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Item Type	Article
Authors	Al Hasani, Zahra;Nayak, Jagdeep Kumar;Al Balushi, Noor Juma;Al-Mamun, Abdullah
Citation	Water, 17, 1321
DOI	<a href="https://doi.org/10.3390/w17091321">10.3390/w17091321</a>
Publisher	MDPI
Rights	Attribution-NonCommercial-ShareAlike 4.0 International
Download date	2026-06-10 12:46:04
Item License	<a href="http://creativecommons.org/licenses/by-nc-sa/4.0/">http://creativecommons.org/licenses/by-nc-sa/4.0/</a>
Link to Item	<a href="https://hdl.handle.net/10344/31481">https://hdl.handle.net/10344/31481</a>

Review

# Prospect of Conductive Materials in the Anaerobic Digester Matrix for Methane Production: Electron Transfer and Microbial Communication

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**Abstract:** Anaerobic digestion (AD) converts organic waste into methane-rich biogas but often faces performance issues due to organic acid and ammonium nitrogen accumulation. This hinders methanogen growth and reduces methane production. Recent studies show that incorporating conductive materials (CMs) into the AD matrix can mitigate these issues by facilitating electron transfer between microorganisms. This process accelerates the oxidation of organic acids and ammonium ions, enhancing methane recovery. The effectiveness of CMs depends on their type, porosity, surface morphology, and conductivity, which foster a symbiotic microbial community. This comprehensive review paper aimed to (i) describe the influence of CMs on the growth and enrichment of the AD microbial community, (ii) quantify the enhancement of biodegradation and methane generation, and (iii) observe syntrophic interactions and interspecies electron transfer. The review also summarized the impact of different conductive materials on methane generation and the effect of operational parameters, e.g., dose, size, and external voltage application, on the conductive electrodes. The study summarized that the different conductive materials have different influences, and their application in the AD matrix has to be realistic based on availability and economic benefits.

**Keywords:** anaerobic digestion; conductive materials; electrode; direct interspecies electron transfer; indirect interspecies electron transfer



Academic Editor: Catherine N. Mulligan

Received: 13 February 2025  
Revised: 31 March 2025  
Accepted: 8 April 2025  
Published: 28 April 2025

**Citation:** Al Hasani, Z.; Nayak, J.K.; Al Balushi, N.J.; Al-Mamun, A.; Samal, K. Prospect of Conductive Materials in the Anaerobic Digester Matrix for Methane Production: Electron Transfer and Microbial Communication. *Water* **2025**, *17*, 1321. <https://doi.org/10.3390/w17091321>

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## 1. Introduction

The explosive growth of industrialization and urbanization, accompanied by excessive consumption, has caused an increase in waste production. As a result, millions of tons of diversified organic and complex wastes are produced annually from agricultural, municipal, and industrial sources. Biodegradable wastes are cost-effective resources for producing biofuels through several energy-harvesting methods [1]. Waste-to-energy harvesting methods are mostly either biochemical or thermochemical processes or a combination of both. Anaerobic digestion (AD), composting, landfilling, and microbial electrochemical technologies are emerging biochemical processes, whereas pyrolysis, gasification, and incineration technologies are renowned thermochemical processes [2]. AD is a practical approach for treating biodegradable waste, offering both waste reduction and energy recovery benefits compared to incineration and landfilling [3].

AD is a series of naturally occurring bioprocesses through which a particular group of microorganisms degrade organic materials and convert them into biogas [4]. AD consists of four main phases: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Each step is governed by specific microbes based on the organic composition of wastes, as well as several operating factors of biogas generation and recovery [5]. The generated biogas is a mixture of CH<sub>4</sub> (50–75%), CO<sub>2</sub> (25–50%), NH<sub>3</sub> (1–2%), H<sub>2</sub> (0–2%), N<sub>2</sub> (0–1%), and a trace amount of H<sub>2</sub>S [6]. Since commercial AD plant designs were introduced in the early 1990s, the AD of biodegradable waste has attracted widespread interest.

Biogas production by AD faces limitations, including extended hydraulic retention time, insufficient removal of organic matter, and suboptimal methane production [7]. The biological breakdown of complex organics and macromolecules into simple organics and micromolecules is a rate-limiting process. Depending on the type of waste, the process is even inhibited by the intermediate formation and accumulation of by-products (NH<sub>3</sub>, H<sub>2</sub>S) from nitrogen-rich and protein-rich organics [8–10]. Additionally, accumulating volatile fatty acids (VFAs) in the AD matrix, which lowers pH, can significantly decrease process efficiency. Low pH inhibits methanogen growth by reducing methanogenic activity, resulting in further VFA accumulation. Eventually, the system deteriorates, creating conditions that make AD unsuitable [11]. For example, due to acid accumulation, a significant decrease in pH from 7.8 to 5.5 after one week has been reported, which causes CH<sub>4</sub> inhibition. In addition, the effluent's total organic carbon (TOC) concentration increased during the continuous operation, indicating the system's poor performance [12].

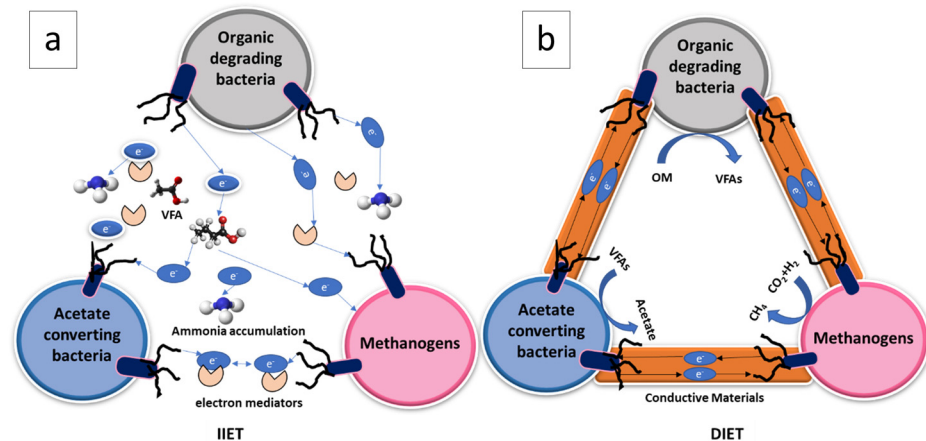
In conventional AD, the microorganisms exchange their metabolically produced electrons only via indirect interspecies electron transfer (IIET) mechanisms. Ineffective IIET is the cause of the limited microbial syntrophic interaction and electron transfer [13]. Adding conductive materials (CMs) into the AD matrix is an emerging approach to improve its performance, offering higher stabilization and methane production rates than conventional AD [14,15]. In traditional AD, low energy efficiency and limited diffusion of electron carriers hinder methanogenesis [16]. However, direct interspecies electron transfer (DIET) enhances electron transfer efficiency using electrical pili (e-pili) and c-type cytochromes, overcoming these limitations [17–20]. CMs support the DIET process by providing excellent conductivity, porosity, large surface area, and redox properties, which facilitate electron transfer among electroactive microorganisms [21–23]. CMs also act as enrichment surfaces for electrogens, forming microbial communities that accelerate the decomposition of organic matter and methane generation. As a result, numerous efforts have been directed toward optimizing methane production by changing the reactor configuration and operating parameters. A few CMs have recently been applied in AD to facilitate DIET [24,25].

Due to limited information on DIET in AD, this review summarized all the possible ways of interspecies and intermolecular e-exchange between the microorganisms and the electrodes for higher biogas recovery. The possible application of the CMs and their efficiency were also presented and graphically shown. The major influencing parameters of CMs, such as particle sizes, dosage, and the external current supply on the AD process, were summarized. The review provided a critical analysis of the impact of CMs on AD performance and their future application. Applying CMs could be an effective solution for the sustainable and efficient development of the AD process.

## 2. Role of Conductive Materials for Electron Transfer

The IET between the fermentative and the methanogenic organisms is the key to understanding the decomposition of complex organics and methane production in conductive material-assisted AD [20,26,27]. First, organics are decomposed electrochemically in the AD

matrix and released  $e^-$ ,  $H^+$ , and  $CO_2$  [28,29]. Then, these products are further converted to methane through two major electron pathways: (i) IIET and (ii) DIET (Figure 1).



**Figure 1.** Interspecies electron transfer pathways (a) IIET and (b) DIET from conductive materials to microbes in AD.

### 2.1. Indirect Interspecies Electron Transfer

Previous studies have shown that the AD system allows methane production through an indirect or mediated electron transfer. It is a mechanism that involves the transfer of electrons between syntrophic microorganisms via redox mediators such as hydrogen, acetate, and formate (Figure 1) [20,30,31]. The involved syntrophic bacteria can produce these mediators. At the same time, most of their methanogenic partners can oxidize these compounds in an anaerobic environment.

