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► **To cite this version:**

Leilei Xiao, Jian Liu, P Senthil Kumar, Meng Zhou, Jiafeng Yu, et al.. Enhanced methane production by granular activated carbon: A review. *Fuel*, 2022, 320, pp.123903. 10.1016/j.fuel.2022.123903 . hal-03614098

**HAL Id: hal-03614098**

**<https://hal.science/hal-03614098>**

Submitted on 19 Mar 2022

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# Enhanced methane production by granular activated carbon: A review

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## ARTICLE INFO

### Keywords:

Anaerobic digestion  
Microbiome  
Methane production  
Granular activated carbon  
Conductive material  
Direct interspecies electron transfer  
Wastewater

## 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 CO<sub>2</sub> 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, acetogenic 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), CO<sub>2</sub> 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 *Methanotheroxiphila* (*Methanosaeta*), are proved with the ability of methane production through direct acetate dismutation [9,13-16]. CO<sub>2</sub> 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 widely used to increase methane production in the AD process, mainly focusing on carbon materials and

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magnetite [26,29]. In addition, some Fe-bearing based materials were used such as ferrihydrite 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 commonly proposed as the potential mechanism [7,31-33]. Promotion of DIET efficiency for CO<sub>2</sub> reduction by forming biofilms or conductive

nanowires was proposed [31,34,35]. However, some evidence supporting the above mechanism is indirect proof [36]. Recently, acetoclastic 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**  
Studies of granular activated carbon (GAC) effect on microbial methanogenesis.

Research object	Inoculum/Substrates	Combined treatment	Organic load	Dose	Predominant bacteria	Predominant methanogens	Ref.
Synthetic brewery wastewater	Granular sludge	Direct voltage /NZVI	5.8 g/L	1 g/L	<i>Ignavibacterium</i>	<i>Methanothrix</i>	[30]
Synthesized Blackwater	Anaerobic digester sludge	Mixing	26.25 g/L	25 g/L	<i>Bacteroidetes</i>	<i>Methanosaeta</i>	[66]
Butanol octanol wastewater	Anaerobic sludge	Exogenous hydrogen	11.76 g/L	5 g/L	<i>Geobacter</i>	<i>Methanosaeta</i>	[108]
Domestic wastewater	Waste sludge/acetate	No	3 g/L	NA	<i>Geobacter</i>	<i>Methanomicrobia</i>	[56]
Swine manure	Anaerobic sludge	No	NA	25 g /L	<i>Tricibacter</i> and <i>Terrisporobacter</i>	<i>Methanosaeta</i> and <i>Methanosarcina</i>	[109]
Synthetic brewery water	Granular sludge	NZVI	7 g/L	0.5–1.5 g/L	<i>Longilinea</i> and <i>Geobacter</i>	<i>Methanosaeta</i> and <i>Methanothrix</i>	[102]
Corn straw	Anaerobic sludge	No	NA	5 g/L	<i>Firmicutes</i>	<i>Euryarchaeota</i>	[110]
Brewery wastewater	Waste sludge/phenol	No	NA	15 g/L	<i>Syntrophorhabdus</i>	<i>Methanosaeta</i>	[50]
Phenol-containing wastewater	Anaerobic sludge/phenol	Exogenous hydrogen	2 g/L	1 g/L	<i>Syntrophus</i> and <i>Syntrophorhabdus</i> ,	<i>Methanobacterium</i>	[43]
Domestic sewage	Waste sludge	NZVI	0.3 g/L	280 mg/g MLVSS	<i>Syntrophobacter</i>	<i>Methanosaeta</i> and <i>Methanobacterium</i>	[102]
Fat, oil and grease lipid-rich wastewater	Anaerobic sludge	No	0.8 g/L	0–15 g/L	<i>Geobacter</i>	<i>Methanosaeta</i>	[111]
	Granular sludge	No	3.3 g/L	0–33 g/L	NA	NA	[112]
Municipal sewage	Waste sludge/glucose	No	0.2 g/L	25 g /L	<i>Geobacter</i> and <i>Syntrophus</i>	<i>Methanobacterium</i>	[58]
Municipal sewage	Waste sludge	No	23 g/L	10 g/L	NA	NA	[72]
Synthetic feed wastewater	Digester sludge/acetate and propionate	ABS particles	0.3 g/L	25%	<i>Syntrophobacter</i>	<i>Methanothrix</i>	[113]
Food waste	Municipal sludge	No	1.1 g/L	1–5 g/L	<i>Thermotogae</i> and <i>Firmicutes</i>	<i>Methanobacterium</i> and <i>Methanolinea</i>	[59]
Synthetic wastewater	Waste sludge/acetate	No	NA	2 g/L	<i>Geobacter</i>	NA	[60]
Swine wastewater	Waste sludge	No	9.2 g/L	15 g/L	<i>Pseudomonas</i>	<i>Methanosaeta</i>	[61]
Municipal sewage	Waste sludge	No	0.5 g/L	25 g/L	<i>Geobacter</i>	<i>Methanosaeta</i>	[62]
Anaerobic soil	Straw	<i>Shewanella. oneidensis</i> MR-1	NA	1 g/L	NA	<i>Methanosarcinaceae</i>	[15]
Food waste	Waste sludge	No	NA	5–15 g/L	NA	NA	[49]
Starch wastewater	Granular sludge	MnO <sub>2</sub>	1 g/L	1.5 g/g MLVSS	<i>Spirochaetaceae</i> , <i>Cloacibacterium</i> , and <i>Treponema</i>	<i>Methanobacterium</i> and <i>Methanosaeta</i>	[47]
Synthetic wastewater	Granular sludge/glucose	<i>Clostridium pasteurianum</i>	NA	10 g/L	NA	NA	[41]
Food waste	Digester sludge	No	4.4 g/L	25 g/L	<i>Syntrophomonas</i>	<i>Methanosarcina</i> and <i>Methanoculleus</i>	[65]
Synthetic wastewater	Digester sludge	No	NA	1 g/L	<i>Geobacter</i>	<i>Methanosarcinales</i>	[57]
Synthetic wastewater	Anaerobic sludge/acetate	nano-Fe <sub>3</sub> O <sub>4</sub>	0.4 g/L	15 g/L	<i>Thermogutta</i>	<i>Methanothrix</i>	[104]
Incineration leachate	Anaerobic sludge	No	40 g/L	75 g/L	<i>Geobacter</i>	<i>Methanosarcina</i>	[45]
Bagasse waste	Digester sludge	No	NA	10–100 g/L	<i>Petrimonas</i>	<i>Methanothrix</i>	[114]
Blackwater	Anaerobic sludge	No	20 g/L	0.5–4 g/L	<i>Clostridiales</i>	<i>Methanosarcina</i>	[83]
Swine manure	Acclimated sludge	No	NA	42.7 g/kg	<i>Clostridium</i>	<i>Methanosarcina</i>	[115]
Synthetic brewery wastewater	Seed sludge/glucose	No	65.3 g/L	5 g/L	<i>Proteiniphilum</i>	<i>Methanosarcina</i>	[116]
Food waste	Anaerobic digester sludge	No	355 g/L	25 g /L	<i>Firmicutes</i>	<i>Methanosarcina</i>	[87]
Feeding medium	Seed sludge/glucose	No	NA	10 g/L	<i>Actinobacteria</i>	<i>Methanosaeta</i>	[117]
Waste activated sludge	Seed sludge	Magnetite	35 g/L	27 g/L	<i>Anaerolineaceae</i>	<i>Methanosaeta</i>	[103]
Artificial wastewater	Digester sludge	No	NA	40 g/L	<i>Geobacter</i>	<i>Methanosaeta</i>	[118]
Organic wastewater	Anaerobic sludge/acetate	No	NA	10 g/L	<i>Gracilibacter</i>	<i>Methanosaeta</i>	[84]
Packing media	Sludge/fructose and polyethylene glycol anaerobic digester	No	3 g/L	NA	<i>Geobacter</i>	<i>Methanosaeta</i>	[119]
Synthetic wastewater		No	0.25 g/L	10 g/L	<i>Geobacter</i>	<i>Methanospirillum</i>	[44]
Co-culture	Ethanol	No	NA	25 g/L	<i>Geobacter metallireducens</i>	<i>M. barkeri</i>	[46]
Co-culture	Ethanol	No	NA	25 g/L	<i>Geobacter metallireducens</i>	<i>M. barkeri</i>	[53]

