using a continuous-fed digestion process should

631   be investigated.

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Table

Table 1: Inhibitors, their functions, effects and exiting counteracting methods

Inhibitor	Function	Inhibition	Counteracting methods
Direct inhibitor			
Heavy metals (Cu^{2+}, Zn^{2+}, Cr^{3+}, Cd, Ni, Pb^{4+} & Hg^{2+})	Part of essential enzymes and drives anaerobic enzymatic reactions Formation of complexes to form unspecific complex compounds (Nies, 1999)	The order of inhibition to the acetogens (Cu>Zn>Cr>Cd>Ni>Pb) and methanogens (Cd>Cu>Cr>Zn>Pb>Ni) (Lin, 1993)	Production of hydrogen sulphide to precipitate as metal sulphide (Gadd & Griffiths, 1977) Co-digestion with another substrate (Pahl et al., 2008) Retention of metal on the cell wall (Jankowska et al., 2006) Lowering permeability of the cell membrane (Jankowska et al., 2006)
Light metals (Na^+, K^+, Mg^{2+}, Ca^{2+}, and Al^{3+})	Required for microbial growth Enhances bacterial cell immobilization (Ca) (Thiele et al., 1990; van Langerak et al., 1998)Formation of adenosine phosphate (ADH) (Na^+)(Dimroth & Thomer, 1989)	Restrict production of double cells (Mg^{2+}) Neutralize cell membrane potential (K^+)(Jarrell et al., 1987) Inhibit acetoclastic methanogens (Na^+) Precipitation of carbonates and phosphates thus destabilizing the buffering system (Ca^{2+}) (van Langerak et al., 1998) Competition with adsorption of other metals (Al^{3+}) (Cabirol et al., 2003)	Acclimation of bacterial cell (Chen et al., 2008) Na^+, Mg^{2+} and NH_4^+ mitigate potassium toxicity(Chen et al., 2008)
Chlorophenols and Halogenated aliphatic	Reduction of pathogens	Interference with cellular energy transduction Disruptions of proton gradient through the cell membrane (Chen et al., 2008) Methanogens are greatly inhibited (Chen et al., 2014)	Removal of contaminant using activated carbon (Liu et al., 2010)
Pesticides and antibiotic	-	Inhibition of protein and cell Wall Synthesis Alteration of Cell Membranes Antimetabolite Activity(Neu, 1984)Inhibits methanogens (Alvarez et al., 2010; El-Gohary et al., 1986)	Removal of contaminant using biochar (Yao et al., 2013)
Lignocellulose	-	Inhibition of anaerobic digestion process (Furfural > 5-	Acclimation of the bacterial cell (Palmqvist & Hahn-

hydrolysate		HMF>phenol) Damage of DNA Distortion of the glycolytic pathway (Palmqvist & Hahn-Hagerdal, 2000).	Hagerdal, 2000).
Indirect inhibitor			
Volatile fatty acids (VFAs)	Methane production	Reduces pH at high concentration Acidity of the system	pH adjustment Reduce organic loading rate
Long-chain fatty acids (LCFAs)	-	Distorting the electron transport system in the cell membrane of the bacterial cell(Hanaki et al., 1981) Suspension of bacterial cell Contributes to foaming during interaction with filamentous microorganisms in an anaerobic condition(Ganidi et al., 2009)	Acclimation of bacterial cell(Rinzema et al., 1994) Co-digestion with lipid-free substrate
Limonene	-	Increases permeability of cell membrane and causes leakage of cell content (Burt, 2004)	Acclimation of bacterial cell Removal of essential oil Thermophilic operation Co-digestion with crude glycerol (Mizuki et al., 1990; Martin et al., 2010; Martín et al., 2013)
Sulfide $SO_4^{2-} + 4H_2$ $= H_2S + 4H_2O$ $+ 2OH^-$ $SO_4^{2-} + CH_3COOH$ $= H_2S + 2HCO_3^-$	co-enzyme production, ferredoxin and other compounds(Khan & Trottier, 1978).	Compete with acetate users for acetate utilization Corrosion of pipes and engine Inhibition of methanogens Khan and Trottier (1978)	Acclimation of the bacterial cell Removal of sulphide (Song et al., 2001)
Inorganic nitrogen $NH_4^+ + OH^-$ $\leftrightharpoons HCO_3^- + H_2O$ $CO_2^+ + H_2O + OH^-$ $= HCO_3^- + H_2O$	Availability of nitrogen as nutrient (Liu & Sung, 2002)	Proton imbalance (NH$_3$-N) Inhibit methane producing enzymes (NH$_4$-N) Methane production will be inhibited Accumulation of VFAs	Bacterial cell immobilization (Sasaki et al., 2011) Acclimation of bacterial cell (Chen et al., 2008) pH adjustment (Angelidaki & Ahring, 1993) Addition of trace element (Banks et al., 2012) Dilution of feedstock (Kelleher et al., 2002) Adjustment of the C/N ratio (Resch et al., 2011)