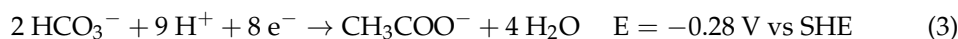
**By hydrogen mediators:** Many studies have focused on the typical pathway through the reduction of  $H_2$  (hydrogenotrophic methanogens) [32,33].  $H_2$  is produced and consumed continuously by anaerobic microorganisms. Therefore, when the  $H^+$  is produced, it is reduced to  $H_2$  by hydrogen-producing bacteria. Then, methane produced electroactivity in biofilm or through hydrogen-utilizing microorganisms, such as *Methanobacterium formicium* and *Methanobrevibacter arborophilus* in the bulk solution, in which hydrogen serves as an electron carrier between hydrogen-producing bacteria and hydrogenotrophic methanogens in the biofilm, which converts the  $H_2$  and  $CO_2$  into methane as shown in Equations (1) and (2) [34].



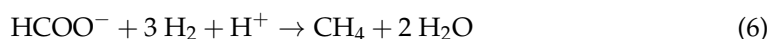
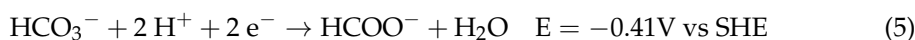
This reaction is unspontaneous, which requires an energy supply from an external source to attribute the electron's flow [35]. A recent study has supplied different voltages of 0.1, 0.3, 0.5, 0.7, and 0.9 V to investigate the possible methane synthesis pathway in bioelectrochemical anaerobic digestion (BEAD). Their findings indicate four possible routes of hydrogenotrophic methanogen for methane production, which are (1) hydrogenotrophic methanogenesis by cathode-attached archaea such as *M. flavescens* or *M. thermautotrophicus*, which produce  $CH_4$  using  $H_2/CO_2$  that has been produced through fixed or suspended biofilms, (2) hydrogenotrophic methanogenesis via suspended biofilms of archaea, (3) electrochemical hydrogenotrophic methanogenesis via archaea fixed to the cathodic electrode, which may accept  $e^-$  from the electrode and produce  $CH_4$  by utilizing  $H^+/CO_2$  in anode reaction, (4) hydrogenotrophic methanogenesis by DIET, in which they produce  $CH_4$  by the cooperation of fermentative microbes such as *A. halophilus* or *C. saudiense* [36].

**By formate and acetate:** Some other mediators, mostly formate and acetate, could be produced biochemically or bio-electrochemically, as shown in Equations (3)–(6). Then, the mediators are transformed into CH<sub>4</sub> via methanogens [37,38]. Both formate and acetate may be produced biochemically during the acetogenesis process by oxidizing propionate and butyrate [12]. The e-transfer by formate is sometimes considered the significant path of e-exchange. The role of formate as a mediator has been proven in a reactor treating whey; the primary electron transfer mechanism in flocs was by formate 90 μM formate per hour rather than hydrogen [39].

Acetate-mediated methanogenesis:



Formate-mediated methanogenesis:

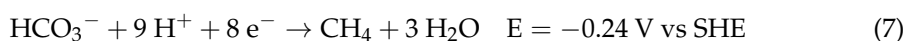


Even though formate and hydrogen have the same principle of e<sup>−</sup> transfer to methanogenic archaea, their chemical and physical properties are different in a way that favors hydrogen over formate. Due to the lower solubility of hydrogen compared to formate, hydrogen creates a high concentration gradient between the syntrophic microorganisms. In addition, the diffusion rate of hydrogen is larger than the formate diffusion. The rate of diffusion caused by the mediators has been significantly restricted by the concentration difference at which redox reactions are thermodynamically possible [40]. To facilitate the growth and metabolism of syntrophic microorganisms, H<sub>2</sub> or formate (HCOO<sup>−</sup>) will be utilized as a reducing agent by methanogens quickly. Hydrogenotrophic methanogenesis consumes hydrogen at very low concentrations, whereas hydrogen-producing bacteria's metabolism is inhibited at high hydrogen concentrations. Therefore, hydrogenotrophic methanogenesis is also inhabited [31]. For instance, a study using H<sub>2</sub>/CO<sub>2</sub> as a substrate shows that the diffusion of H<sub>2</sub> and its accumulated partial pressure directly affect hydrogenotrophic methanogenesis. The same study has concluded that CH<sub>4</sub> production is mainly caused by the mass transfer of accumulated molecular H<sub>2</sub> rather than the biofilm activity or voltage supply, where the electron produced in the anode is used to produce H<sub>2</sub> [35].

Apart from H<sub>2</sub>, formate and acetate are significant electron transfer agents, and other mediators exist, such as flavins and humic substances. One strategy could favor the production of CH<sub>4</sub> by increasing the accumulation of intermediate by-products, such as H<sub>2</sub> and CH<sub>3</sub>COO<sup>−</sup>. Nevertheless, recent studies show that electron transfer could be possible without a mediator through DIET [41,42].

## 2.2. Direct Interspecies Electron Transfer

DIET is a mutualistic interactive (syntrophy) metabolic process in which metabolically produced electrons have been exchanged directly between the microbial cells using no external redox mediators, such as molecular H<sub>2</sub> or formate. Studies showed that some microorganisms could exchange electrons in direct contact, requiring no mediator to shuttle electrons (Figure 1b) [27,43]. In this process, CO<sub>2</sub> is reduced to CH<sub>4</sub> by methanogens that directly utilize the electrons (Equation (7)).



In the last decade, studies summarize three specific mechanisms that have been identified for DIET. The DIET has been achieved by (1) microbial conductive nanowires [44], (2) electron transport proteins [45], and (3) conductive materials (CMs) [46].

(1) By nanowires (e-pili or conductive filaments): The concept of conductive filaments or pili was first discovered in *Geobacter* sp. (*Geobacter metallireducens* and *Geobacter sulfurreducens*). *Geobacter* is a recognized anaerobic metal oxidizing species that is capable of exchanging electrons directly through the electroactive conductive pili (e-pili) [47]. The conductive pili are considered one of the key cellular organs for extracellular  $e^-$  transfer to reduce the electron acceptors outside the cells or at the anodes [19,48]. The study revealed that the electron transfer between bacterial species through DIET in the AD process eliminates the need for  $H_2$  as the principal interspecies electron transporter. However, the DIET can also occur in aerobic conditions where the terminal electron acceptor could be oxygen, proton, nitrate, or sulfate, unlike  $CO_2$  in anaerobic conditions. The efficient way for DIET is that the exoelectrogenic microbes should be close enough to transfer the electron to electrotroph microbes. However, the study also revealed that the maximum distance covered by the pili was one centimeter.

(2) Conductive proteins or c-cytochromes: Another DIET occurs through the conductive redox proteins. The outer membrane c-type cytochrome of some electroactive bacterial communities is capable of transferring electrons from  $e^-$ -donating bacteria to  $e^-$ -accepting bacteria using electro-motive force [44]. For example, in syntrophic co-cultures of *G. sulfurreducens* and *G. metallireducens*, electrons were transferred via membrane-bound structures (c-type cytochrome) that acted as biological electrical connections. *Methanosaeta* and *Methanosarcina* are the only genera of methanogens with membrane-bound cytochromes that can significantly play a role in DIET [49]. However, most methanogens, including other *Methanosarcina* species, lack membrane-bound multiheme cytochromes like MmcA and require different mechanisms for transferring electrons [45].

(3) Externally added CMs: The third type of DIET production of methane was observed in AD-containing CMs [50]. CMs, such as hydrochar and granular active carbon (GAC), provide a surface for cell attachment, thus increasing the exchange of electrons. For instance, GAC acted as an electrical conduit for DIET between *G. metallireducens* and *G. sulfurreducens*, enabling electron sharing between the two species, even when the co-culture was initiated with *G. sulfurreducens* strains that were incapable of producing pili or the pilin-associated c-type cytochrome OmcS [51]. These materials have higher conductivity than organic and biological materials (i.e., conductive c-cytochromes and e-pili); thus, CMs are preferentially used for IET. Particularly, the utilization of CMs is beneficial for facilitating long-distance electron transfer as CMs provide higher conductivity between cells than bio-electrical connections. Furthermore, DIET through CMs presents an ecological benefit compared to DIET through biological connections since synthesizing extracellular electron conduits (e.g., conductive nanowires) necessitates a large energy investment. For example, the IET between fermentative bacteria and methanogens archaea was improved in an anaerobic digester assisted with graphite felt, which resulted in enhancement in the organic matter removal and biogas production [36]. The details about the efficiency of other CMs are discussed in Section 3.