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 CO<sub>2</sub> 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 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

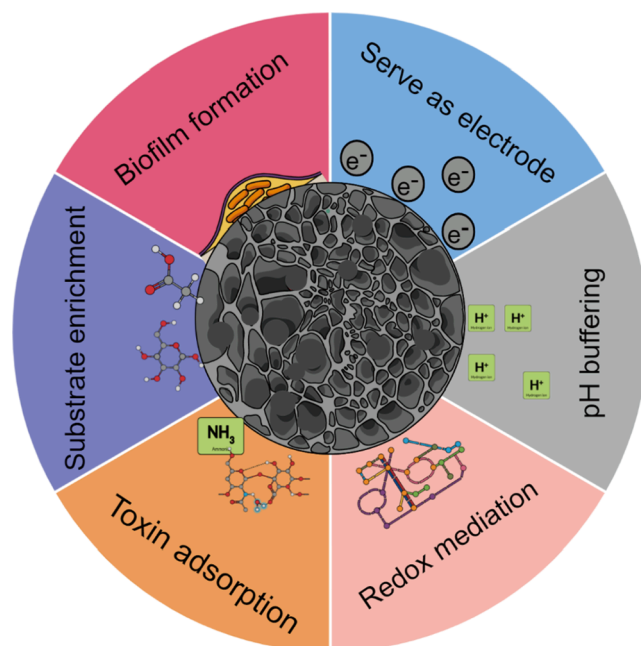


Fig. 2. Other positive effects of granular activated carbon (GAC) on methanogenic progress. GAC fixes microbes to form biofilms, enrich substrate, adsorb toxic materials, act as electrode, buffer pH variation and mediate redox power, which contributes to the enhancement of methanogenesis.

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].

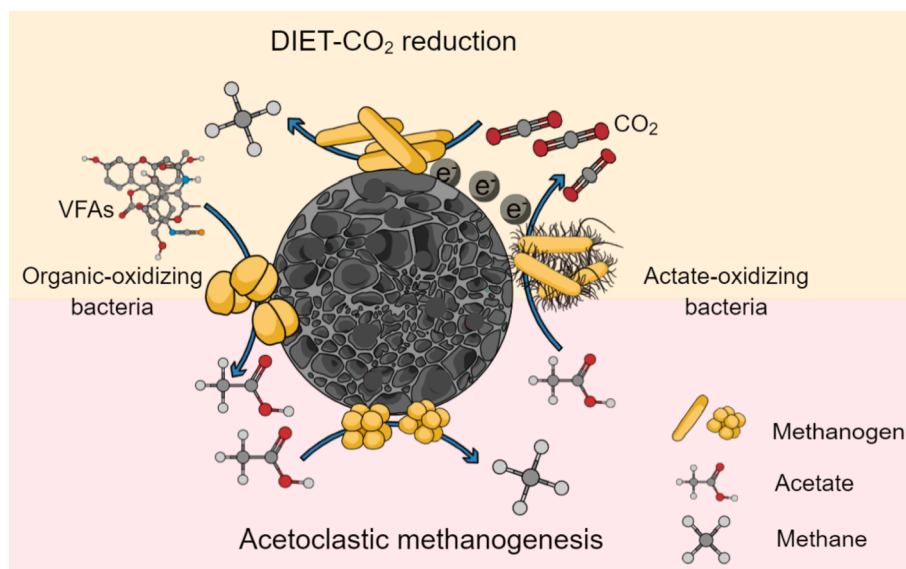


Fig. 1. Effects of granular activated carbon (GAC) on methanogenesis. GAC promotes DIET coupled CO<sub>2</sub> reduction to perform methanogenesis (upper); and acetoclastic methanogenesis is also stimulated through diverse strategies (lower). DIET: Direct interspecies electron transfer, VFAs: volatile fatty acids.

### 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 production 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 electricigens [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 methanogens [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 CO<sub>2</sub> 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 mechanism.

## 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 adsorbed 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 Pb<sup>2+</sup> and Ni<sup>2+</sup> 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]. H<sub>2</sub>S 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 H<sub>2</sub> 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].

