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Review

Overview of Enhancing Sludge Anaerobic Digestion Through Exogenous Materials: From Non-Recyclable to Recyclable Materials

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Abstract

The introduction of exogenous materials offers a highly promising technical approach for enhancing the performance of sludge anaerobic digestion (AD). This review systematically presents the mechanisms and application effects of carbon-based materials, metal-based materials, inorganic mineral materials, and metal–carbon composites in enhancing sludge AD. In-depth mechanism analysis revealed that these materials primarily enhance both methane yields and system stability through multiple synergistic mechanisms, such as mediating interspecies electron and proton transfer, promoting biofilm formation as microbial carriers, and adsorbing inhibitors while enhancing the buffering capacity of the system. However, a critical analysis indicated that the inherent limitations of various materials in engineering applications, particularly in terms of stability and recyclability, are the fundamental obstacles hindering the engineering implementation of this technology. Based on the above analysis, this review further proposes that the field is shifting from a sole pursuit of efficiency enhancement to a paradigm that balances efficiency and sustainability. Developing new recyclable and circular material systems with both high efficiency and excellent recycling potential is crucial for promoting the development of sludge AD technology towards a green, low-carbon, and resource-cycling direction, and also provides key scientific and technological support for the circular economy transformation of the sludge treatment system.

Keywords: anaerobic digestion; exogenous materials; sludge; recyclability; electron and proton transfer; magnetic materials

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1. Introduction

With the acceleration of global urbanization and the widespread adoption of wastewater treatment facilities, the generation of waste-activated sludge continues to rise, posing a significant challenge for its safe, efficient, and resource-oriented disposal [1]. Anaerobic digestion (AD) is a highly promising sludge treatment technology capable of simultaneously achieving sludge stabilization, reduction, and energy recovery in the form of methane [2]. However, conventional sludge AD often faces intrinsic limitations, including the complex structure of sludge, low hydrolysis efficiency of organic matter, and poor system stability, resulting in relatively low methane yields (average methane yield < 40% of the theoretical value) and a long reaction cycle (>20 days) [3]. To overcome these limitations, the addition

of exogenous materials to the AD system has emerged as an effective enhancement strategy [4]. These materials primarily optimize microbial community structure and strengthen metabolic pathways through facilitating interspecies electron and proton transfer, serving as microbial carriers [5], adsorbing inhibitory substances, and enhancing system buffering capacity, thereby improving overall AD performance [6].

To date, extensive research has been conducted on various exogenous materials to enhance sludge AD, encompassing carbon-based materials [7], metal-based materials [8], inorganic mineral materials [9], as well as more structurally and functionally complex metal-carbon composite materials [10]. Nevertheless, most materials face practical challenges related to non-recyclability, susceptibility to loss, high costs, or potential secondary pollution, which hinder their large-scale and sustainable engineering application. Consequently, research on AD enhancement materials is undergoing a shift from a single-use paradigm toward a concept of recyclability and circular utilization. The development of novel materials that combine high enhancement efficiency with excellent recovery potential is crucial for advancing sludge AD technology toward greener, low-carbon, and sustainable development.

This review aims to systematically summarize research progress on the enhancement of sludge AD by exogenous materials, with a particular focus on elucidating the evolving trend from non-recyclable to recyclable material systems. To ensure transparency and reproducibility, a systematic literature search was conducted using the Web of Science, Scopus, and Google Scholar databases, covering the period from 2000 to 2025. The search employed keywords including "anaerobic digestion", "sludge", "exogenous materials", "carbon-based materials", "metal-based materials", "inorganic minerals", "metal-carbon composites", "recyclable materials", "interspecies electron transfer", and "direct interspecies electron transfer". Studies were included if they focused on the application of exogenous materials in sludge anaerobic digestion and reported relevant performance metrics (e.g., methane yield, volatile fatty acids (VFAs) conversion, microbial community shifts). Articles not written in English, conference abstracts, and studies lacking quantitative data were excluded. A total of 120 relevant studies were identified and critically evaluated. The remainder of this review is structured as follows. Section 2 outlines the fundamental principles and critical bottlenecks of sludge AD. Section 3 dissects the core mechanisms by which exogenous materials enhance AD performance, including electron/proton transfer, microbial immobilization, and adsorption/buffering. Section 4 critically evaluates the application effectiveness of various exogenous materials—categorized as carbon-based materials, metal-based materials, inorganic mineral materials, metal-carbon composites, and recyclable material systems—with particular attention to their enhancement performance and, where applicable, recoverability. Finally, the future design directions of recyclable materials are outlined in Section 5, aiming to provide a theoretical reference for the research, development, and application of high-performance, sustainable materials for AD enhancement.