It is worth highlighting that DIET is more energy-efficient than IIET, as the latter consumes energy during intermediates and electron transfer formation. For example, Tan et al. (2021) reported that DIET-dominated systems showed three-fold higher methane yield rates and accelerated digestion of oleate compared to IET-reliant systems [52]. However, there are some energy losses in DIET, which can be traced to the electron transfer energy requirements of electron-donating and electron-accepting redox cofactors [40]. Also, the

IIET can cause VFA accumulation and ammonia accumulation, which will prevent methane generation and affect the efficiency of the AD system.

### 3. Types of Conductive Materials Applied in Anaerobic Digestion

Conductive materials serve as the backbone of the electron transfer mechanism via nonbiological connections, which facilitate the electron transfer between the exoelectrogenic fermentation bacteria and the electrophilic methanogenic archaea [53,54]. The addition of CM could improve AD’s overall performance, including organics removal efficiency, VFA utilization, and methane production [55,56]. During the past decade, researchers have used various configurations of CMs, including conductive particles, conductive powders, and conductive electrodes, to boost the methane production rates from the AD system [57]. According to the Scopus database ([www.scopus.com](http://www.scopus.com)), using “Conductive materials for anaerobic digestions” as a keyword, more than 145 articles were published throughout (2015–2025). The search was narrowed by focusing on particles form of carbon-based CM (Table 1), metals-based CM (Table 2), and composited conductive materials (Table 3). Further, the articles were screened and analyzed for relevant information, such as the size/dosage of conductive materials (Table 4) and substrate type with methane production.

CM physiochemical characteristics distinctly influence microbial communities and bio-electrocatalytic processes. Therefore, in selecting CMs, they must have specific features like large active surface area for more electron transfer, high electrical conductivity, extremely electrochemically catalytic activity, and good mechanical stability. In addition, they should be corrosion-resistant, low-cost, and environmentally friendly. Figure 2 summarizes different materials used as external conductive materials in 2015–2025. The most widely used materials can be classified into three groups: (i) carbon-based materials, (ii) metal-based materials, and (iii) composite materials of both carbon and metal additives.

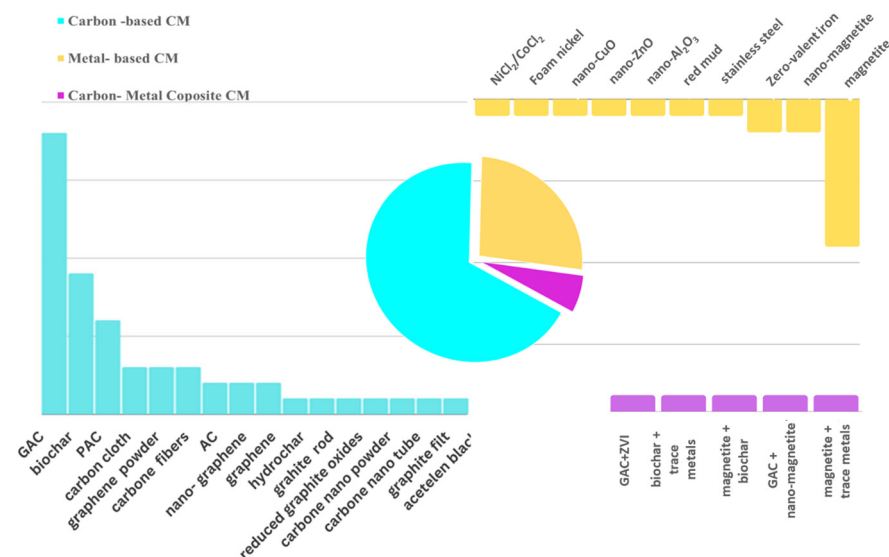


Figure 2. Different external conductive materials used in different studies (2015–2025).

#### 3.1. Carbon-Based Materials

Carbon-based materials are generally used as additives as they provide high electrical conductivity, good biocompatibility, and high corrosion–mechanical strength resistance [58,59]. Carbon materials show a wide range of electron transport properties, which have stimulated basic research and application for the development of microbial electrochemical systems (MESs). The electrical properties of carbon materials are strongly correlated with structural features. The charge transfer may vary from 1D structures to 3D structures [60]. Furthermore, the structural variability of carbon materials allows them to

be used in various forms in BES [61]. Carbon-based CMs, such as carbon felt [62], cloth [63], fibers [64], and graphite rods [65], can be fabricated and manipulated to generate unique properties and provide unique CMs. For example, the graphite felt (compared to stainless-steel bar) improves the DIET between the syntrophic microorganisms for organic waste removal and production of biogas [36]. Additionally, carbon materials can be produced in large quantities at a low cost, making them an ideal option for affordable applications in energy generation devices such as BESs [58].

As illustrated in Figure 2, the widely held studies have primarily focused on the impact of carbon-based CMs to enhance AD performance. Figure 2 shows that the most commonly used carbon CM are granular activated carbon (GAC) and biochar. Biochar is a carbon-rich by-product produced by the high-temperature combustion of biomass (between 300 and 1000 °C) in environments with limited oxygen levels in a process known as gasification or without oxygen as in pyrolysis, whereas GAC is a biochar that has undergone chemical or physical activation [66]. Even though biochar has a conductivity that is 1000 times lower than GAC, it promotes DIET in the co-cultures of *G. metallireducens* with *G. sulfurreducens* or *Methanosarcina barkeri* when ethanol was used as an electron donor [67]. However, its characteristics rely on the biomass source and various process conditions such as temperature, atmosphere, and heating rate [66,68,69].

Since the early efforts of applying CMs to AD, biochar and GAC have been widely used as absorbents for eliminating organic chemicals, metals, taste, and odors from waste and wastewater. Their conductive properties, along with their large surface area, high porosity, and surface chemistry that interacts with molecules possessing specific functional groups, enhance their capabilities as an adsorbent. As a result, GAC, as well as biochar, has four significant influences on the AD process: electroactive biofilm formation, reduced redox potential, DIET enhancement, and boosted methane generation [70]. GAC enhanced methane production by promoting DIET through the development of an electroactive biofilm; microbes attached to GAC, thereby reducing the interspecies distance between the syntrophic microorganisms, which improved the mass transfer (i.e., acids, H<sub>2</sub>) and facilitated the DIET, thus improving methanogenesis [70–72]. At the same time, it reduces redox potential from −223 mV to −470 mV. The methanogenic activity requires a redox potential of less than 200 mV. This activity is almost negligible when the redox potential exceeds 200 mV [73]. These findings indicate that adding GAC to biodigesters improves AD performance [70]. However, its ability to enhance AD performance should be explained in terms of a combination of substrate type and dose concentration, as these two components have a major influence on the CMs and could inhibit their performance.

The adsorption characteristics of biochar and GAC restricted the bioavailability of certain organic compounds, leading to a reduction in methane yield [74]. Yet, generating the specific intermediate metabolic compounds may inhibit methane generation in the digester; GAC could adsorb them and increase methane generation [72]. However, complex substrates, such as food waste, fat, oil, and grease, may restrict GAC function as a conductive conduit. For example, lipids may accumulate on the surface of GAC, thereby preventing electroactive bacteria from directly interacting with it [71,75]. To date, research on enhancing methanogenesis using GAC has primarily focused on analyses conducted in high-strength wastewater, such as waste activated sludge [76], food waste [73], and lipid-rich wastewater [71,77,78]. Their findings revealed that the main issue limiting GAC function in methane conversion was the low efficiency of acidogenesis. Therefore, these observations indicated that DIET was unlikely to be involved in the direct decomposition of complex organic waste, even in the presence of CM, but it might act efficiently if acidogenesis was fully functional [79]. Therefore, the concentration of CM additives must be correlated to the substrate type and strength (more details are discussed in Section 4.1).

Apart from GAC and biochar, other carbon CMs maintained a compatible performance in enhancing AD processes and methane production. Table 1 shows various carbon-based CMs treating several types of waste. Due to the variation in each experimental substrate properties, the operation condition, and data representation, each experiment has been analyzed separately. Each methane yield was compared to its control from the same experiment with the same operation condition and data representation, and % of enhancement in methane production was obtained. For example, Zhao et al. (2015) investigated the influence of several carbon-based materials, such as graphite rods, carbon cloths, and biochar, on CH<sub>4</sub> production from synthesized wastewater and found that CH<sub>4</sub> increased by 10%, 43%, and 33%, respectively [65]. These observations suggest variations in the effectiveness of carbon materials in increasing methane production.

Overall, while carbon CMs hold promise for enhancing AD processes by improving DIET and microbial activity, their large-scale application is limited by their relatively low electrical conductivity and mechanical strength [58]. In addition, the compatibility of carbon CMs with existing reactor materials and anaerobic digestion processes must be thoroughly tested. Some materials may corrode or degrade over time in the harsh anaerobic digestion environment, causing operational issues and possibly contaminating the digestate.