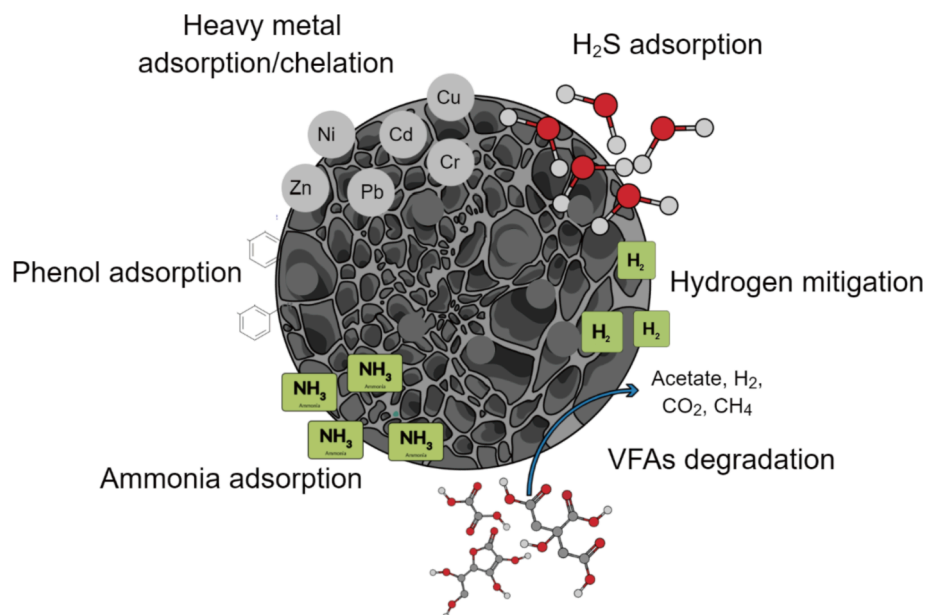
GAC showed promising effects during the treatment of wastewater with toxic organics like aromatic and nitrogen organics. GAC adsorbed the highly toxic compounds in the system to release the inhibition and enrich syntrophic bacteria to accelerate the degradation of the toxic compounds [26]. For example, 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.





**Fig. 3.** Anaerobic digestion inhibitors are removed by granular activated carbon (GAC). GAC decreases heavy metals through adsorption or chelation. H<sub>2</sub>S, ammonia, and phenol are removed by GAC through adsorption. GAC accelerated the degradation of volatile fatty acids and mitigate its inhibition of methanogenesis.

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<sup>-2</sup> [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 recalcitrant azo 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 voltammogram 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<sup>-1</sup> 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<sup>-1</sup>, 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/

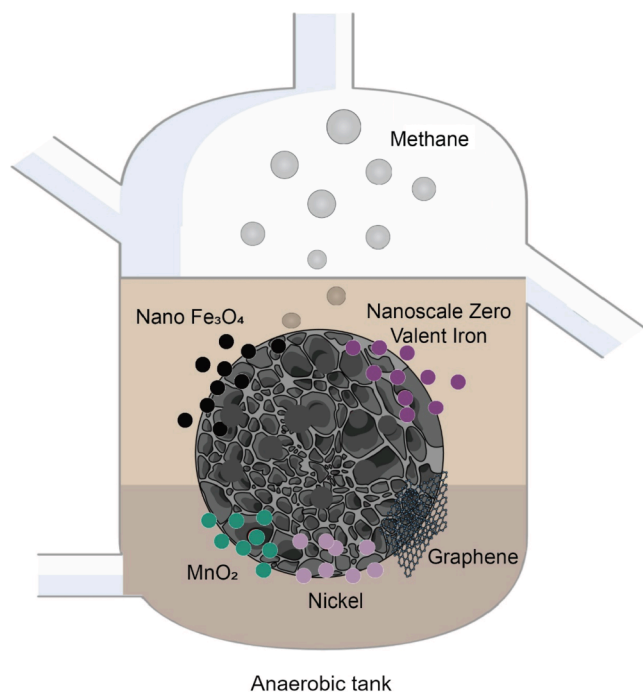


Fig. 4. Nanomodifications of granular activated carbon (GAC) to improve the anaerobic digestion performance.

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 reactivity 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  $\text{Fe}^{2+}$ , 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 hydrolysis by enriching iron-reducing bacteria, while GAC enhanced DIET between iron-reducing bacteria and methanogens. Nano- $\text{Fe}_3\text{O}_4$ /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- $\text{MnO}_2$  composite increased 36% of methane production [47]. GAC- $\text{MnO}_2$  composite enhanced extracellular polymeric substance secretion but inhibited humic substances. The methanogenesis was enhanced through the redox cycle of  $\text{Mn}^{4+}/\text{Mn}^{2+}$ . 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- $\text{Fe}_3\text{O}_4$  modified GAC [107]. However, it is worthy to note that GAC modification also showed negative effects. A recent study showed that GAC@ $\text{Fe}_3\text{O}_4$  and GAC@- $\text{V}_3\text{O}_7\cdot\text{H}_2\text{O}$  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  $\text{CO}_2$  reduction.
- The hydrolysis, acidogenesis, and acetogenesis 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  $^{13}\text{C}$  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 nano-materials, 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.

### Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (42077025) and Youth Innovation Promotion Association, CAS (2021213).

### References

- [1] Hao X, Wei J, van Loosdrecht MCM, Cao D. Analysing the mechanisms of sludge digestion enhanced by iron. *Water Res* 2017;117:58–67. <https://doi.org/10.1016/J.WATRES.2017.03.048>.
- [2] Zan F, Huang H, Guo G, Chen G. Sulfite pretreatment enhances the biodegradability of primary sludge and waste activated sludge towards cost-effective and carbon-neutral sludge treatment. *Sci Total Environ* 2021;780:146634.
- [3] Zhen G, Lu X, Kato H, Zhao Y, Li YY. Overview of pretreatment strategies for enhancing sewage sludge disintegration and subsequent anaerobic digestion: Current advances, full-scale application and future perspectives. *Renew Sust Energ Rev* 2017;69:559–77. <https://doi.org/10.1016/J.RSER.2016.11.187>.
- [4] Evans PN, Boyd JA, Leu AO, Woodcroft BJ, Parks DH, Hugenholtz P, et al. An evolving view of methane metabolism in the Archaea. *Nat Rev Microbiol* 2019;17(4):219–32. <https://doi.org/10.1038/s41579-018-0136-7>.
- [5] Xiao L, Lichtfouse E, Senthil Kumar P. Advantage of conductive materials on interspecies electron transfer-independent acetoclastic methanogenesis: A critical review. *Fuel* 2021;305:121577.
- [6] Zhang J, Zhao W, Zhang H, Wang Z, Fan C, Zang L. Recent achievements in enhancing anaerobic digestion with carbon-based functional materials. *Bioresour Technol* 2018;266:555–67. <https://doi.org/10.1016/J.BIORTECH.2018.07.076>.