2. Fundamental Principles and Critical Bottlenecks of Sludge AD

AD is a complex microbial process that converts organic matter in sludge into biogas under anaerobic conditions. This process essentially involves the sequential coupling and microbial synergy of four biochemical stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis [11]. During the hydrolysis stage, particulate organic matter is decomposed into soluble monomers. In the subsequent acidogenesis stage, these monomers are fermented primarily into VFAs, alcohols, methyl compounds, H_2, and CO_2. In the acetogenesis stage, syntrophic acetogenic bacteria further convert metabolic products into acetate and H_2. Simultaneously, methyl compounds are further transformed into small

molecular substrates such as methanol, methylamines, and dimethyl sulfide, which can be directly utilized by methanogens. Finally, methanogenic archaea generate methane through acetoclastic (Equation (1)), hydrogenotrophic (Equation (2)), or methylotrophic (Equation (3)) pathways [12]. The metabolic activities of microbial communities at each stage are tightly coupled, and their overall efficiency depends heavily on the efficient transfer of interspecies metabolites and energy [13].

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad (1)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 3H_2O \quad (2)$$

$$4CH_3OH \rightarrow 3CH_4 + CO_2 + 2H_2O \quad (3)$$

However, conventional sludge AD faces multiple bottlenecks in practical applications, which constrain its treatment efficiency and stability (Figure 1). Figure 1 illustrates the bottlenecks happened at each stage of AD. Firstly, the low efficiency of interspecies electron and proton transfer during the acetogenesis stage constitutes a thermodynamic bottleneck, as shown in Figure 1. In syntrophic metabolism, electron transfer between syntrophic acetogens and hydrogenotrophic methanogens relies on the diffusion of H_2 or formate, which is intrinsically slow and highly sensitive to hydrogen partial pressure [14]. This limitation often leads to VFA accumulation, thereby inhibiting the methanogenesis process [11]. Second, the system lacks sufficient shock resistance and environmental buffering capacity. When the organic loading rate increases or microbial metabolism becomes unbalanced, the production rate of VFAs may exceed their consumption rate, triggering a sharp decline in system pH (acidification) [6]. Concurrently, high concentrations of free ammonia (NH_3) generated from the degradation of nitrogenous organic matter, such as proteins in the sludge, can exert toxic inhibition on methanogens [15]. Finally, the retention of functional microorganisms and the stability of the community structure are challenging. Slow-growing methanogenic archaea are easily washed out in continuous-flow systems, and microorganisms lacking attachment carriers struggle to form dense syntrophic consortia, resulting in poor system resilience and slow recovery from disturbances [5]. These bottlenecks collectively lead to the common issues of low methane yield, prolonged reaction cycles, and operational instability in conventional sludge AD processes. From an economic perspective, these technical deficiencies translate into higher energy costs, increased reactor volume requirements, and reduced overall process profitability, which together limit the widespread adoption of conventional AD at industrial scale. To specifically overcome these limitations, the addition of exogenous materials with specific physicochemical properties has emerged as an effective enhancement strategy. A detailed discussion of the economic implications and life cycle considerations associated with the use of exogenous materials is provided in Section 5.