**Table 1.** Carbon-based conductive materials.

	Material	Reactor	Substrate	Methane CH <sub>4</sub> Production	% CH <sub>4</sub> Increased	Ref.
1	GAC PAC	UASB	Synthetic brewery wastewater	60% 70%	60 70	[12]
2	Graphite rods Carbon cloth Biochar	UASB	Artificial wastewater	23 mL 30 mL 28 mL	10 43 33	[65]
3	GAC	Continuous-flow AD	Synthetic wastewater	35.7 mL	78	[72]
4	GAC	TAD	Artificial dairy wastewater	1232.5 ± 27.8 mL	6	[79]
5	Carbon nanotube GAC	Batch	Glucose	0.48 mL/g VSS 0.67 mL/g VSS.	44 56	[80]
6	Graphene	Batch	Ethanol	695.0 ± 9.1 mL/g	25	[41]
7	Biochar	Batch	Food waste	92–110% of initial VFA	12.8	[69]
8	GAC	Batch	Nejayote wastewater	26 L/kg VS	34	[70]
9	Biochar	Batch	Swine manure	593.1 ± 50.4 mL	39	[81]
10	Carbon fibers	Batch	Propionate and butyrate	800 mL	100	[82]
11	GAC	Batch	Acetic acid Ethanol	176.7 (±1.4) mL 168.9 (±1.6) mL	31	[83]
12	GAC	Batch	Fat, oil, and grease	Max: 108 ± 11 L/kg VS	50–80	[71]
13	Graphite felt	ASBRs	Artificial wastewater	537.1 ± 6.4 mL/d	16.7	[25]
14	Carbon fibers	Batch	Ethanol	205 ± 32 mL/g sCOD	50	[64]
15	GAC	UASB	Raw incineration leachate	0.27 m <sup>3</sup> /kg COD	-	[84]

Table 1. Cont.

	Material	Reactor	Substrate	Methane CH <sub>4</sub> Production	% CH <sub>4</sub> Increased	Ref.
16	PAC	Batch	Brewery spent yeast	675 L/kg VS	69	[74]
17	Nano-carbon powder	Batch	Sewage sludge	593.94 mL/g VS	16.9	[85]
18	AC	Pilot-scale reactor	Food waste	413 ± 25 mL/g VS	88	[86]
19	Graphite powder AC	Batch	Glucose	750.9 mL 740.1 mL	−4 −5	[87]
20	GAC	Batch	Kitchen waste lipid–rapeseed oil	3300.6 nmol/L	10	[77]
21	GAC	Batch	Liquid swine manure Raw swine manure	23.6 ± 0.7 mL 165.7 ± 6.4 mL	33 10.8	[88]
22	GAC	Batch	Rural wastewater	16.7 mL	23.4	[89]
23	Acetylene black Hydrochar	Batch	Vinegar Residue	94.0 ± 20 mL/g VS 50.3 ± 18.5 mL/g VS	232 76.8	[90]
24	Nano-graphite GAC Carbon cloth	Batch	Waste fat, oil, and grease	168 mL 167.3 mL 179.3 mL	14 9 22	[78]
25	Biochar	Batch	Sewage sludge and food waste	335.7 ± 7.1 mL/g VS	23	[91]
26	Carbon fiber	Batch	Synthetic glucose	83 ± 3 mL/g COD	-	[92]
27	Biochar	Semi-continuous	Kitchen wastes	Max: 956.1 ± 65.7 mL	42	[93]
28	GAC PAC	Batch	Synthesized blackwater	Max: 318 ± 28 mL/g COD Max: 229 mL/g COD	8 −1	[94]
29	Biochar	Batch	Chicken manure	260 mL/g VS	31	[95]
30	Graphene oxide Carbonnanotubes	Semi-continuous	MSW and sewage sludge	0.211 NL/gVS 0.206 NL/gVS	13.4 10.7	[46]

GAC: granular activated carbon; PAC: powder activated carbon; AC: activated carbon; VS: volatile solid; UASB: up-flow anaerobic sludge blanket; TAD: two-phase anaerobic digestion; VSS: volatile suspended solids; ASBR: two anaerobic sequencing batch reactors; sCOD: soluble chemical oxygen demand.

### 3.2. Metal-Based Materials

Various Metallic conductive additives have been used in AD applications, such as stainless steel (plate, mesh, and scrubber), nickel sheet, and titanium plate. Metal-based electrodes were widely applied in bio-electrochemical applications due to their mechanical strength, low electric resistance, and easy fabrication. Nevertheless, they have a lower specific surface area than carbon-based materials and are susceptible to corrosion due to continual electron transport [96,97]. According to Figure 2, the most commonly used metal-based CM is magnetite (Fe<sub>3</sub>O<sub>4</sub>). It has gained attention in AD for its potential to enhance methane production. Magnetite electrical conductivity varies due to the mixed valence state of iron ions (Fe<sup>2+</sup> and Fe<sup>3+</sup>). The bulk magnetite is typically in the range of 10<sup>2</sup> to 10<sup>4</sup> S/m, while for nanoparticles, the conductivity varies widely and is often lower than that of bulk material. It can range from 10<sup>−1</sup> to 10<sup>2</sup> S/m, depending on the specific synthesis method, particle size, and surface characteristics [73,98]. Magnetite serves as an electron

shuttle and participates in redox reactions, which facilitate the electron transfer process. For instance, using magnetite during anaerobic treatment fed by tryptone increased  $\text{CH}_4$  production from acetate by 12.8% and accelerated the hydrolysis/acidification process [99]. Moreover, nanoscale magnetite particles improved  $\text{CH}_4$  generation from acetate in a dose-independent way while enriching unique microbial consortiums from paddy soil. However, increasing the magnetite concentration did not affect the lag phase time, methane yield, or production rate [100]. Table 2 shows the magnetite effect and other forms of metal-based CM effect on %  $\text{CH}_4$  compared to the control. It shows that magnetite has a positive effect in increasing methane generation. However, the percentage varies with the type of substrate and operation condition. Therefore, the use of magnetite as CMs in AD should be in consideration of these two variables. More details are discussed in Section 4.

Other forms of metal-based nanoparticles have significantly enhanced methane production through both DET and IET pathways. For example, nano zero-valent iron (nZVI) played a dual role by enhancing IET via hydrogen and DIET, which helped maintain the efficiency of AD for treating high-solid food wastes [101]. Furthermore, trace metals, also known as micronutrients, play a crucial role in AD processes. It provides bacteria with nutrients and improves enzyme activity, enhancing bacterial growth [11]. These metals, which include metals like iron (Fe), cobalt (Co), nickel (Ni), selenium (Se), molybdenum (Mo), and zinc (Zn), are essential for the metabolic activities of microorganisms involved in the AD process [102]. For example, the decomposition of complex organics with the addition of conductive Fe(III)/Fe(III)-Fe(II) oxides/sulfate was followed by considerable hydrogen generation, increasing hydrogen partial pressure, and enrichment of hydrogen-utilizing methanogens. These uncertain variables may restrict the use of Fe(III)/Fe(III)-Fe(II) oxides/sulfate in syntrophic metabolism via the conventional IHT [79]. For instance, a reduction of 2% in accumulative methane generation was noted upon the use of Fe(II) sulfate in comparison to control (Table 2). However, there were definite advantages of supplementing anaerobic digestion with Fe(III)/Fe(III)-Fe(II) oxides. Recent research has shown that Fe(III) oxides can expedite the decomposition of some recalcitrant contaminants into simple like benzene and its homologs in both pure and mixed cultures [103,104]. This may be considered a technique for improving biodegradability and reducing toxicity by degrading the resistant pollutants found in industrial effluent [79,105].

Although trace metals are essential at low concentrations, excessive amounts can be toxic to methanogens, impairing AD performance. The presence of nanometals in AD processes can be stimulatory, inhibitory, or even toxic, depending on their concentrations (Section 4.1). Adding metal-based materials generally resulted in a lower percentage increase in  $\text{CH}_4$  production, not exceeding 48% in most studies (as shown in Table 2). In some cases, such as in the study of [85], Table 2, the addition of nano-ZnO and nano-CuO led to reductions in methane production by 90.2% and 17%, respectively. Trace metals would adhere to the cell surface and those suspended in the water would generate reactive oxygen species (ROS) when interacting with water. Specifically, CuO produced superoxide anions, while ZnO produced hydroxyl radicals. Increased intracellular ROS levels can damage cell membranes and cause bacterial cytoplasmic leakage. In addition to the negative impact on proteins and cell intermediates, it demonstrates precisely why nano-CuO and nano-ZnO had negative effects on the AD process, particularly methane generation [85]. Similarly, treating primary sludge with the addition of  $\text{NiCl}_2/\text{CoCl}_2$  reduces methane by 3.9% compared to the control group due to the toxicity of trace elements, e.g., nickel (II), cobalt (II), and their mixture to microorganisms [106]. However, some studies show that  $\text{Al}_2\text{O}_3$  has a non-toxic impact on biogas and methane production [107,108]. Chen et al. report a 23.40% increase in methane production compared to the control (Table 2). This

might be due to the weak solubility, large surface area, and appropriate pore structure of trace  $\text{Al}_2\text{O}_3$ , which provides a good carrier for an anaerobic medium [85].