- [7] Wang W, Lee D-J. Direct interspecies electron transfer mechanism in enhanced methanogenesis: A mini-review. *Bioresour Technol* 2021;330:124980.
- [8] Sasidhar KB, Kumar PS, Xiao L. A critical review on the two-stage biohythane production and its viability as a renewable fuel. *Fuel* 2022;317:123449.
- [9] Sarker S, Lamb JJ, Hjelme DR, Lien KM. Overview of recent progress towards in-situ biogas upgradation techniques. *Fuel* 2018;226:686–97. <https://doi.org/10.1016/J.FUEL.2018.04.021>.
- [10] Liu Y, Whitman WB. Metabolic, phylogenetic, and ecological diversity of the methanogenic archaea. *Ann NY Acad Sci* 2008;1125:171–89. <https://doi.org/10.1196/ANNALS.1419.019>.
- [11] Conrad R. Quantification of methanogenic pathways using stable carbon isotopic signatures: A review and a proposal. *Org Geochem* 2005;36(5):739–52. <https://doi.org/10.1016/j.orggeochem.2004.09.006>.
- [12] Prakash D, Chauhan SS, Ferry JG. Life on the thermodynamic edge: Respiratory growth of an acetotrophic methanogen. *Sci Adv* 2019;5(8).
- [13] Holmes DE, Smith JA. Biologically produced methane as a renewable energy source. *Adv Appl Microbiol* 2016;97:1–61. <https://doi.org/10.1016/BS.AAMBS.2016.09.001>.
- [14] Xiao L, Liu F, Xu H, Feng D, Liu J, Han G. Biochar promotes methane production at high acetate concentrations in anaerobic soils. *Environ Chem Lett* 2019;17(3):1347–52. <https://doi.org/10.1007/s10311-019-00863-3>.
- [15] Xiao L, Liu F, Lichtfouse E, Zhang P, Feng D, Li F. Methane production by acetate dismutation stimulated by *Shewanella oneidensis* and carbon materials: An alternative to classical CO<sub>2</sub> reduction. *Chem Eng J* 2020;389:124469. <https://doi.org/10.1016/j.cej.2020.124469>.
- [16] Rasapoor M, Young B, Brar R, Sarmah A, Zhuang W-Q, Baroutian S. Recognizing the challenges of anaerobic digestion: Critical steps toward improving biogas generation. *Fuel* 2020;261:116497.
- [17] Stams AJM, Plugge CM. Electron transfer in syntrophic communities of anaerobic bacteria and archaea. *Nat Rev Microbiol* 2009;7(8):568–77. <https://doi.org/10.1038/nrmicro2166>.
- [18] Wang Z, Wang T, Si B, Watson J, Zhang Y. Accelerating anaerobic digestion for methane production: Potential role of direct interspecies electron transfer. *Renew Sust Energ Rev* 2021;145:111069.
- [19] Li L, Xu Y, Dai X, Dai L. Principles and advancements in improving anaerobic digestion of organic waste via direct interspecies electron transfer. *Renew Sust Energ Rev* 2021;148:111367.
- [20] Barua S, Dhar BR. Advances towards understanding and engineering direct interspecies electron transfer in anaerobic digestion. *Bioresour Technol* 2017;244:698–707. <https://doi.org/10.1016/J.BIORTECH.2017.08.023>.
- [21] Sieber JR, Le HM, McInerney MJ. The importance of hydrogen and formate transfer for syntrophic fatty, aromatic and alicyclic metabolism. *Environ Microbiol* 2014;16(1):177–88. <https://doi.org/10.1111/1462-2920.12269>.
- [22] Lovley DR. Syntrophy goes electric: Direct interspecies electron transfer. *Annu Rev Microbiol* 2017;71(1):643–64.
- [23] Summers ZM, Fogarty HE, Leang C, Franks AE, Malvankar NS, Lovley DR. Direct exchange of electrons within aggregates of an evolved syntrophic coculture of anaerobic bacteria. *Science* 2010;330(6009):1413–5.
- [24] Ajay CM, Mohan S, Dinesha P, Rosen MA. Review of impact of nanoparticle additives on anaerobic digestion and methane generation. *Fuel* 2020;277:118234.
- [25] Kumar AN, Dissanayake PD, Masek O, Priya A, Ki Lin CS, Ok YS, et al. Recent trends in biochar integration with anaerobic fermentation: Win-win strategies in a closed-loop. *Renew Sust Energ Rev* 2021;149:111371.
- [26] Abbas Y, Yun S, Wang Z, Zhang Y, Zhang X, Wang K. Recent advances in bio-based carbon materials for anaerobic digestion: A review. *Renew Sust Energ Rev* 2021;135:110378.
- [27] Cruz Viggì C, Rossetti S, Fazi S, Paiano P, Majone M, Aulenta F. Magnetite particles triggering a faster and more robust syntrophic pathway of methanogenic propionate degradation. *Environ Sci Technol* 2014;48(13):7536–43.
- [28] Martins G, Salvador AF, Pereira L, Alves MM. Methane production and conductive materials: A critical review. *Environ Sci Technol* 2018;52(18):10241–53. <https://doi.org/10.1021/acs.est.8b01913>.
- [29] Kumar V, Nabaterega R, Khoei S, Eskicioglu C. Insight into interactions between syntrophic bacteria and archaea in anaerobic digestion amended with conductive materials. *Renew Sust Energ Rev* 2021;144:110965.
- [30] Sun M, Jiang H, Zhang Z, Lv M, Liu G, Feng Y. Coupling direct voltage and granular activated carbon modified nanoscale zero valent iron for enhancing anaerobic methane production. *Chemosphere* 2022;286:131840.
- [31] Lu J-S, Chang J-S, Lee D-J. Adding carbon-based materials on anaerobic digestion performance: A mini-review. *Bioresour Technol* 2020;300:122696.
- [32] Nguyen LN, Vu MT, Abu Hasan Johir Md, Pernice M, Ngo HH, Zdzarta J, et al. Promotion of direct interspecies electron transfer and potential impact of conductive materials in anaerobic digestion and its downstream processing - a critical review. *Bioresour Technol* 2021;341:125847.
- [33] Xiao L, Liu F, Liu J, Li J, Zhang Y, Yu J, et al. Nano-Fe<sub>3</sub>O<sub>4</sub> particles accelerating electromethanogenesis on an hour-long timescale in wetland soil. *Environ Sci Nano* 2018;5(2):436–45.
- [34] Lee Y-J, Lee D-J. Impact of adding metal nanoparticles on anaerobic digestion performance - A review. *Bioresour Technol* 2019;292:121926.
- [35] Yin Q, Wu G. Advances in direct interspecies electron transfer and conductive materials: Electron flux, organic degradation and microbial interaction. *Biotechnol Adv* 2019;37(8):107443.
- [36] van Steendam C, Smets I, Skerlos S, Raskin L. Improving anaerobic digestion via direct interspecies electron transfer requires development of suitable characterization methods. *Curr Opin Biotechnol* 2019;57:183–90. <https://doi.org/10.1016/j.copbio.2019.03.018>.