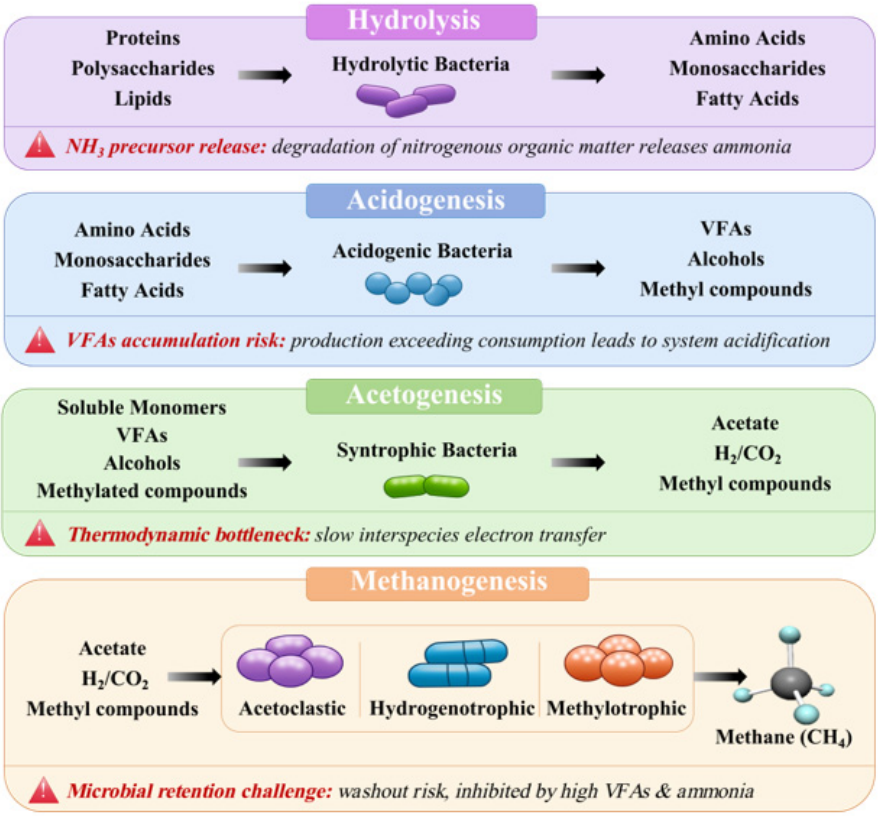

Figure 1. The basic principles and practical application bottlenecks of anaerobic digestion of sludge.

3. Mechanisms of Exogenous Materials in Enhancing Sludge AD

Currently, the relevant mechanisms of exogenous materials enhancing sludge anaerobic digestion are mainly classified into three categories (Figure 2): facilitating electron and proton transfer, microbial immobilization and biofilm formation, and providing system buffering and adsorbing inhibitors. The three major bottlenecks identified above—namely, the thermodynamic limitation of interspecies electron transfer, system instability caused by the accumulation of VFAs and ammonia, and the poor retention of functional microorganisms—correspond to three core reinforcement mechanisms of exogenous materials. As illustrated in Figure 2, conductive materials can overcome the thermodynamic barrier of electron transfer by mediating direct interspecies electron transfer. Materials with buffering capacity and adsorption functionality can neutralize acidic metabolites and immobilize inhibitory substances, thereby mitigating system acidification and ammonia inhibition. Meanwhile, materials featuring good biocompatibility and porous structures provide attachment sites for functional microorganisms, promoting biofilm formation and the construction of syntrophic consortia, thus enhancing microbial retention. These mechanisms are systematically discussed in the following sections.

3.1. Facilitating Electron and Proton Transfer

Extracellular electron transfer (EET) is a key microbial process in anaerobic digestion, enabling electron exchange across the cell envelope and thereby facilitating syntrophic metabolism and methanogenesis. In anaerobic consortia, EET not only supports the redistribution of reducing equivalents among functional microorganisms and maintains redox balance and energy flow, but also offers critical advantages. It accelerates electron flux between syntrophic partners, alleviates thermodynamic and kinetic limitations associated with VFAs oxidation, and enhances process stability by reducing dependence on diffusible carriers and strict low hydrogen partial pressure. These features promote tighter metabolic

coupling between fermentative bacteria and methanogens, ultimately favoring methane production. When EET occurs between different microbial species, it is referred to as interspecies electron transfer (IET) [16,17].

