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Enhanced methane production by granular activated carbon: A review

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ABSTRACT

Biomethane production by anaerobic digestion is an efficient technology to treat organic waste and produce clean energy. A growing number of studies has attempted to use carbon-based materials to enhance methane production performance. Granular activated carbon (GAC) is commonly used due to its low price and high efficiency. Moreover, the high conductivity of GAC favors direct interspecies electron transfer (DIET) coupled with CO2 reduction to accelerate electromethanogenesis. GAC has also other properties such as porosity, which may influence microbial methanogenesis. But the comprehensive contributions to microbiome function were hardly summarized. Herein, we review the effects of GAC on anaerobic carbon mineralization, with focus on conductivity, adhesion, adsorption, pH buffering, and redox mediation. The findings are also applicable to natural ecosystems, such as soils and sediments. We also discuss modification of GAC by nanomaterials to enhance anaerobic performance. We suggest practical GAC applications in anaerobic digestion and energy conservation.

1. Introduction

Methane, a greenhouse gas as well as clean energy, is a crucial gas for the global climate. Biomethane production from biomass decomposition through anaerobic digestion (AD) is considered a carbon–neutral process [1-3]. The anaerobic digestion process consists of four steps such as hydrolysis, acidogenesis, acetogenesis, and methanogenesis, which involves microbiome hydrolytic bacteria, acid-producing bacteria, aceticogenic bacteria, and methanogens, respectively [4-6]. With a series of reactions in these microbes, biomass composed of macromolecular organic matter will be degraded into small molecules, such as acetate, hydrogen, carbon dioxide, and most importantly, methane. AD improvement strategies have been developed such as operating conditions tuning, biogas upgrading, and two-stage anaerobic digestion [7-9]. However, these strategies are not widely applied because of their tedious parameter tuning procedures, excess energy, and capital expenditure. The industrial application of biomethane production requires a better understanding of related factors controlling its emissions and feasible AD improvement strategies. (See Table 1.)

Methanogenesis is the last stage of AD to produce biomethane, achieved by methanogens mainly belonging to the archaeal phylum Euryarchaeota [4,10]. Three methanogenesis processes were identified in methanogens: acetate dismutation (acetoclastic methanogenesis), CO2 reduction, and methylotrophic methanogenesis. For natural ecosystems, acetoclastic methanogenesis generally accounts for about two-thirds of global biomethane production [11,12]. Only two archaeal genera, Methanosarcina and Methanothrix (Methanosaeta), are proved with the ability of methane production through direct acetate dismutation [9,13-16]. CO2 reduction requires microbiome syntrophic interactions between methanogens and fermentative bacteria, which provide indispensable electron transfer during this process [17-19]. The interspecies electron transfer (IET) can be achieved through two mechanisms: mediated interspecies electron transfer (MIET) which ferry electrons from bacteria to archaea through small molecules as electron shuttle, represented by hydrogen and formate [9,16,20,21]. Direct interspecies electron transfer (DIET) transfers electrons through direct contact of conductive pili (e-pili) or conductive proteins such as c-type cytochromes [22-26]. DIET showed better electron transfer efficiency than MIET because of the diffusion limitation of electron shuttles [16,27,28].

Conductive materials (CMs) are wildly used to increase methane production in the AD process, mainly focusing on carbon materials and...
magnetite [26,29]. In addition, some Fe-bearing based materials were used such as ferricydrate and Nano-Zero-Valent-Iron (NZVI). For example, Sun et al. improved methane yield in an anaerobic reactor by 10% with NZVI particles [30]. The increase of DIET efficiency is used such as ferrihydrite and Nano-Zero-Valent-Iron (NZVI). For commonly proposed as the potential mechanism [7,31-33]. Promotion of DIET efficiency for CO₂ reduction by forming biofilms or conductive nanowires was proposed [31,34,35]. However, some evidence supporting the above mechanism is indirect proof [36]. Recently, acetoelastic methanogenesis is also proved to be enhanced by conductive materials evidenced by pure culture experiments [37-40] and isotope tracing analysis in anaerobic soils and anaerobic sludges [14,15,41]. These results imply diverse mechanisms of CMs on the AD process and