- [37] Fu L, Zhou T, Wang J, You L, Lu Y, Yu L, et al. NanoFe<sub>3</sub>O<sub>4</sub> as solid electron shuttles to accelerate acetotrophic methanogenesis by *Methanosarcina barkeri*. *Front Microbiol* 2019;10:388.
- [38] Salvador AF, Martins G, Melle-Franco M, Serpa R, Stams AJM, Cavaleiro AJ, et al. Carbon nanotubes accelerate methane production in pure cultures of methanogens and in a syntrophic coculture. *Environ Microbiol* 2017;19(7):2727–39. <https://doi.org/10.1111/1462-2920.13774>.
- [39] Xiao L, Zheng S, Lichtfouse E, Luo M, Tan Y, Liu F. Carbon nanotubes accelerate acetoclastic methanogenesis: From pure cultures to anaerobic soils. *Soil Biol Biochem* 2020;150:107938. <https://doi.org/10.1016/j.soilbio.2020.107938>.
- [40] Yu J, Liu J, Senthil Kumar P, Wei Y, Zhou M, Vo D-V, et al. Promotion of methane production by magnetite via increasing acetogenesis revealed by metagenome-assembled genomes. *Bioresour Technol* 2022;345:126521.
- [41] Xiao L, Sun R, Zhang P, Zheng S, Tan Y, Li J, et al. Simultaneous intensification of direct acetate cleavage and CO<sub>2</sub> reduction to generate methane by bioaugmentation and increased electron transfer. *Chem Eng J* 2019;378:122229. <https://doi.org/10.1016/j.cej.2019.122229>.
- [42] Caizán-Juanarena L, Sleutels T, Borsje C, ter Heijne A. Considerations for application of granular activated carbon as capacitive bioanode in bioelectrochemical systems. *Renew Energ* 2020;157:782–92. <https://doi.org/10.1016/J.RENENE.2020.05.049>.
- [43] He C, Liu T, Ou H, Yuan S, Hu Z, Wang W. Coupling granular activated carbon and exogenous hydrogen to enhance anaerobic digestion of phenol via predominant syntrophic acetate oxidation and hydrogenotrophic methanogenesis pathway. *Bioresour Technol* 2021;323:124576.
- [44] Lee JY, Lee SH, Park HD. Enrichment of specific electro-active microorganisms and enhancement of methane production by adding granular activated carbon in anaerobic reactors. *Bioresour Technol* 2016;205:205–12. <https://doi.org/10.1016/J.BIORTECH.2016.01.054>.
- [45] Lei Y, Sun D, Dang Y, Feng X, Huo Da, Liu C, et al. Metagenomic analysis reveals that activated carbon aids anaerobic digestion of raw incineration leachate by promoting direct interspecies electron transfer. *Water Res* 2019;161:570–80.
- [46] Rotaru A-E, Shrestha PM, Liu F, Markovaita B, Chen S, Nevin KP, et al. Direct interspecies electron transfer between *Geobacter metallireducens* and *Methanosarcina barkeri*. *Applied and Environ Microbiol* 2014;80(15):4599–605. <https://doi.org/10.1128/AEM.00895-14>.
- [47] Yang Bo, Xu H, Liu Y, Li F, Song X, Wang Z, et al. Role of GAC-MnO<sub>2</sub> catalyst for triggering the extracellular electron transfer and boosting CH<sub>4</sub> production in syntrophic methanogenesis. *Chem Eng J* 2020;383:123211.
- [48] Rotaru AE, Posth NR, Löscher CR, Miracle MR, Vicente E, Cox RP, et al. Interspecies interactions mediated by conductive minerals in the sediments of the iron rich meromictic Lake La Cruz, Spain. *Limnologia* 2019;38:21–40. <https://doi.org/10.23818/LIMN.38.10>.
- [49] Johnravindar D, Liang B, Fu R, Luo G, Meruvu H, Yang S, et al. Supplementing granular activated carbon for enhanced methane production in anaerobic digestion of post-consumer substrates. *Biomass Bioenergy* 2020;136:105543.
- [50] Li Q, Gao X, Liu Y, Wang G, Li Y-Y, Sano D, et al. Biochar and GAC intensify anaerobic phenol degradation via distinctive adsorption and conductive properties. *J Hazard Mater* 2021;405:124183.
- [51] Wu Yu, Wang S, Liang D, Li N. Conductive materials in anaerobic digestion: From mechanism to application. *Bioresour Technol* 2020;298:122403. <https://doi.org/10.1016/j.biortech.2019.122403>.
- [52] Chen S, Rotaru A-E, Liu F, Phillips Jo, Woodard TL, Nevin KP, et al. Carbon cloth stimulates direct interspecies electron transfer in syntrophic co-cultures. *Bioresour Technol* 2014;173:82–6.
- [53] Liu F, Rotaru AE, Shrestha PM, Malvankar NS, Nevin KP, Lovley DR. Promoting direct interspecies electron transfer with activated carbon. *Energy Environ Sci* 2012;5:8982–9. <https://doi.org/10.1039/C2EE22459C>.
- [54] Chen S, Rotaru A-E, Shrestha PM, Malvankar NS, Liu F, Fan W, et al. Promoting interspecies electron transfer with biochar. *Sci Rep* 2015;4(1). <https://doi.org/10.1038/srep05019>.
- [55] Lin R, Cheng J, Zhang J, Zhou J, Cen K, Murphy JD. Boosting biomethane yield and production rate with graphene: The potential of direct interspecies electron transfer in anaerobic digestion. *Bioresour Technol* 2017;239:345–52. <https://doi.org/10.1016/J.BIORTECH.2017.05.017>.
- [56] Kang H-J, Lee S-H, Lim T-G, Park H-D. Effect of microbial community structure in inoculum on the stimulation of direct interspecies electron transfer for methanogenesis. *Bioresour Technol* 2021;332:125100.
- [57] Kang H-J, Lee S-H, Lim T-G, Park H-D. Effect of inoculum concentration on methanogenesis by direct interspecies electron transfer: Performance and microbial community composition. *Bioresour Technol* 2019;291:121881.
- [58] Zhang Y, Guo B, Zhang L, Zhang H, Liu Y. Microbial community dynamics in granular activated carbon enhanced up-flow anaerobic sludge blanket (UASB) treating municipal sewage under sulfate reducing and psychrophilic conditions. *Chem Eng J* 2021;405:126957.
- [59] Wang M, Qian Y, Zhu Y, Yong X, Jia H, Wong JWC, et al. Enhancing the performance and stability of the co-anaerobic digestion of municipal sludge and food waste by granular activated carbon dosing. *Energy Fuels* 2020;34(12):16284–93.
- [60] Lee S-H, Kang H-J, Lim T-G, Park H-D. Magnetite and granular activated carbon improve methanogenesis via different metabolic routes. *Fuel* 2020;281:118768.
- [61] Romero RM, Valenzuela EI, Cervantes FJ, Garcia-Reyes RB, Serrano D, Alvarez LH. Improved methane production from anaerobic digestion of liquid and