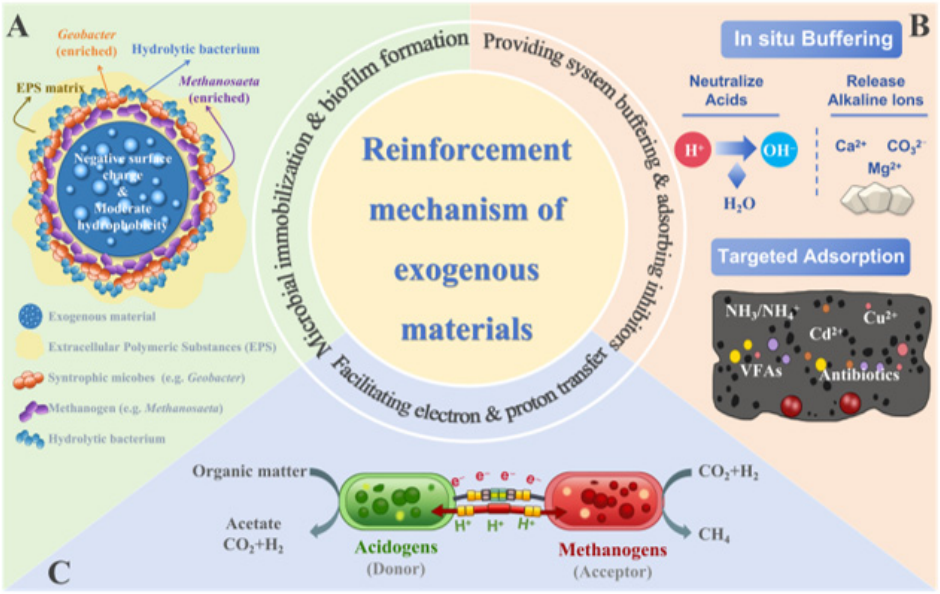

Figure 2. Reinforcement mechanisms of exogenous materials on anaerobic digestion of sludge. (**A**) Microbial immobilization and biofilm formation; (**B**) Providing system buffering and adsorbing inhibitors; (**C**) Facilitating electron and proton transfer.

In the complex microbial syntrophic network of anaerobic digestion, IET serves as the core energy transfer pathway driving the ultimate conversion of organic matter into methane [18]. During this process, electrons flow from donor microorganisms (e.g., acidogens) to acceptor microorganisms (e.g., methanogens) [19]. Efficient IET is crucial for overcoming the inherent thermodynamic barriers in syntrophic reactions. For instance, propionate oxidation is thermodynamically unfavorable under standard conditions ($\Delta G^{0\prime} > 0$), and only becomes exergonic when coupled with hydrogenotrophic methanogenesis and when hydrogen partial pressure is maintained below approximately 10^{-4} atm [14]. Therefore, IET sustains the redox equilibrium of the system, ensuring the rapid consumption of intermediate metabolites such as VFAs and the efficient synthesis of methane.

Currently, IET is understood to occur mainly through two mechanisms, including mediated IET (MIET) and direct IET (DIET) [20]. MIET relies on diffusible redox carriers to transfer electrons between microorganisms. Its primary forms include interspecies hydrogen/formate transfer (IHT/IFT) with H_2 or formate as electron carriers, and the electron shuttle mechanism utilizing small molecule redox mediators [21]. However, MIET efficiency is often constrained by carrier diffusion rates and environmental hydrogen partial pressure [22]. In contrast, DIET represents a more efficient and direct mode of electron exchange [23]. Electroactive microorganisms can directly transfer electrons to syntrophic partners through physical contact or via biological nanowires composed of conductive pili, without relying on soluble mediators [24]. This process primarily depends on cell-surface conductive components, specifically *c*-type cytochromes (*c*-Cyts) and conductive pili (e-pili) [25,26].

Modeling studies suggest that DIET can achieve electron transfer rates several orders of magnitude higher than MIET via hydrogen diffusion, particularly when intercellular distance is reduced through material-mediated aggregation [20,27]. Conductive materials with high electrical conductivity (e.g., graphene, magnetite) effectively mediate DIET, whereas materials with low conductivity primarily support MIET [28]. By minimizing

extracellular diffusion limitations and bypassing H_2 partial pressure constraints, DIET enables faster electron flux and reduces dependence on hydrogen/formate turnover. These features make DIET particularly advantageous in high-load or stressed anaerobic systems, where rapid electron dissipation is essential for maintaining microbial cooperation and methanogenic activity. Therefore, the promotion of EET, especially DIET, is widely regarded as a key biological basis for the enhancement of AD performance by exogenous conductive materials [27].