Overall, many scientists have worked on improving the surface area and conductivity of conductive additives to maximize the methane yield at a reasonable cost. The utilization of metal-based CMs in AD shows potential for increasing methane production. However, practical challenges such as toxicity, cost, and environmental sustainability must be carefully managed, and further research and practical evaluations are required to optimize its utilization and understand its long-term implications.

**Table 2.** Metal-based conductive materials applied in AD.

	Material	Reactor	Substrate	Methane Production	% $\text{CH}_4$ Increased	Ref.
1	Magnetite nanoparticles	Batch	Propionate	-	12	[109]
		CSTR	Butyrate	-	22	
2	Magnetite ( $\text{Fe}_3\text{O}_4$ )	TAD	Artificial dairy wastewater	$939.6 \pm 73.2$ mL	38	[79]
3	Magnetite ( $\text{Fe}_3\text{O}_4$ )	ASBR	Tryptone-based high-strength wastewater	$70.8 \pm 7.6$ mL	12.2	[99]
4	Magnetite	ASBR	Fischer–Tropsch wastewater	$7.46 \pm 0.24$ L		[110]
5	Red mud with 45.46% hematite	Batch	Waste activated sludge	$1.41 \pm 0.02$ mmol/g VSS	$35.52 \pm 2.6$	[111]
6	Magnetite	Batch	Fat, oil, and grease	Max: $72 \pm 9$ L/kg VS		[71]
7	Nano- $\text{Al}_2\text{O}_3$ Nano-ZnO Nano-CuO	Batch	Sewage sludge	627.11 mL/g VS	23.40	[85]
				49.57 mL/g VS	−90.20	
				420.03 mL/g VS	−17.30	
8	Foam nickel	Batch	Ethanol	Max: 94.5 mL/g	14.50	[27]
9	Zero-valent iron	Batch	Food waste	Max: 778.2 mL/g VS		[101]
10	Magnetite Iron(II) sulfate	Batch	Glucose	786.5 mL	1	[92]
				760.5 mL	−2	
12	$\text{Fe}_3\text{O}_4$	Batch	Antibiotic fermentation residue	280 mL/g VS	48	[112]
13	Zero-valent iron Magnetite ( $\text{Fe}_3\text{O}_4$ )	Batch	Sewage sludge and food waste	$272.6 \pm 11.0$ mL/gVS	45	[91]
				$394.0 \pm 6.3$ mL/g VS	16	
14	Nano zero-valent iron	Batch	Artificial wastewater	309.89 mL/g COD	24	[113]
15	Micron zero-valent Iron Micron-magnetite	Batch	Chicken manure	276 mL/g VS	31	[95]
				288 mL/g VS	37	
16	Red mud	Batch	Kitchen waste	75.31 mL/g VS	201	[14]

CSTR: continuous stirred tank reactor; VS: volatile solid; TAD: two-phase anaerobic digestion; VSS: volatile suspended solids; ASBR: two anaerobic sequencing batch reactors.

### 3.3. Modified Conductive Materials

Generally, the conductive additives are modified through various strategies to (i) enhance the surface area, (ii) enhance the biocompatibility of CMs, and (iii) improve electron transfer between microorganisms and the electrodes [114]. The commonly used

strategies include composite material, pretreatment of existing materials, the addition of nanoparticles, and functional groups [53].

An ideal external CM should have the following characteristics: high specific surface area, high conductivity, strong chemical stability (including corrosion resistance), excellent biocompatibility, exceptional mechanical strength, good processability and scalability, minimal environmental impact, including manufacturing footprint and recyclability, and inexpensive. However, both carbon-based and metal-based materials fail to fully satisfy these requirements. As a result, combining the best of these two materials with the best surface modification strategies can result in intriguing composite CMs. Recently, a composite material has been integrated to enhance the performance of CMs associated with AD. The composite CMs may be added as (i) carbon–carbon composite, (ii) metal–metal composite, and (iii) carbon–metal materials, as shown in (Table 3). Carbon felt, carbon paper, and carbon cloth have been used as additives to improve the surface area of electrodes [58]. For instance, a two-time increase in CH<sub>4</sub> production was reported in a microbial reverse-electrodialysis methanogenesis cell enhanced with a carbon-black-modified carbon cloth electrode [115].

As mentioned earlier, GAC/biochar application is constrained by the slow rate of hydrolysis and acidification. Magnetite has been shown in earlier research to facilitate hydrolysis and acidification while potentially inhibiting methanogenesis. Moreover, studies demonstrated that the addition of ZVI enhanced sludge treatment [116,117]. Feng et al. (2014) report that ZVI boosted the generation of VFAs by 37.3% during hydrolysis and acidification [118]. Therefore, GAC was modified by the addition of magnetite by the coprecipitation method to produce a novel material called magnetic granular activated carbon (MGAC). The MGAC demonstrated excellent conductivity, electron transfer rate, and CH<sub>4</sub> generation. The MGAC had a conductivity of  $(17.5 \pm 0.6 \text{ mS cm}^{-1})$ , which was 2.03 times higher than the GAC's  $(8.6 \pm 0.3 \text{ mS cm}^{-1})$  [119]. With the same concept, GAC coated with nZVI resulted in a 14.29% increase in CH<sub>4</sub> production (Table 3) and magnetite–biochar by 23% (Table 3).

Similarly, metallic electrodes are frequently used in BESs owing to their low electrical resistance and simplicity of fabrication. However, they could readily corrode due to continual electron transport [96]. On the other hand, carbonaceous electrodes offer strong corrosion resistance and are cost-effective. Therefore, to manage food waste in AD, a copper foam, which has exceptional mechanical strength and electrical conductivity, was incorporated with carbon nanotubes, a material with high bioaffinity and low electric resistance, through electrophoretic deposition and screen-printing techniques. The modified foam CM enriched and activated the electroactive bacteria, thereby activating the DIET for methane synthesis, resulting in 338.1 mL CH<sub>4</sub>/L vs. the control's 181.0 mL CH<sub>4</sub>/L. Furthermore, the modified foam CM has the advantages of both materials, suggesting a high potential for application in BES methane generation from food waste [120]. Adding composite CMs is a promising approach to enhance AD performance. However, more investigation is needed on composite materials that achieve the previous properties.

**Table 3.** Composite conductive materials applied in AD.

	Material	Reactor	Substrate	Methane Production Without Modifications	Methane Production with Modification	% CH <sub>4</sub> Increased	Ref.
1	GAC with nano-Fe <sub>3</sub> O <sub>4</sub> (magnetic granular activated carbon)	Batch	Low-strength wastewater	3.0 ± 0.4 mL, over a cycle	4.7 ± 0.2 mL	57	[119]
2	Biochar without trace metals Biochar + trace metals	Batch	Food waste	358.5 ± 21.2 mL/g VS	386.6 ± 16.8 mL/g VS	8 23	[102]
3	GAC and nZVI combined	Batch	Synthetic brewery water	—	Cum: 122.16 mL/g COD	14.29	[121]
4	Magnetite—biochar	Batch	Artificial dairy wastewater	No biochar (54.4 mg/day)	66.7 mL/day	23	[122]
5	ZVI/AC	Batch	Dichlorophen synthetic wastewater	20 mL	253.41 mL	1167	[15]
6	Biochar/ZVI	Batch	Chicken manure	210 mL/g VS	314 mL/g VS	50	[95]
7	g-C <sub>3</sub> N <sub>4</sub> /polyaniline *	Batch	Wastewater	60.5 mL	110 mL	82	[123]

Notes: GAC: granular activated carbon, VS: volatile solid, CUM: cumulative, COD: chemical oxygen demand, CNTs: multi-walled carbon nanotubes, \* carbon-carbon composite.