Table 1

<table>
<thead>
<tr>
<th>Research object</th>
<th>Inoculum/Substrates</th>
<th>Combined treatment</th>
<th>Organic load</th>
<th>Dose</th>
<th>Predominant bacteria</th>
<th>Predominant methanogens</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
<td>Synthetic brewery wastewater</td>
<td>Granular sludge</td>
<td>Direct voltage /NZVI</td>
<td>5.8 g/L</td>
<td>1 g/L</td>
<td>Ignavibacterium</td>
<td>Methanobacterium</td>
<td>[30]</td>
</tr>
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<td>Synthesized Blackwater</td>
<td>Anaerobic digester sludge</td>
<td>Mixing</td>
<td>26.25 g/L</td>
<td>25 g/L</td>
<td>Bacteroidetes</td>
<td>Methanoseta</td>
<td>[66]</td>
</tr>
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<td>Butanol octanol wastewater</td>
<td>Anaerobic sludge</td>
<td>Exogenous hydrogen</td>
<td>11.76 g/L</td>
<td>5 g/L</td>
<td>Geobacter</td>
<td>Methanoseta</td>
<td>[108]</td>
</tr>
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<td>Waste sludge/acetate</td>
<td>No</td>
<td>3 g/L</td>
<td>NA</td>
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<td>Methanocellulosa</td>
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<td>NA</td>
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<td>Treibacter and Terrisporobacter</td>
<td>Methanosaeta and Methanosarchaeota</td>
<td>[109]</td>
</tr>
<tr>
<td>Synthetic brewery wastewater</td>
<td>Granular sludge</td>
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<td>0.5-1.5 g/L</td>
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<td>Fervicutes</td>
<td>Euryarchaeota</td>
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<td>No</td>
<td>15 g/L</td>
<td>1 g/L</td>
<td>Syntrophobactera</td>
<td>Methanoseta</td>
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<td>Phenol-containing wastewater</td>
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<td>2 g/L</td>
<td>1 g/L</td>
<td>Syntrophus and Syntrophobacter</td>
<td>Methanobacterium</td>
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</tr>
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<td>0.3 g/L</td>
<td>280 mg/g MLVSS</td>
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<td>[102]</td>
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<td>0-15 g/L</td>
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<td>[121]</td>
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<tr>
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<td>No</td>
<td>0.2 g/L</td>
<td>25 g/L</td>
<td>Geobacter and Syntrophus</td>
<td>Methanobacterium</td>
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<td>23 g/L</td>
<td>10 g/L</td>
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<td>ABS particles</td>
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<td>Syntrophobacter</td>
<td>Methanobacterium</td>
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<td>1.1 g/L</td>
<td>1-5 g/L</td>
<td>Thermotogae and Firmicutes</td>
<td>Methanobacterium and Methanolinea</td>
<td>[59]</td>
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<td>NA</td>
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<td>NA</td>
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<td>15 g/L</td>
<td>Pseudomonas</td>
<td>Methanoseta</td>
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<td>No</td>
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<td>25 g/L</td>
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<td>[62]</td>
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<td>Shewanella oneidensis MR-1</td>
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<td>Methanobacterium</td>
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<td>5-15 g/L</td>
<td>NA</td>
<td>NA</td>
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<td>MnO₂</td>
<td>1 g/L</td>
<td>1.5 g/g MLVSS</td>
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<td>Methanoseta</td>
<td>[47]</td>
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<td>Granular sludge/glucose</td>
<td>Clostridium pasteurianum</td>
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<td>10 g/L</td>
<td>NA</td>
<td>NA</td>
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<td>Digester sludge</td>
<td>No</td>
<td>4.4 g/L</td>
<td>25 g/L</td>
<td>Sympothomonas</td>
<td>Methanosarina and Methanocalculus</td>
<td>[65]</td>
</tr>
<tr>
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<td>Digester sludge</td>
<td>No</td>
<td>NA</td>
<td>1 g/L</td>
<td>Geobacter</td>
<td>Methanobacterium</td>
<td>[57]</td>
</tr>
<tr>
<td>Synthetic wastewater</td>
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<td>nano-Fe₃O₄</td>
<td>0.4 g/L</td>
<td>15 g/L</td>
<td>Thermoddota</td>
<td>Methanobacterium</td>
<td>[104]</td>
</tr>
<tr>
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<td>Anaerobic sludge</td>
<td>No</td>
<td>40 g/L</td>
<td>75 g/L</td>
<td>Geobacter</td>
<td>Methanosarina</td>
<td>[45]</td>
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</tr>
<tr>
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<td>5 g/L</td>
<td>Proteiniphilum</td>
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<td>[116]</td>
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<tr>
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<td>25 g/L</td>
<td>Firmicutes</td>
<td>Methanosarina</td>
<td>[87]</td>
</tr>
<tr>
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<td>Seed sludge</td>
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<td>26 g/L</td>
<td>Acinetobacter</td>
<td>Methanosarina</td>
<td>[117]</td>
</tr>
<tr>
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<td>NA</td>
<td>40 g/L</td>
<td>Geobacter</td>
<td>Methanosarina</td>
<td>[118]</td>
</tr>
<tr>
<td>Organic wastewater</td>
<td>Anaerobic sludge/acetate</td>
<td>Sludge/fructose and polyethylene glycol</td>
<td>No</td>
<td>10 g/L</td>
<td>Graeciliseta</td>
<td>Methanobacterium</td>
<td>[84]</td>
</tr>
<tr>
<td>Packing media</td>
<td>Sludge/glucose</td>
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<td>NA</td>
<td>Geobacter</td>
<td>Methanobacterium</td>
<td>[119]</td>
</tr>
<tr>
<td>Synthetic wastewater</td>
<td>Anaerobic digester sludge</td>
<td>No</td>
<td>0.25 g/L</td>
<td>10 g/L</td>
<td>Geobacter</td>
<td>Methanospirillum</td>
<td>[44]</td>
</tr>
<tr>
<td>Co-culture</td>
<td>Ethanol</td>
<td>No</td>
<td>25 g/L</td>
<td>Geobacter metallireduccens</td>
<td>M. barkeri</td>
<td>[46]</td>
<td></td>
</tr>
<tr>
<td>Co-culture</td>
<td>Ethanol</td>
<td>No</td>
<td>25 g/L</td>
<td>Geobacter metallireduccens</td>
<td>M. barkeri</td>
<td>[53]</td>
<td></td>
</tr>
</tbody>
</table>