- raw fractions of swine manure effluent using activated carbon. *J Water Process* 2020;38:101576.
- [62] Zhang Y, Zhang L, Guo B, Zhou Y, Gao M, Sharaf A, et al. Granular activated carbon stimulated microbial physiological changes for enhanced anaerobic digestion of municipal sewage. *Chem Eng J* 2020;400:125838.
- [63] Park JH, Park JH, Je Seong H, Sul WJ, Jin KH, Park HD. Metagenomic insight into methanogenic reactors promoting direct interspecies electron transfer via granular activated carbon. *Bioresour Technol* 2018;259:414–22. <https://doi.org/10.1016/J.BIORTECH.2018.03.050>.
- [64] Yang Y, Zhang Y, Li Z, Zhao Z, Quan X, Zhao Z. Adding granular activated carbon into anaerobic sludge digestion to promote methane production and sludge decomposition. *J Clean Prod* 2017;149:1101–8. <https://doi.org/10.1016/J.JCLEPRO.2017.02.156>.
- [65] Chowdhury B, Lin L, Dhar BR, Islam MN, McCartney D, Kumar A. Enhanced biomethane recovery from fat, oil, and grease through co-digestion with food waste and addition of conductive materials. *Chemosphere* 2019;236:124362.
- [66] Shekhar Bose R, Chowdhury B, Zakaria BS, Kumar Tiwari M, Ranjan Dhar B. Significance of different mixing conditions on performance and microbial communities in anaerobic digester amended with granular and powdered activated carbon. *Bioresour Technol* 2021;341:125768.
- [67] Xu S, Han R, Zhang Y, He C, Liu H. Differentiated stimulating effects of activated carbon on methanogenic degradation of acetate, propionate and butyrate. *Waste Manage* 2018;76:394–403. <https://doi.org/10.1016/J.WASMAN.2018.03.037>.
- [68] Li J, Xiao L, Zheng S, Zhang Y, Luo M, Tong C, et al. A new insight into the strategy for methane production affected by conductive carbon cloth in wetland soil: Beneficial to acetoclastic methanogenesis instead of CO<sub>2</sub> reduction. *Sci Total Environ* 2018;643:1024–30. <https://doi.org/10.1016/j.scitotenv.2018.06.271>.
- [69] Yang P, Tan G-Y, Aslam M, Kim J, Lee P-H. Metatranscriptomic evidence for classical and RuBisCO-mediated CO<sub>2</sub> reduction to methane facilitated by direct interspecies electron transfer in a methanogenic system. *Sci Rep* 2019;9(1).
- [70] Pham TH, Aelterman P, Verstraete W. Bioanode performance in bioelectrochemical systems: recent improvements and prospects. *Trends Biotechnol* 2009;27(3):168–78.
- [71] Watanabe K. Recent developments in microbial fuel cell technologies for sustainable bioenergy. *J Biosci Bioeng* 2008;106(6):528–36.
- [72] Jiang Q, Liu He, Zhang Y, Cui M-H, Fu Bo, Liu H-b. Insight into sludge anaerobic digestion with granular activated carbon addition: Methanogenic acceleration and methane reduction relief. *Bioresour Technol* 2021;319:124131.
- [73] Bose S, Kumar PS, Vo D-V, Rajamohan N, Saravanan R. Microbial degradation of recalcitrant pesticides: a review. *Environ Chem Lett* 2021;19(4):3209–28.
- [74] Muthu Kumara Pandian A, Rajasimman M, Rajamohan N, Varjani S, Karthikeyan C. Anaerobic mixed consortium (AMC) mediated enhanced biosynthesis of silver nano particles (AgNPs) and its application for the removal of phenol. *J Hazard Mater* 2021;416:125717.
- [75] Monisha RS, Mani RL, Sivaprakash B, Rajamohan N, Vo D-V. Green remediation of pharmaceutical wastes using biochar: a review. *Environ Chem Lett* 2022;20(1): 681–704.
- [76] Zhao W, Yang H, He S, Zhao Q, Wei L. A review of biochar in anaerobic digestion to improve biogas production: Performances, mechanisms and economic assessments. *Bioresour Technol* 2021;341:125797.
- [77] Eeshwarasinghe D, Loganathan P, Vigneswaran S. Simultaneous removal of polycyclic aromatic hydrocarbons and heavy metals from water using granular activated carbon. *Chemosphere* 2019;223:616–27. <https://doi.org/10.1016/J.CHEMOSPHERE.2019.02.033>.
- [78] Sirianuntapiboon S, Ungkaprasattha O. Removal of Pb<sup>2+</sup> and Ni<sup>2+</sup> by bio-sludge in sequencing batch reactor (SBR) and granular activated carbon-SBR (GAC-SBR) systems. *Bioresour Technol* 2007;98(14):2749–57.
- [79] Bertin L, Lampis S, Todaro D, Scoma A, Vallini G, Marchetti L, et al. Anaerobic acidogenic digestion of olive mill wastewaters in biofilm reactors packed with ceramic filters or granular activated carbon. *Water Res* 2010;44(15):4537–49.
- [80] Ou HW, Fang ML, Chou MS, Chang HY, Shiao TF. Long-term evaluation of activated carbon as an adsorbent for biogas desulfurization. *J Air Waste Manag Assoc* 2020;70(6):641–8. <https://doi.org/10.1080/10962247.2020.1754305>.
- [81] Rattanapan C, Boonsawang P, Kantachote D. Removal of H<sub>2</sub>S in down-flow GAC biofiltration using sulfide oxidizing bacteria from concentrated latex wastewater. *Bioresour Technol* 2009;100(1):125–30.
- [82] Ngo T, Shahsavari E, Shah K, Surapaneni A, Ball AS. Improving bioenergy production in anaerobic digestion systems utilising chicken manure via pyrolysed biochar additives: A review. *Fuel* 2022;316:123374.
- [83] Florentino AP, Sharaf A, Zhang L, Liu Y. Overcoming ammonia inhibition in anaerobic blackwater treatment with granular activated carbon: the role of electroactive microorganisms. *Environ Sci Water Res Technol* 2019;5(2):383–96. <https://doi.org/10.1039/C8EW00599K>.
- [84] Usman M, Hao S, Chen H, Ren S, Tsang DCW, O-Thong S, et al. Molecular and microbial insights towards understanding the anaerobic digestion of the wastewater from hydrothermal liquefaction of sewage sludge facilitated by granular activated carbon (GAC). *Environ Int* 2019;133:105257.
- [85] Dai C, Yang L, Wang J, Li D, Zhang Y, Zhou X. Enhancing anaerobic digestion of pharmaceutical industries wastewater with the composite addition of zero valent iron (ZVI) and granular activated carbon (GAC). *Bioresour Technol* 2022;346: 126566.
- [86] Wang Z, Zhang C, Watson J, Sharma BK, Si B, Zhang Y. Adsorption or direct interspecies electron transfer? A comprehensive investigation of the role of biochar in anaerobic digestion of hydrothermal liquefaction aqueous phase. *Chem Eng J* 2022;435:135078.