## 4. Operation Conditions Affecting Conductive Materials Performance

### 4.1. Effects of Sizes and Concentrations of Added Conductive Materials

Many recent studies have demonstrated that particle size and concentration of CMs influence AD performance [12,124,125]. The particle size of CMs significantly enhances methane production. Smaller CMs have a better surface area-to-volume ratio, which improves microbial colonization and electron transfer efficiency. This enhanced contact surface benefits microbial attachment and activity, resulting in improved anaerobic digestion efficacy [126]. For illustration, smaller-sized powder activated carbon (PAC) outperformed granular activated carbon (GAC) under higher organic loading due to the enormous mesopores in the PAC that facilitated the colonization of specific bacteria, like the syntrophic VFAs-oxidizing bacteria and *Methanosarcina* sp., which improved the syntrophic relationship between bacteria and methanogens [12].

Furthermore, nanoparticles (NPs) have shown significant potential because of their elevated surface area and conductivity. However, their use raises concerns regarding potential cell-level side effects. Studies have demonstrated that certain nanoparticles, particularly metal nanoparticles (Section 3.2), can adversely affect microbial communities, reducing their viability and activity [127]. NiCl<sub>2</sub>/CoCl<sub>2</sub> elements had minimal effects on the performance of AD at a dose of 10 mg/L, although toxic effects on methanogens were reported at a dose of 100 mg/L [106]. Mitigation methods and more studies into the effects of nanoparticles are necessary to ensure the safe and efficient utilization of these particles.

Nevertheless, the effect of CM depends on the concentration of particles added concerning the substrate available in the digester. Table 4 demonstrates the CMs with different dosages and the associated methane production with optimum dosage. For example, increasing GAC concentration up to 8.0 g/L significantly impacted the lag phase and peak

time for methane generation from oleate synthesis wastewater. However, no considerable impact was observed in the maximum methane yield in comparison to various GAC concentrations and controls [52]. Another study revealed that assisted black water with GAC (33.5 g/L) varied depending on the dilution factor applied during black water preparation; methane potential was enhanced by 53.1% in 1 L, while in 5 L and 9 L conditions, the methane production was remarkably reduced to 16.1 and 9.6%, respectively [128]. The effect of GAC varies depending on particle concentration added to the substrate available to be converted to methane. At a large amount of GAC, the adsorption of substances to GAC disadvantaged the AD steps before methanogenesis, depleting the substrate for methane production and ultimately causing process failure [52,128]. Therefore, reactors assisted with AC show higher efficiencies, mostly higher than 90%. TOC removal [12]. According to the data in this review, the optimal concentration of AC for treating synthesis waste feedstock is between 0.2 and 5 mg/L, while the optimal concentration for treating actual waste feedstock varies based on the complexity of the waste, with the optimal range being between 10 and 20 g/L.

As stated earlier, enhancing the carbon-based nanoparticles with the metal-based nanoparticles could solve the material's adsorption to GAC. Comparing various concentrations of GAC/nZVI in the synthetic brewery water AD (1.3 L) shows that the COD degradation and total CH<sub>4</sub> yield improved by 9.38% and 14.29%, respectively, at a concentration of 1 g/L. On the other hand, using composite GAC/nZVI at the same concentration reduced the methane yield [121]. Microbial community analysis indicates that adding GAC/nZVI increased total methanogen contents from 74.7% to 81.74% at the general level. Furthermore, it could neutralize certain VFAs to generate more H<sub>2</sub> and decrease the alkalinity, reducing CO<sub>2</sub> to CH<sub>4</sub>, resulting in higher methane production of about 26.9% compared to the control [129]. Applying a low concentration of CM could not be enough to increase methane production. For example, 0.1 g/L of HC failed to aggregate microorganisms. As a result, they were partially loaded on the HC surface, more scattered, and unable to interact effectively, resulting in lower methane yield [90].

However, even when adopting the optimal concentration, the material characteristics (electrical conductivity, surface area) are the key determining factors when comparing conductive materials. For example, it was observed that the optimal dose of graphene increased methane production than the optimal activated charcoal addition (even at a concentration of 20.0 g/L). The following factors can explain these findings: (1) graphene has a much higher electrical conductivity than activated charcoal, leading to improved electron transfer efficiency in DIET; (2) graphene has a much smaller micro size, resulting in a larger specific surface area and better contact with microorganisms [41]. Consequently, based on the type of waste, choosing the appropriate concentration of the external CMs will significantly influence the efficacy of anaerobic digestion. Hence, additional research should be conducted to identify the minimum effective dosage of CMs.

**Table 4.** Conductive materials with different dosages and the associated methane production with optimum dosage (\*).

	Material	Dosage (mg/L)	Reactor	Substrate	Methane Production	% CH <sub>4</sub> Increased	Ref.
1	Nano-graphene	30 120 *	Continuous-flow AD	Synthetic wastewater	12.8 ± 0.4 mL/g VSS/d	17 51.4	[130]
2	Powder activated carbon	1000	Batch	Primary sludge	150.6 ± 1.3 mL/g VS	10.8	[106]
		15,000 *			151.6 ± 1.3 mL/g VS		
		20,000			146.9 ± 1.2 mL/g VS		
	Graphite powder	200			150.7 ± 1.5 mL/g VS	13.70	
		100			150.7 ± 1.4 mL/g VS		
		500			149.0 ± 1.3 mL/g VS		
Magnetite	50 *	145.7 ± 1.3 mL/g VS	9.7				
	100	145.1 ± 1.3 mL/g VS					
	200	140.4 ± 1.3 mL/g VS					
NiCl <sub>2</sub> /CoCl <sub>2</sub>	10/10 *	137.2 ± 1.3 mL/g VS	−4				
	100/100	102.8 ± 0.8 mL/g VS					
3	Powder activated carbon	2240	Batch	Sewage sludge	211 mL/g VS	49	[131]
		4480					
	11,210 *	195.7 mL/g VS			7.80		
	2240						
Powder graphene	4480						
	11,210 *						
4	Granular activated carbon	10,000	Batch	Wheat husk and sewage sludge	263 mL/g VS	22	[59]
		20,000 *					
	30,000	273 mL/g VS			27		
	40,000						
GBC	50,000						
5	Granular activated carbon	0/0.5/2 */4/ 8/16/25/33	Batch	Lipid-rich wastewater (oleate)	2980.7 ± 185.5 mg CH <sub>4</sub> COD/L	31	[52]
6	Reduced graphene oxide	10	Batch	Municipal organic solid waste	Max: 816 ± 14 mL/gVS	50	[132]
		20 *					
		30					
7	Nano-sized magnetite particles	4600	TAD	Acetate	0.96 mol CH <sub>4</sub> /mol acetate	80	[100]
		18,500					
		37,000					
		74,000					
8	Stainless steel	200	UASB	Artificial wastewater	159.9 mL/d	7.5	[133]
		500 *				24.6	
		800				10.8	

VS: volatile solid, UASB: up-flow anaerobic sludge blanket, reactors, cod: chemical oxygen demand, TAD: two-phase anaerobic digestion.

#### 4.2. External Voltage Supply in Conductive Matrix and Methane Production Potential

Voltage can be supplied to the CM to expedite the DIET between the syntrophic microorganisms to produce methane. According to Guo et al. (2017), supplying a voltage in the bio-electrochemical-assisted AD (BEAD) promotes the community structure of *Geobacter* sp. and *Methanosarcina* sp., which participate in DIET in the bulk sludge, producing 18% more methane than conventional AD. As a result, BEAD improves process stability and the efficiency of methane production [134]. Similarly, higher methane production rates were obtained when introducing voltage supply to food waste and acetate digesters. The

voltage affects the DIET, which promotes methane production [35]. Table 5 summarizes the previous study of bio-electrochemical performance in AD systems.

Furthermore, two sets of anaerobic reactors were used to interpret the impact of voltage on the DIET via CM, either with or without voltage supply, on a pair of graphite rods as electrodes. The results indicated that a voltage supply of 0.39 V on the graphite rods in the anaerobic reactors could increase the methane production rate via hydrogenotrophic methanogens by 168% more than when no voltage was applied. However, the applied voltage led to a reduced amount of methane production, as some of the electrons transferred to the cathode were used for biomass synthesis instead of methane production. Meanwhile, in the reactors without applied voltage, methane production was primarily driven by DIET [135]. Park et al. (2020) reported similar experimental results, stating that the voltage supply has no significant effect on hydrogenotrophic methanogenesis. This indicates that electrons were not utilized to convert methane directly but to generate H<sub>2</sub> [35].

Studies have demonstrated that BEAD and AD performed similarly once the steady state was attained [136]. Consequently, studies highlighted that intermittent voltage supply was a more effective technique for improving BEAD's energy efficiency than continuous voltage supply [136,137]. Cho et al. (2019) conducted the first experimental study, presenting evidence that intermittent voltage supply showed 36.6% higher methane yield than continuous voltage supply. Furthermore, it increased the overall energy efficiency to 111% [138].