Note: NA, not available. MLVSS: mixed liquid volatile suspended solids.
biomethane production. GAC, a typical conductive material, faultlessly shows these complex effects (Fig. 1).

Activated carbon is normally from raw material, such as coal, wood, and coconut shell [42]. According to the particle size, activated carbon is generally classified as granular activated carbon (GAC) and powdered activated carbon. GAC has a relatively larger particle size and a smaller external surface compared to activated carbon powdery. It is widely used in industrial field because of its outstanding adsorbing capacity, high mechanical strength, and excellent chemical stability. Most of the GACs used in the AD process are bio-carbon original, such as coconut shells. Thus, the industrial-scale application of GAC is economically feasible and environmentally friendly. It was concluded that GAC enhanced biomethane production through DIET coupled CO₂ reduction because of the high conductivity (Fig. 1) [43-47]. However, the diverse effects of GAC, such as adsorption and adhesion, may concurrently play an important role (Fig. 2). At present, the use of CMs in the AD process is reviewed through different perspectives. Yet, given the lack of study on advances towards methanogenesis affected by GAC in anaerobic digestion, this review focuses on the potential functions of GAC on AD enhancement. Diverse mechanisms were proposed, and a combined effect expect DIET was summarized and discussed.

2. Advantages of granular activated carbon on methanogenesis

Most studies observed promising improvements concerning substrate degradation and biomethane production. This prosperity was frequently attributed to the increased DIET based on the high conductivity of GAC and evidenced by microbial abundance analysis. Apart from conductive effects, the porous structure creates an excellent adsorbent to enrich substrates and potentially remove toxic compounds, and to facilitate biofilm-forming. GAC is suitable for electron storage thus serves as a capacitor to accept or release electrons. Other properties such as pH buffering, and redox mediator cannot be ignored in play a role in the AD improvement (Fig. 2).