Figure captions

Figure 1 Schematic representation of the anaerobic digestion process (Amaya et al., 2013)

Figure 2 A model of mechanisms of a chemical attack on the bacterial cell (Ibraheem & Ndimba, 2013).

Figure3 Summary of proposed mechanisms for adsorption on biochars (Adapted from; Tan et al., 2015)

Figure 4 Macroscopic representation of the features of carbon surface chemistry (Radovic et al., 2001)

Figure 5 The potential benefits of biochar in enhancing anaerobic digestion and digestate quality
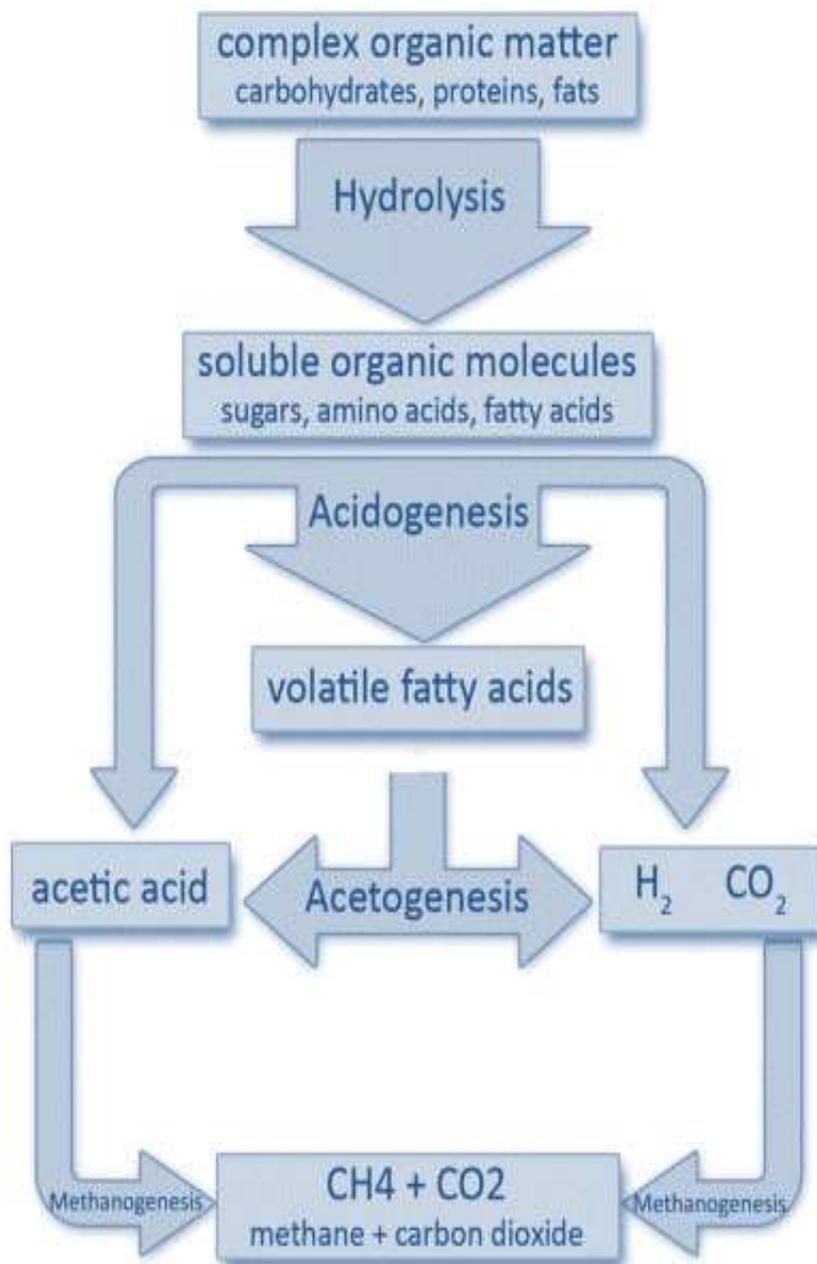
Figure 1
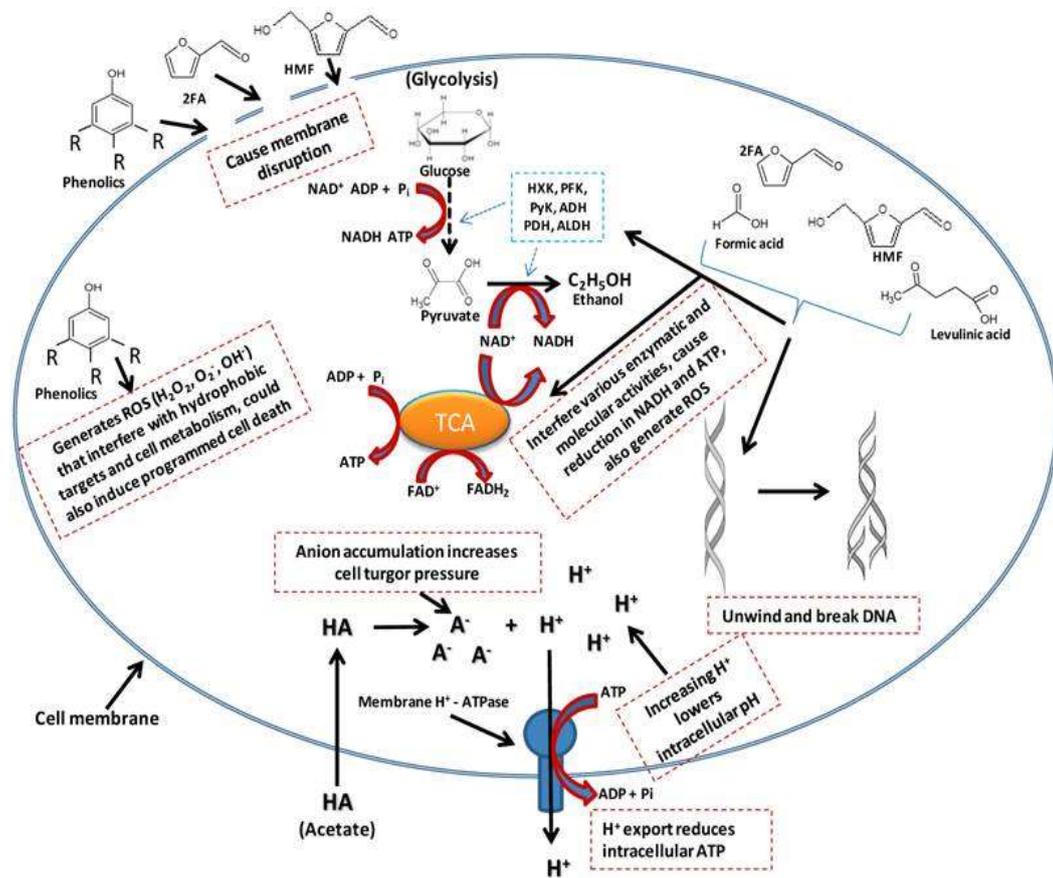
Figure 2
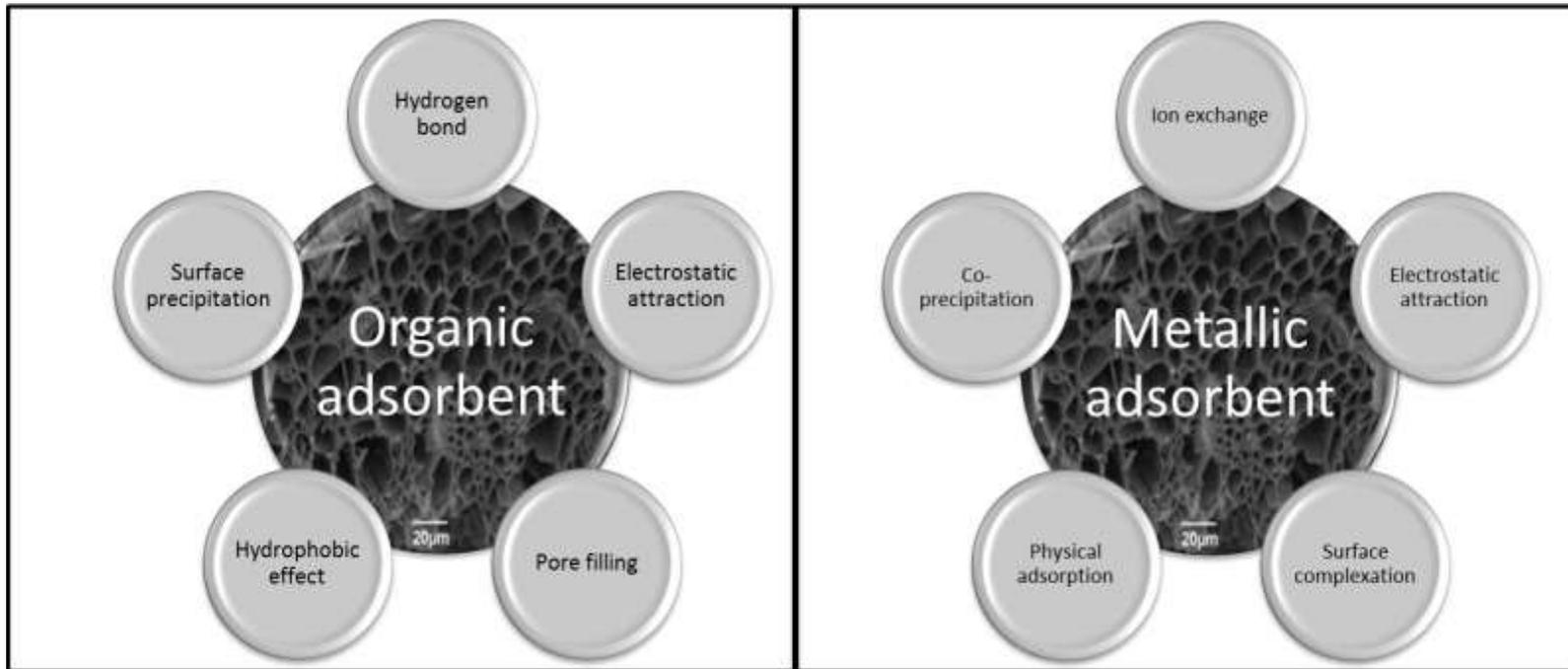
Figure 3

Figure 4

Figure 5