In addition to electron transfer, proton transfer is also a crucial factor influencing the efficiency of methanogenic metabolism [29]. The establishment of a proton motive force (PMF) serves as the direct driving force for microorganisms to synthesize adenosine triphosphate (ATP) via ATP synthase [30]. In many key biochemical reactions, electron transfer is coupled with proton translocation, which is known as proton-coupled electron transfer (PCET) [31]. By synchronizing the migration of charges, PCET effectively lowers the activation energy barrier of redox reactions and enhances energy conversion efficiency (Figure 3) [31]. PCET is widely found in respiratory chain complexes (e.g., Complexes I, III, and IV) and specialized enzyme systems in methanogens [32], such as heterodisulfide reductase (Hdr) [33].

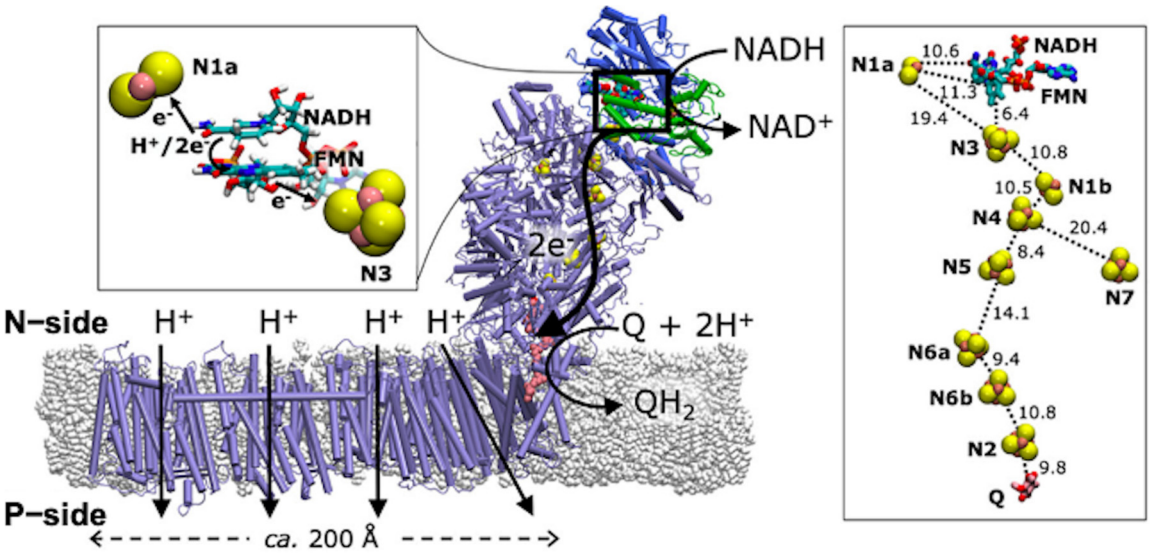

Figure 3. Proton-coupled electron transfer (PCET) in respiratory chain Complex I. Complex I (NADH: ubiquinone oxidoreductase) catalyzes NADH oxidation, transferring electrons through FMN and FeS clusters to reduce quinone (Q) to quinol (QH_2). Concurrently, this electron transfer drives proton pumping across the membrane, generating proton motive force (PMF) that powers ATP synthesis. This exemplifies how PCET synchronizes electron and proton flow to enhance energy conversion efficiency in methanogenic metabolism [31].

Recent evidence demonstrates that specific exogenous materials can facilitate PCET in sludge AD. For example, magnetic porous microspheres substantially increased cytochrome c content, F_{420} coenzyme activity, and proton motive force, indicating enhanced electron-proton coupling [5,34]. MOF-based composites improved both electron transfer and proton conductivity through their metal nodes and ordered pore structures, thereby accelerating acetate-to-methane conversion [35]. Biochar containing quinone/hydroquinone moieties undergoes reversible redox cycling, enabling simultaneous electron storage and proton buffering that supports PCET while maintaining local pH homeostasis [36].