2.1. Conductive effects

GAC conductivity is normally larger than iron oxides but lower than nano-scale carbon materials [5,48]. It, however, possesses various advantages compared to nano-scale carbon materials, such as being low-price and pollution-free. The relatively high electron transfer capacity of GAC currently meets the demand for electrical conductivity in the anaerobic digestion process. As an example, GAC replaces the function of e-pili and cytochromes to promote electron transfer efficiency and result in high biomethane production by 145% and short lag phase by 2 days [49,50]. The enhancement effect, however, is not invariably proportional to conductivity. In pure co-cultures, carbon cloth showed a similar promoting effect even with a 10-fold higher conductivity [51-53]. Biochar materials with 3 orders of magnitude less conductive than GAC manifested almost the same enhancements on anaerobic digestion [54]. Consequently, conductivity promoting the AD process may have an upper threshold [20].

![Fig. 1.](image1.png) **Fig. 1.** Effects of granular activated carbon (GAC) on methanogenesis. GAC promotes DIET coupled CO₂ reduction to perform methanogenesis (upper); and acetoclastic methanogenesis is also stimulated through diverse strategies (lower). DIET: Direct interspecies electron transfer, VFAs: volatile fatty acids.

![Fig. 2.](image2.png) **Fig. 2.** Other positive effects of granular activated carbon (GAC) on methanogenic progress. GAC fixes microbes to form biofilms, enrich substrate, adsorb toxic materials, act as electrode, buffer pH variation and mediate redox power, which contributes to the enhancement of methanogenesis.
2.1.1. Promoting interspecies electron transfer efficiency

It is widely shared that conductive materials improved AD performance through enhanced DIET efficiency [7,55]. DIET was observed in co-culture with Geobacter species and methanogenic Methanosarcina barkeri via conductive pili or cytochromes [46,53]. However, the detailed mechanism of DIET is still ambiguous [20,22]. Kang et al. showed that the effect of GAC on AD performance is independent of the inocula composition, and GAC promoted biomethane production through enrichment of DIET-related bacteria and methanogens on its surface [56,57]. Zhang et al. observed a 20% increase in methane production by GAC addition in up-flow anaerobic sludge blankets [58]. The increase was attributed to enhanced DIET because of the enrichment of Geobacter and Methanobacterium on the surface of GAC. A 12.14% increase in biomethane production by GAC on food waste treatment was reported [59], where DIET participant Geobacter increased close to an order of magnitude. Enhancement of biomethane performance by GAC with Geobacter was found somewhere else, where 49.8% of the organisms on the surface of GAC were Geobacter species [60]. Romero et al. linked the biomethane increase to the abundant archaeal Methanosaeta which was increased by 13.2% with GAC addition [61]. Zhang et al. demonstrated increased sludge conductivity from a high proportion of Geobacter, with an increased expression of pilA in response to GAC addition [62]. Lei et al. observed that GAC addition led to an outstanding AD performance with four times higher methane production and two times reduced start-up time [45]. Metagenomic analysis showed an enrichment of DIET-related species such as Geobacter and Methanosarcina, and genes such as e-pili components and c-type cytochrome, OMCs, implying an enhancement of DIET. Similarly, a methane production increase of 72% by GAC was attributed to increased genes of pilA and OMCs with metagenomic analysis [63]. Some weaker promotion, 17.4% higher, on biomethane production, was evidenced by the enrichment of hydrogen-utilizing methanogens and Geobacter [64]. Lee et al. showed a higher efficiency, 80% increase, with the presence of GAC based on the enrichment of Geobacter, Methanospirillum, and Methanolinea [44].

Obviously, GAC favors microbiome activities and electron transfer among electro-active bacteria and methanogens (Fig. 1), thus promoting biogas production through enhanced DIET or the enrichment of DIET-related microbes. However, a pile of studies did not observe an increase of DIET and/or electriciens [64-67], implying diverse effects of GAC on AD performance.

2.1.2. Promoting acetoclastic methanogenesis

A pure culture study proved that conductive materials accelerated acetoclastic methanogenesis through the enhancement of electron transfer within cells [39]. Moreover, considering the first step of acetate dismutation, which requires adenosine triphosphate (ATP) to activate acetate, the transfer of extracellular electrons is particularly beneficial for acetoclastic methanogenesis [68].