- [87] Ryue J, Lin L, Liu Y, Lu W, McCartney D, Dhar BR. Comparative effects of GAC addition on methane productivity and microbial community in mesophilic and thermophilic anaerobic digestion of food waste. *Biochem Eng J* 2019;146:79–87. <https://doi.org/10.1016/J.BEJ.2019.03.010>.
- [88] Zhang L, Zhang J, Loh KC. Activated carbon enhanced anaerobic digestion of food waste – Laboratory-scale and Pilot-scale operation. *Waste Manage* 2018;75: 270–9. <https://doi.org/10.1016/J.WASMAN.2018.02.020>.
- [89] Capson-Tojo G, Moscoviz R, Ruiz D, Santa-Catalina G, Trably E, Rouez M, et al. Addition of granular activated carbon and trace elements to favor volatile fatty acid consumption during anaerobic digestion of food waste. *Bioresour Technol* 2018;260:157–68.
- [90] Brandão Lavender M, Pang S, Liu D, Jourdin L, ter Heijne A. Reduced overpotential of methane-producing biocathodes: Effect of current and electrode storage capacity. *Bioresour Technol* 2022;347:126650.
- [91] Liu B, Williams I, Li Y, Wang L, Bagtzoglou A, McCutcheon J, et al. Towards high power output of scaled-up benthic microbial fuel cells (BMFCs) using multiple electron collectors. *Biosens Bioelectron* 2016;79:435–41.
- [92] Kalathil S, Lee J, Cho MH. Efficient decolorization of real dye wastewater and bioelectricity generation using a novel single chamber biocathode-microbial fuel cell. *Bioresour Technol* 2012;119:22–7. <https://doi.org/10.1016/J.BIORTECH.2012.05.059>.
- [93] Liu S, Song H, Wei S, Yang F, Li X. Bio-cathode materials evaluation and configuration optimization for power output of vertical subsurface flow constructed wetland — Microbial fuel cell systems. *Bioresour Technol* 2014;166: 575–83. <https://doi.org/10.1016/J.BIORTECH.2014.05.104>.
- [94] van der Zee FP, Bisschops IAE, Lettinga G, Field JA. Activated carbon as an electron acceptor and redox mediator during the anaerobic biotransformation of azo dyes. *Environ Sci Technol* 2003;37(2):402–8.
- [95] Guo K, Freguia S, Dennis PG, Chen X, Donose BC, Keller J, et al. Effects of surface charge and hydrophobicity on anodic biofilm formation, community composition, and current generation in bioelectrochemical systems. *Environ Sci Technol* 2013;47(13):7563–70.
- [96] Ren G, Chen P, Yu J, Liu J, Ye J, Zhou S. Recyclable magnetite-enhanced electroethanogenesis for biomethane production from wastewater. *Water Res* 2019;166:115095.
- [97] Tiwari SB, Dubey M, Ahmed B, Gahlot P, Khan AA, Rajpal A, et al. Carbon-based conductive materials facilitated anaerobic co-digestion of agro waste under thermophilic conditions. *Waste Manage* 2021;124:17–25.
- [98] Lee J-Y, Yun J, Kim TG, Wee D, Cho K-S. Two-stage biogas production by co-digesting molasses wastewater and sewage sludge. *Bioprocess Biosyst Eng* 2014; 37(12):2401–13.
- [99] Florentino AP, Xu R, Zhang L, Liu Y. Anaerobic digestion of blackwater assisted by granular activated carbon: From digestion inhibition to methanogenesis enhancement. *Chemosphere* 2019;233:462–71. <https://doi.org/10.1016/J.CHEMOSPHERE.2019.05.255>.
- [100] Li D, Song L, Fang H, Li P, Teng Y, Li Y-Y, et al. Accelerated bio-methane production rate in thermophilic digestion of cardboard with appropriate biochar: Dose-response kinetic assays, hybrid synergistic mechanism, and microbial networks analysis. *Bioresour Technol* 2019;290:121782.
- [101] Sun M, Zhang Z, Liu G, Lv M, Feng Y. Enhancing methane production of synthetic brewery water with granular activated carbon modified with nanoscale zero-valent iron (NZVI) in anaerobic system. *Sci Total Environ* 2021;760:143933.
- [102] Xu H, Liu Y, Yang Bo, Jia L, Li X, Li F, et al. Inhibitory effect of released phosphate on the ability of nano zero valent iron to boost anaerobic digestion of waste-activated sludge and the remediation method. *Chem Eng J* 2021;405:126506.
- [103] Peng H, Zhang Y, Tan D, Zhao Z, Zhao H, Quan X. Roles of magnetite and granular activated carbon in improvement of anaerobic sludge digestion. *Bioresour Technol* 2018;249:666–72. <https://doi.org/10.1016/J.BIORTECH.2017.10.047>.
- [104] Song X, Liu J, Jiang Q, Zhang P, Shao Y, He W, et al. Enhanced electron transfer and methane production from low-strength wastewater using a new granular activated carbon modified with nano-Fe<sub>3</sub>O<sub>4</sub>. *Chem Eng J* 2019;374:1344–52. <https://doi.org/10.1016/j.cej.2019.05.216>.
- [105] Kim K-R, Kang J, Chae K-J. Improvement in methanogenesis by incorporating transition metal nanoparticles and granular activated carbon composites in microbial electrolysis cells. *Int J Hydrogen Energy* 2017;42(45):27623–9.
- [106] Cheng P, Zhou Y, Liu Y. Synthetic effect of zero-valent iron and granular activated carbon on methane production from pentachlorophenol wastewater. *Desalin Water Treat* 2021;237:226–32. <https://doi.org/10.5004/DWT.2021.27741>.
- [107] Wan H, Wang F, Chen Y, Zhao Z, Zhang G, Dou M, et al. Enhanced Reactive Red 2 anaerobic degradation through improving electron transfer efficiency by nano-Fe<sub>3</sub>O<sub>4</sub> modified granular activated carbon. *Renewable Energy* 2021;179:696–704.
- [108] Liu T, Ou H, Su K, Hu Z, He C, Wang W. Promoting direct interspecies electron transfer and acetoclastic methanogenesis for enhancing anaerobic digestion of butanol octanol wastewater by coupling granular activated carbon and exogenous hydrogen. *Bioresour Technol* 2021;337:125417.
- [109] Xiao Y, Yang H, Zheng D, Liu Y, Zhao C, Deng L. Granular activated carbon alleviates the combined stress of ammonia and adverse temperature conditions during dry anaerobic digestion of swine manure. *Renew Energy* 2021;169:451–60. <https://doi.org/10.1016/J.RENENE.2021.01.021>.
- [110] Liu Y, Qian Y, Yong X, Jia H, Wei P, Zhou J. Effects of granular activated carbon and temperature on the viscosity and methane yield of anaerobically digested of corn straw with different dry matter concentrations. *Bioresour Technol* 2021;332: 125109.
- [111] He X, Guo Z, Lu J, Zhang P. Carbon-based conductive materials accelerated methane production in anaerobic digestion of waste fat, oil and grease. *Bioresour Technol* 2021;329:124871.