The experiment results showed that close circuits (CCs) produced significantly more methane than open circuits (OCs), with CCs producing 1.4 times more methane than OCs. Moreover, CCs were able to continue producing methane even when the applied voltages were reduced. To justify the results, the authors mentioned that the microbial communities and electron transfer pathways were already established. Therefore, accelerating biogas production in bio-electrochemical anaerobic reactors by starting with high voltage at first and then operating at low voltage might be an energy-efficient technique [34].

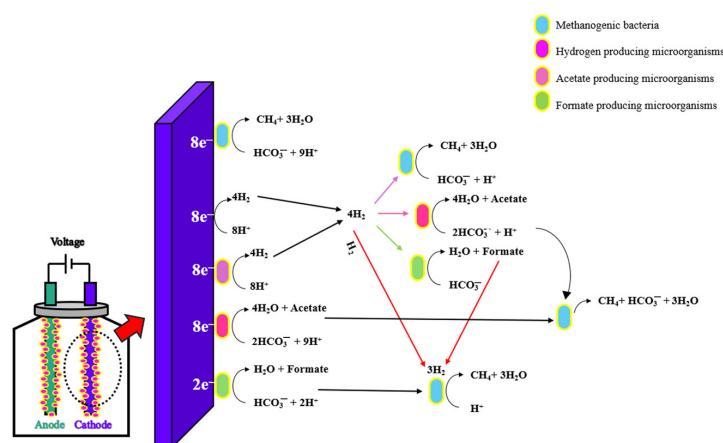
#### 4.2.1. Optimal Voltage Supply

The optimal voltage supplied on the cathode in a bio-electrochemical reaction depends upon the reaction's thermodynamics and the system's internal potential losses [36]. Previous studies suggested that applying voltage above an optimal range significantly inhibits microbial activity [7]. Thus, many studies have tried to supply a suitable voltage for the bio-electrochemical reaction on the electrode. For example, a recent study examining the influence of various voltage supplies on anaerobic digester performance assisted with the bio-electrolysis of agricultural waste combined with wastewater for biogas production. Their study applied several voltages, 20 mV, 40 mV, 80 mV, and 120 mV, to the digester (Table 5). The COD removal rate and organic conversion to methane increased at varied applied voltages. The optimal voltage supply was found at 40 mV, yielding  $175.17 \pm 81.39$  mL/g COD. However, the applied voltage changed the structure and population of the microbial community. Bacterial growth at the electrode can be inhibited by voltages above or below an optimal value, reducing methane yield [7]. Likewise, Yu et al. (2019) applied different voltage supplies from 0.1 to 0.9 V to treat swine manure (Table 5) [36]. They reported that the COD and TOC removal efficiency increased as the voltage rose from 0.1 to 0.7 V, affecting total biogas and methane yields. A reactor obtained the maximum biogas and methane yields with 0.7 V, 3081 mL/L, and 2175 mL/L, respectively. Since the methanogen and fermenter activity increased electrochemically in the BES, methane was produced from acetotrophic methanogens and hydrogenotrophic methanogens [36].

The variation in the optimal voltage range was probably due to the internal resistance differences caused by various electrode characteristics and reactor designs [139]. Therefore, the impact of voltage supply will vary from one system to another based on the BEAD system condition. Unfortunately, up to now, there is no quantitative knowledge of how these variables interact to affect BEAD performance.

#### 4.2.2. Cathode Potential

The applied cathode potential influences the structure of microbial communities in the BES [140]. Bio-electrochemical methane production from  $\text{CO}_2$  is possible through DET or IET through hydrogen, acetate, or formate (Figure 3). It has been reported that the cathode potentials for DET and IET-hydrogen are between  $-0.6$  V vs. NHE and  $-1.0$  V vs. NHE [30,141]. A study shows that methane could be produced by both DET and indirectly via bio-electrochemical hydrogen produced when a higher cathode potential of  $-0.59$  V vs. NHE was applied [142]. Generally, the standard cathode potentials for bio-electrochemical hydrogen and acetate productions are  $-0.41$  V vs. NHE and  $-0.28$  V vs. NHE, respectively. Another possible mechanism is the electrochemical reduction of  $\text{CO}_2$  to formate. However, the occurrence of such a reaction involves a low cathode potential of about  $-0.1$  V vs. NHE. Therefore, the reaction is implausible with a higher cathode potential [38]. The cathode potential defines the amount of energy available for bio-electrochemical reactions. Lower cathode potential (more negative values) empowers more energy to be used in bio-electrochemical reactions, resulting in higher production rates. A study used a cathode potential of  $-0.7$  V and  $-0.9$  V vs. NHE to investigate the mechanisms of bio-electrochemical methane production [38]. It was hypothesized that at  $-0.7$  V vs. NHE, electron transfer can be either directly or indirectly via mediators. Whereas at  $-0.9$  V vs. NHE, electron transfer is primarily indirect via hydrogen [30]. However, the results indicate methane is most likely generated indirectly through intermediates rather than through electron transfer at  $-0.7$  V vs. NHE cathode potential. Methane production was predominately by indirect hydrogen and acetate mediators, while no observation was found for formate mediators [38].



**Figure 3.** Bio-electrochemical  $\text{CH}_4$  production through DET and IET through hydrogen, acetate, and formate.

A major drawback of methane production using BESs is the need for a power source to supply enough voltage to overcome the significant electrode overpotential [115]. Furthermore, in terms of energy input, DIET requests the least minimum electrical energy input compared to all other mechanisms, followed by indirect electron transfer via formate, hydrogen, and acetate [143]. Therefore, producing methane directly rather than indirectly via  $\text{H}_2$ , acetate, or formate is preferable.

Table 5. Bio-electrochemical performance in AD system.

BEAD (Process Type)	Feedstock	Operation Condition	Anode Material	Cathode Material	T (°C)	Power Mode (V)	Methane Content in Biogas	Ref.
Direct biochemical methanation Hydrogenotrophic/ electromethanogenesis Hydrogenotrophic/ electromethanogenesis	Synthetic substrate	(1) Single large brush without electrodes (FB) (2) Half large brush with 2 electrodes operated in a closed circuit (HB-CC) (3) Half large brush with 2 electrodes operated in an open circuit (HB-OC) (4) Two electrodes with a closed circuit and no large brush (NB-CC)	Carbon fiber brush	Stainless- steel brush	35	0.8	253 ± 16 mL 240 ± 22 248 ± 15 232 ± 63	[34]
DIET DIET Hydrogenotrophic methanogenesis	Food waste Acetate H <sub>2</sub> /CO <sub>2</sub>	Testing for SMA of AD, BEAD, with voltage and without voltage	Graphite carbon mesh coated with Ni	Graphite carbon mesh (metal catalyst)		0.4	0.325 L/g 0.335 0.328 0.345 0.345	[35]
Hydrogenotrophic methanogenesis	Swine manure	V (0.1–0.9), and opt is (0.7), then opt (0.7) with different temperatures (25–45)	Graphite felt	Graphite felt	35 25 35 45	- 0.7 0.7 0.7	2197 mL/L 2229 2993 3691	[36]
Acetate methanogenesis	Wastewater+ wheat straw	Different voltage supplies 0.02–0.12 V	Graphite	Graphite	37	0.02 0.04 0.08 0.12	8270.28 ± 163.2 362.07 ± 480.2 16,349.17 ± 742.9 12,314.29 ± 626. 11,054.6 ± 480.6	[38]
Indirect methanogenesis via hydrogen and acetate	Mixed culture	Different cathode potentials –0.7 V and –0.9 V vs. NHE	Platinum- coated titanium mesh	Graphite felt	31 ± 1	–0.7 –0.9	5200 mL	[7]

Table 5. Cont.