Isotope tracing experiments showed that over 90% of the methane was produced from acetoclastic methanogenesis [15,41]. Moreover, CMs may simultaneously accelerate DIET coupled CO₂ reduction and acetate dismutation in complex microbial communities [41]. Yang et al. demonstrated an increase of acetoclastic methanogenesis by GAC, evidenced by metatranscriptomic analysis that acetate dismutation genes were highly induced by GAC [69]. In anyway, the enhancement of the acetate pathway is a recent finding. More research is needed to confirm its reliability and dig underlying mechanisms.

2.2. Adsorption and adhesion effects

2.2.1. Adsorption of organic substrates

GAC is a porous material with large surface area, strong adsorption and adhesion ability [70,71]. The absorbed substrates such as acetate and/or hydrogen are easily accessible by methanogens attached to GAC, thus reducing the lag phase of AD treatment [20]. Sun et al. proposed that the enhancement of the GAC reactor by a 10% increase of methane production was mainly due to the adsorption of extracellular polymeric substances by activated carbon within the first 6 h of reaction [30]. Jiang et al. noted that GAC preferred absorbing large molecular weight substances (e.g., proteins, polysaccharides) rather than small molecules (e.g., glucose, volatile fatty acids (VFAs)), resulting in up to 30% shorter lag phase [72]. Collectively, GAC promoted AD performance through adsorption of organic substrates to accelerate hydrolysis and acidogenesis processes.

2.2.2. Adsorption of toxic compounds

The microbial community, microbiome, encounters a multitude of inhibitors during the AD process, such as heavy metals, ammonia, sulfate, organic solvents, and the high pressure of hydrogen, which can be removed by absorbents [73-75]. The large surface area of GAC provides a powerful absorbent to break the inhibition (Fig. 3). Heavy metals are often over-presented in waste sludge, which strongly inhibited the activity of the microbes [76]. The removal of heavy metals by GAC in anaerobic digestion has been well constructed. For example, the Pb²⁺ and Ni²⁺ adsorption capacities of GAC in bio-sludge were at 840 ± 20 and 720 ± 10 mg/g [77,78]. GAC adsorbed phenolic inhibitors to promote methane production [79]. Detoxification of phenols by GAC was also observed recently, which was proposed as the reason for the methanogenic acceleration [72]. The removal efficiency of phenol-like toxic compounds by GAC through adsorption was up to 100% [72]. H₂S produced during fermentation is harmful to the methanogenesis process. Reassuringly, it can be removed by adsorption of GAC [80] or by sulfide oxidizing bacteria attached on the GAC surface [81].

Food waste (FW) contains high concentration of nitrogen which is converted to ammonia by bacteria [82]. GAC reduced the ammonia concentration during FW digestion and increased methane production [65]. Furthermore, Zhang et al. demonstrated that GAC protected the microbial system from sulfate inhibition [58], which is also true for ammonia inhibition removed by adsorption [83]. Except for soluble substances, the disinhibition effect of GAC towards high H₂ pressure during the AD process also benefited biomethane production [62]. Accumulation of VFAs produced during the hydrolysis step decreased the pH of the system and inhibit methane production. Recent studies proved that GAC accelerated the degradation of VFAs, thus reduced the inhibition effect [45,49].

GAC showed promising effects during the treatment of wastewater with toxic organics like aromatic and nitrogen organics. GAC adsorbed the highly toxic compounds in the system to release the inhibition and enrich syntrophic bacteria to accelerate the degradation of the toxic compounds [26]. For example, the use of GAC in the treatment of high-strength organic wastewater increased the removal efficiency of N-heterocyclic compounds, acids and aromatic compounds to more than 95% [84]. Dai et al. showed that GAC composite increased 11% methane production during pharmaceutical wastewater treatment and enhanced the pharmaceutical intermediates degradation [85]. At present, it is not clear which role is the more important, adsorption or DIET. According to published studies, most focused on DIET rather than adsorption. However, a recent study proposed that the adsorption capacity of GAC played a more key role than DIET based on Random Forest modeling [86].