Thus, efficient electron transfer coupled with robust PMF constitutes the core driving force of the methanogenesis process. The introduction of exogenous materials can optimize this electron-proton coupling process from multiple dimensions by providing

proton conduction sites, enhancing local buffering capacity, or regulating interfacial charge distribution, thereby synergistically improving the overall performance and stability of the system [5].

3.2. Microbial Immobilization and Biofilm Formation

Sludge AD systems often operate in a suspended state, where microorganisms are susceptible to washout with the effluent. This poses a significant challenge, particularly for key functional microorganisms with long growth cycles and slow replication rates, such as methanogenic archaea. The difficulty in achieving effective colonization and enrichment of these microbes severely constrains the long-term stability and metabolic flux of the system. The introduction of exogenous materials provides stable attachment carriers, effectively promoting microbial immobilization and biofilm formation through physical shielding and chemical induction [37]. The diverse physicochemical properties of exogenous materials serve as the core drivers for early microbial proliferation and colonization. The high specific surface area and porous structure of certain materials provide an ideal ecological niche for microorganisms, protecting them from hydraulic shear forces and washout [38]. Furthermore, the hydrophobicity and surface functional groups of specific materials interact with the hydrophobic components or charges on microbial cell membranes via electrostatic attraction and Van der Waals forces, thereby accelerating biofilm growth kinetics [39].

Biofilm formation is a process involving microbial attachment, proliferation, and the secretion of extracellular polymeric substances (EPS) on carrier surfaces, ultimately forming a structured and high-density microbial aggregate [40]. The interior of the biofilm develops unique microenvironmental heterogeneity, characterized by distinct substrate concentration gradients and redox potential gradients, which provide a spatial foundation for syntrophic interactions among microorganisms at different trophic levels [41]. For instance, in the outer layers of the biofilm, hydrolytic and acidogenic bacteria degrade macromolecular organic matter to obtain energy. In the inner layers, closer to the carrier surface, where anaerobic conditions are more stringent, hydrogen-producing acetogens and methanogens are densely enriched, significantly shortening the physical distance between species [5]. This compact spatial arrangement not only enhances the efficiency of IHT/IFT but also creates favorable microenvironmental and physical contact conditions for material-mediated DIET [42].

Material surface properties—particularly surface charge, hydrophobicity, and roughness—exert quantifiable effects on biofilm architecture and microbial community composition. Materials with moderately negative surface charge facilitate stable biofilm formation through electrostatic bridging with divalent cations (Ca^{2+}, Mg^{2+}) in EPS, while moderately hydrophobic surfaces (water contact angle 60–90°) preferentially enrich syntrophic consortia by balancing initial cell attachment and substrate diffusion [38,39]. High-throughput sequencing studies have revealed that conductive materials reshape microbial ecology by enriching electroactive bacteria such as *Geobacter* (relative abundance increasing from <1% to 3–8%) and DIET-capable methanogens such as *Methanosaeta* (increasing from 10–15% to 25–35%), while reducing the proportion of hydrogenotrophic *Methanosarcina* [19,21]. This community shifts toward DIET-based syntrophy, which correlates with enhanced methane production rates and improved process stability under high organic loading conditions.

In summary, by strengthening microbial immobilization, exogenous materials not only resolve the bottleneck of functional microbiota washout but also achieve efficient metabolic synergy by optimizing the spatial organization of the microbial community, thereby significantly improving the treatment efficiency and methane production rate of the AD system.

3.3. Providing System Buffering and Adsorbing Inhibitors

In practical operations, sludge AD systems frequently encounter challenges such as pH fluctuations [43], accumulation of intermediate metabolites [44], and inhibition by toxic substances [45], which severely compromise system stability and methane yield. Exogenous materials effectively enhance the buffer capacity and reduce the concentration of inhibitors through their unique ion exchange capacity, surface functional groups, and porous adsorption characteristics, thereby improving the shock resistance and long-term operational stability of the AD system [8,46].