BEAD (Process Type)	Feedstock	Operation Condition	Anode Material	Cathode Material	T (°C)	Power Mode (V)	Methane Content in Biogas	Ref.
Hydrogenotrophic methanogen Acetate methanogenesis	Synthetic wastewater	R1 (control)	Graphite rod (Gr)	(Gr)/(PPy) MnO <sub>2</sub> NPs/PPy	20 20 12	- 0.4 0.4	R1 (10.2 ± 0.8)	[144]
		R2 (graphene/PPy)					R2 (13.0 ± 1.8)	
		R3 (MnO <sub>2</sub> nanoparticles/PPy) at 3 phases					R3 (14.3 ± 1.4)	
		P1 (0 V/20 C) (0.4 V/20 C) (0.4 V/12 C)					R1 (21.7 ± 0.5) R2 (27.2 ± 1.8) R3 (30.0 ± 1.1) R1 (12.3 ± 1.1) R2 (27.2 ± 1.8) R3 (17.1 ± 0.8)	
Hydrogenotrophic and H <sub>2</sub> -dependent methylotrophic methanogens	Food waste	R1 (1–364 d), OLR (2–3) R2 (365–598 d), OLR (4.0) R3 (599–795 d), OLR (6.0) R4 (796–950 d), OLR (8.0) R5 (951–1086 d) OLR (10) kg/m <sup>3</sup> ·d	Graphite carbon mesh coated with Ni	Graphite carbon mesh coated with Ni (metal catalyst)	35	0.5	18.6 ± 0.9 L/d 35.0 ± 2.6 52.6 ± 4.3 65.0 ± 4.3 75.8 ± 3.2	[145]
H <sub>2</sub> -dependent methylotrophic methanogens. Hydrogenotrophic methanogens.	Food waste	R1 (electrodes w/biofilm) R2 (electrodes w/biofilm) R3 (electrodes w/biofilm) R4 (electrodes w/obiofilm)	Graphite	Graphite	35	0.3	62.1 ± 2.1 L/d 18.5 ± 2.8 13.0 ± 0.4 not produced	[146]
H <sub>2</sub> -dependent methylotrophic and hydrogenotrophic methanogens	Food waste	R1 (2.0) kg-COD/m <sup>3</sup> . d R2 (3.0) R3 (4.5) R4 (6.0)	Stainless- steel SUS304	Stainless- steel SUS304.	19.8 ± 2.9	0.3	0.24 ± 0.07 L/d 0.34 ± 0.07 0.42 ± 0.12 0.15 L/d	[147]
Indirect methanogenesis	Food waste	R1 (2) R2 (4) R3 (6) OLR (kg COD/m <sup>3</sup> . d)	GC coated with Ni	GC coated with Ni, Fe, and Cu	35–37	0.5	16 ± 4.59 35 ± 3.87 53 ± 6.32	[148]

R: reactor, COD: chemical oxygen demand, W/: with, OLR: organic loading rate, NPs: nanoparticles.

## 5. Critical Analysis of Conductive Materials Applications

Regardless of the successful experimental application of DIET in AD through the addition of CMs, demonstration projects and amplification studies have shown potential improvements in methane production. However, these studies lack comprehensive data to confirm DIET as the primary mechanism, and experimental verification remains insufficient. Due to the complexity of reactor operation control, it is difficult to ensure that CMs influence the designated AD system. The effect of applying CMs varies with different operating parameters, such as temperature, organic loading, and feedstock type [43]. These inconsistencies can be related to the conductive additive's various physical and electrical characteristics, impacting their interactions with microorganisms and electrocatalytic activity [69,82]. For instance, DIET helped balance the syntrophic metabolism rate under temperature shock [80].

Anaerobic digestion is typically supplemented with CMs; however, this approach is not economically scalable. The cost of producing and manufacturing CMs is an important concern in their large-scale application. Generally, carbon-based materials are cheaper than metal-based materials. Biochar production is easy and inexpensive compared to other CMs, considerably decreasing labor expenses. However, yet, biochar cannot be reused. Other carbon-based materials, such as carbon cloth, stabilize operations for longer periods, considerably lowering operating expenses [149]. Although carbon nanotubes and graphene have been discovered to enhance DIET substantially, their production costs are rather costly, making large-scale adoption economically prohibitive. For example, adding 1 g/L of carbon nanotubes to an anaerobic reactor system cost around USD 100,000/m<sup>3</sup>, which is substantially more expensive than adding 50 g/L AC (USD 15–150/m<sup>3</sup>) [26]. As a result, bio-based carbon materials such as biochar, AC, and carbon cloth are the ideal additions to AD systems due to their low preparation costs and ability to be prepared directly from waste biomass. Magnetic-biochar is a composite material made of magnetic iron and carbon with lower operational costs than biochar or AC in AD systems. However, plenty of study is still necessary to uncover the roles of the various materials functionalities and to preferentially integrate more effective ones. Furthermore, the carbon material's stability is critical and must be related to its structure, porosity, and surface chemistry. Understanding the degradation mechanisms of the carbon material and other composite is difficult and unsolved.

The processing of materials is another relevant topic from a technological point of view. For instance, integrating carbon materials into other components to design functional or structural materials is critical in transferring fundamental knowledge into technological applications. This is especially important when attempting to apply new nanomaterials or composite nanomaterials. Because of the nanometer scale size of the particles, handling the materials can be extremely difficult in many cases, requiring special body protection. The conductive material may be lost during the digester discharge. Yet, there is no effective method to prevent the material washout during the discharge. Recycling and reuse of conductive materials may be an effective strategy, but the complex technical operation and high investment cannot be ignored. Some studies have suggested that conductive materials designed as packed beds inside the reactor should be considered to promote DIET continually. However, this approach usually incurs considerable costs for the maintenance of equipment and construction of the reactor.

Introducing CMs into AD reactors enhances methane production and system stability but raises several environmental concerns, such as material persistence, accumulation, and downstream environmental contamination. CMs can modify the characteristics of the resulting digestate. Potentially making further treatment easier or more difficult, it is essential to evaluate the impact on downstream processing before using this approach

on a large scale. For example, some CMs, such as carbon-based materials (e.g., AC, graphite) or metal oxides, are non-biodegradable and may accumulate in ecosystems if not properly managed. Reusability challenges and incomplete recovery could lead to long-term environmental contamination; for instance, the leaching of heavy metals or residual nanoparticles into effluent streams could contaminate water bodies or agricultural soils, posing risks to aquatic life and human health. Moreover, the adsorption properties of materials like AC may strip nutrients or bind to beneficial organic compounds. Current studies emphasize the need to optimize material dosage, improve recovery methods, and assess long-term ecological impacts. Combining chemical–biological treatments or developing biodegradable alternatives could reduce risks.

Scaling CM-assisted AD required rigorous environmental and economic evaluations to ensure sustainability. There are limited techno-economic analyses (TEAs) specifically addressing the scale-up of CM-assisted AD. Most existing TEAs focus on conventional AD or co-digestion processes without incorporating the costs and benefits specific to CMs. This highlights a significant gap in understanding the economic viability of scaling up CM-assisted AD systems. However, preliminary TEA was performed by Tiwari et al. (2021) to assess the use of GAC and GBC in thermophilic anaerobic co-digestion of agro-waste [59]. They found that these materials improved biogas yield and process stability, and their preliminary TEA indicated that their addition may not be economically feasible without further innovations in material engineering or cost-reduction strategies. Furthermore, no existing LCA studies specific to CM-assisted AD are directly cited in the provided literature, indicating a critical research gap. Techno-economic analysis and LCA are critical to ensure that the environmental benefits of enhanced biogas production outweigh the potential emissions or resource use associated with CM production and disposal before scaling up.

The primary focus for advancing CM-assisted AD technology should ideally balance material optimization, reactor design, and techno-economic analysis (TEA), as each plays a critical role in addressing different challenges. However, the emphasis depends on the current stage of development and specific bottlenecks in the technology. However, if resources are limited, the initial focus should be on material optimization, which forms the foundation for improving reactor performance and overall efficiency. Once robust materials are identified, efforts can shift toward optimizing reactor design to maximize their potential. Finally, TEA should be continuously performed to guide decisions and ensure economic viability throughout the development process.

## 6. Conclusions

AD process is a well-implemented conventional sludge treatment technology instead of much operational inhibition, such as VFA accumulation, insufficient interspecies electron transfer, and ammonia accumulation. AD with CMs will provide a large and stable surface for electron transfer and microbial colony growth, as well as a stimulator for buffering capacity and an increase in DIET between methanogens and fermentative bacteria. The principle of electron transfer is well described in this article and the changes in the electron transfer path are well presented. The impact of CM type and their doses are well represented; however, dosage optimization needs to be explored more in the future. The excessive dosage could also inhibit the AD process. More work on cost-effective conductive materials and techno-economic analysis of the CM-assisted AD should be conducted. A thorough investigation of the relationships between CM physicochemical properties and AD performance is urgently required. To implement CM-assisted AD on a pilot scale and an industrial scale, an energy balance and life cycle assessment study needs to be performed. To know more about the efficiency of CMs, fed-batch and continuous studies should be conducted.

**Author Contributions:** Z.A.H.: Conceptualization, Methodology, Software, Validation, Writing—Original Draft; J.K.N.: Writing—Review and Editing, Supervision, Conceptualization; N.J.A.B.: Visualization, Review and Editing; A.A.-M. and K.S.: Supervision, Writing—Review and Editing. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Data Availability Statement:** Data are unavailable.

**Acknowledgments:** The authors would like to acknowledge Sultan Qaboos University (SQU), Central Instrumental Lab.

**Conflicts of 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. All authors confirm that they have no conflicts of interest to declare.

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