2.2.3. Adhesion effect

The porous structure of GAC attaches and immobilizes microbes on its surface to form biofilms [49]. Biofilm on the surface shortens the physical distance among microbes, thus facilitating substance exchange and favoring syntrophic interactions. Moreover, the attachment of microbes on GAC also substantially altered the structure of the microbial community, which has a crucial impact on methane production [87,88].

Recent achievements in enhancing anaerobic digestion with carbon-based materials noted that the biofilm formed on GAC promoted the VFAs degradation by 5–10 days and supplied ample substrates to the methanogens, which favored archaeal survival [89]. Chowdhury et al.
demonstrated that GAC promoted methane production by serving as microbial aggregated supports instead of promoting DIET [65]. Other examples showed that GAC improved AD performance by enriching syntrophic bacteria on its surface to accelerate acetogenesis process [67].

2.3. Capacitor analogue

The conductive effect of GAC refers to its activity to transfer electrons through one partner to another. In addition to serving as a conductive substance, GAC serves as a capacitor analogue, which refers to its electron storage capacity to provide or accept electrons [90]. GAC also acted as excellent electrode component concerning its high surface area and electrical conductivity to construct microbial fuel cells [91]. The possibility of a wide variety of microbes accepting electrons directly from GAC was proved in different electrochemical systems [92,93]. As an example, use of GAC-biocathode in Microbial Fuel Cells (MFC) achieved a high power density of 55.05 mW⋅m⁻² [93]. Recently, Sun et al. demonstrated a more 10% methane yield through a strategy combined with direct voltage and GAC/Nanoscale Zero Valent Iron (NZVI) composites, implying the potential use of GAC as an electrode component or capacitor analogue in AD systems [30].

2.4. Redox mediation

GAC is used as an efficient redox mediator for syntrophic interaction in various environments. For instance, GAC mediated the reduction of recalcitrantazo dyes from electrons released by the oxidation of organic acids [94]. Lee et al. demonstrated that GAC addition improved the microbial oxidizing ability with a higher peak on the cyclic voltamogram measurement, resulting 1.8-fold higher methane production rate [44]. The height of the peak indicated the accumulation of redox-active components, which were observed in different systems [95,96]. Similar results were observed with GAC/NZVI composites increasing 10% methane production, which did not affect the type of redox reaction but enriched oxidation and reduction substances in the system [88].

2.5. pH regulation

AD process requires a stable and neutral pH environment where the substrates are soluble and stably accessible to keep high activities and growth of microbiome [49]. The acidogenesis step produces a large amount of VFAs, which sharply decreases pH value. GAC can serve as a pH buffer because of its high adsorption capacity of VFAs and simultaneously promote the degradation of VFAs, thus stabilizing the pH variations and enhancing substrate production for methanogens. Wang et al. demonstrated that 1 g⋅L⁻¹ GAC in the AD system effectively stabilized the pH value, resulting in a 12% increase of methane production and reduced AD start-up time by about 5 days [59]. The pH buffering capacity of GAC was also observed at a concentration up to 20 g⋅L⁻¹, which showed the best performance that enhanced the methane production by 27% [97]. During a two-stage digestion process, GAC addition maintained the pH of the reactor at 8.0, which reduced the hydraulic retention time from 84 to 56 h [98].

3. Disadvantages of GAC on methanogenesis

The studies about the effect of GAC on methanogenesis are not exactly the same, and the optimal dose of GAC is still unclear. Kang et al. showed the cumulative methane production between the GAC and control reactors with no difference [57]. Some studies reversely showed inhibition effects of GAC on AD performance with up to 30% decrease of methane production [72,99,100]. While the GAC concentration exceeded 8.0 g/L, maximum methane production decreased 20–50% compared to the control [55]. It was speculated that a large amount of GAC adsorbed COD substances and reduced available substrates for methane conversion. Similarly, Chowdhury et al. proposed a reducing effect of GAC due to the adsorption of undesired substances such as lipid, which blocked the contact of microbes with GAC [65]. However, the inhibitory effect of GAC can be mitigated by pre-treatment of the sludge and elevated temperature or combined with other treatments [72]. Although the advantage of GAC is generally acknowledged, negative factors and the corresponding conditions in AD should get more attention.