- [112] Tan LC, Lin R, Murphy JD, Lens PNL. Granular activated carbon supplementation enhances anaerobic digestion of lipid-rich wastewaters. *Renew Energ* 2021;171: 958–70. <https://doi.org/10.1016/J.RENENE.2021.02.087>.
- [113] Kwon D, Lam TYC, Kim M, Tan GYA, Lee PH, Kim J. Combined effect of activated carbon particles and non-adsorptive spherical beads as fluidized media on fouling, organic removal and microbial communities in anaerobic membrane bioreactor. *Membranes* 2021;11:365. <https://doi.org/10.3390/MEMBRANES11050365>.
- [114] Zhao Z, Zhang Y. Application of ethanol-type fermentation in establishment of direct interspecies electron transfer: A practical engineering case study. *Renew Energ* 2019;136:846–55. <https://doi.org/10.1016/J.RENENE.2019.01.055>.
- [115] Xiao Y, Yang H, Yang H, Wang H, Zheng D, Liu Yi, et al. Improved biogas production of dry anaerobic digestion of swine manure. *Bioresour Technol* 2019; 294:122188.
- [116] Xu S, He C, Luo L, Lü F, He P, Cui L. Comparing activated carbon of different particle sizes on enhancing methane generation in upflow anaerobic digester. *Bioresour Technol* 2015;196:606–12. <https://doi.org/10.1016/J.BIORTECH.2015.08.018>.
- [117] Yan W, Shen N, Xiao Y, Chen Y, Sun F, Kumar Tyagi V, et al. The role of conductive materials in the start-up period of thermophilic anaerobic system. *Bioresour Technol* 2017;239:336–44.
- [118] Zhao Z, Li Y, Quan X, Zhang Y. Towards engineering application: Potential mechanism for enhancing anaerobic digestion of complex organic waste with different types of conductive materials. *Water Res* 2017;115:266–77. <https://doi.org/10.1016/J.WATRES.2017.02.067>.
- [119] Mei R, Nobu MK, Narihiro T, Yu J, Sathyagal A, Willman E, et al. Novel *Geobacter* species and diverse methanogens contribute to enhanced methane production in media-added methanogenic reactors. *Water Res* 2018;147:403–12.