4. Treatment of GAC for considerable performance

To further improve the performance of the GAC, modification is considered a viable strategy (Fig. 4). At present, iron-based materials are widely used, such as magnetite and NZVI. Sun et al. constructed GAC/
NZVI composite and applied it in anaerobic reactors [30,101], GAC/NZVI showed better performance than GAC or NZVI. Iron and carbon on the surface of the composite with the attached microbes formed galvanic cells, which enhanced the electrochemical reaction and promoted methanogenesis. GAC/NZVI was also suggested to enhance the redox activity of the sludge by inducing more oxidation and reduction substances to accelerate electron transfer. Some other studies noted that GAC/NZVI reduced the phosphate precipitates by absorbing Fe\(^{2+}\), which relieved the inhibition of methanogenesis [102].

Peng et al. demonstrated that the mixture of magnetite and GAC achieved a 20% increase in methane production [103]. Magnetite enhanced hydroslysis by enriching iron-reducing bacteria, while GAC enhanced DIET between iron-reducing bacteria and methanogens. Nano-Fe\(_3\)O\(_4\)/GAC composites possessed outstanding conductivity and electron transfer efficiency, which led to 3.6 times more methane production than the control group [104]. Yang et al. demonstrated that the GAC-Mn\(_2\)O\(_3\) composite increased 36% of methane production [47]. GAC-Mn\(_2\)O\(_3\) composite enhanced extracellular polymeric substance secretion but inhibited humic substances. The methanogenesis was enhanced through the redox cycle of Mn\(^{3+}\)/Mn\(^{2+}\). Collectively, the combination of different treatments with conductive materials strongly accelerates the performance of methanogenesis. Transition metal nanoparticles such as nickel served as a catalyst to further improve the performance of GAC on methane production [105].

The modification of GAC with other materials also promoted the degradation of toxic compounds. Dai et al. demonstrated that GAC/Zero-Valent-Iron composites increased the degradation of complex pharmaceutical wastes [85]. Cheng et al. showed that adding GAC and ZVI together increased the pentachlorophenol removal efficiency by 50% and methane production by 15% [106]. Anaerobic digestion of azo dye Reactive Red 2 wastewater was enhanced by 117.9% removal efficiency and 167.2% methane production with nano-Fe\(_3\)O\(_4\) modified GAC [107]. However, it is worthy to note that GAC modification also showed negative effects. A recent study showed that GAC@Fe\(_3\)O\(_4\) and GAC@-\(\text{V}_4\text{O}_7\cdot\text{H}_2\text{O}\) did not improve anaerobic digestion performance [40].

5. Perspectives

The effects of conductive materials on the performance of AD system were frequently reviewed. To date, massive attention focuses on the DIET coupled methanogenesis, and a host of conclusions are drawn through indirect evidence. Here we focused on one of the widely used conductive material, GAC, and discussed its potential impacts on methane production. Based on the current research progress, the following aspects still do not attract enough attention and may result in biased conclusions.

- Conductivity acts on extracellular electron flux and affects electron transfer chain within cells, thus possibly accelerating acetoclastic methanogenesis, not only DIET coupled CO\(_2\) reduction.
- The hydrolysis, acidogenic, and acetogenic process provide indispensable substrates to methanogens. Thus, the effects of GAC on these processes, such as biofilm formation, toxin removal, and pH buffering are worth more attention.
- The dosage and the environmental parameters substantially affect the performance of GAC in methane production. Different dosages or external conditions may lead to discrete results.

Though GAC is extensively studied to promote AD performance, the detailed mechanism is still unclear. Compressively studies concerning the crucial aspects, not only DIET, with direct experimental strategies, should be performed. For example, the \(^{13}\)C isotope tracing experiment is useful to classify the actual methanogenesis pathway and substrate utilization [15,33,41]. Advanced omics tools, such as metagenome and metabolomics, provide an avenue to identify the active members and key metabolites contributing to the methanogenesis [40]. Moreover, combining of GAC with other materials, but not limited to nanomaterials, is a promising solution to enhance AD efficiency. Even the use of GAC to promote methane production got promising results. Proper separation methods of GAC from the AD system and safety disposal strategy after AD should be developed before the industrial application.

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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