Methanogens are remarkably sensitive to the environmental pH, with the optimal pH typically required to be maintained between 6.5 and 8.0 [47]. When the organic loading rate is excessive, leading to a VFAs production rate that exceeds the consumption rate by methanogens, a sharp drop in system pH may occur, causing acidification and inhibiting methanogen activity [48]. Certain exogenous materials possess alkaline or acid-base buffering capabilities, enabling them to neutralize excess acidic substances and maintain a stable pH. For instance, biochar exhibits superior pH buffering capacity due to the alkaline ash components and basic surface functional groups formed during its thermochemical production [39]. Similarly, some mineral materials can also stabilize the system pH through the slow release of alkaline substances (e.g., Ca^{2+}, Mg^{2+}, CO_3^{2-}) [49]. Additionally, some composite materials can also regulate the pH of the local microenvironment through the interaction between surface functional groups and protons, thereby further enhancing the acid-base balance ability of the system [50].

The degradation of nitrogenous organic matter, such as proteins in sludge, releases ammonia nitrogen (NH_3/NH_4^+) [51]. High concentrations of free ammonia can penetrate cell membranes, disrupting internal pH balance and enzyme activity [6]. Exogenous materials can effectively reduce the concentration of free ammonia in the system via physical adsorption, ion exchange, or surface complexation [51]. Adsorption studies under AD conditions reveal that materials exhibit varying capacities for inhibitor removal. For example, biochar-based materials demonstrate ammonia adsorption capacities ranging from 10 to 50 mg NH_3-N/g under typical AD temperatures (35–55 °C) and pH conditions (6.5–8.0), with adsorption behavior often following Langmuir or Freundlich isotherms [39,51]. Zeolites show higher selectivity for NH_4^+ through ion exchange mechanisms, achieving removal efficiencies of 60–80% even in the presence of competing cations (Ca^{2+}, Mg^{2+}, K^+) [52]. Additionally, metal ions released by certain metal-based materials during the reaction can form precipitates or complexes with ammonia nitrogen, further decreasing their bioavailability [53].

Beyond ammonia nitrogen, heavy metals, long-chain fatty acids, and antibiotics potentially present in AD systems can also inhibit microbial activity [54]. Leveraging their high specific surface area, abundant pore structures, and active surface sites, exogenous materials chelate cytotoxic organic molecules or heavy metals onto their surfaces or within their pores through physical collisions, hydrophobic interactions, and surface complexation [4]. Adsorption competition effects become significant in complex sludge matrices: VFAs and NH_3 compete for the same adsorption sites on biochar surfaces, with VFAs typically showing higher affinity due to stronger π-π interactions and hydrogen bonding with aromatic structures [4,55]. Multi-component adsorption studies indicate that the presence of VFAs can reduce NH_3 adsorption capacity by 20–40%, necessitating material design that balances multiple inhibitor removal [55]. This adsorption reduces the bioavailability of inhibitors in the aqueous phase, thereby mitigating direct damage to microbial cell membranes and intracellular metabolic enzymes [15,56].

Despite these benefits, it is important to recognize that certain exogenous materials may exhibit adverse effects under specific conditions. For example, graphene oxide (GO)

has been shown to exert dose-dependent cytotoxicity; concentrations above 50 μg/mL can inhibit key methanogenic enzymes such as coenzyme F_{420}, potentially offsetting its adsorption and conductivity benefits [57]. Similarly, excessive dosages of metal-based materials may lead to metal ion accumulation and secondary contamination risks [58]. These potential drawbacks underscore the importance of dosage optimization and material selection in practical applications.

In summary, exogenous materials effectively regulate the physicochemical environment of the AD system through the dual action of in situ buffering and targeted adsorption. This buffering barrier, in conjunction with biofilms, constitutes a multi-layered defense system against external shocks. This not only safeguards the stability of microbial community succession but also provides indispensable preconditions for efficient electron transfer processes. To provide a concise overview of the buffering and adsorption mechanisms discussed above, Table 1 summarizes the primary mechanisms, the most effective materials associated with each mechanism, and their corresponding limitations.

Table 1. Summary of buffering and adsorption mechanisms of exogenous materials.

Mechanism	Most Effective Materials	Limitations	References
pH buffering	Biochar (alkaline ash, surface functional groups); mineral materials (slow release of Ca^{2+}, Mg^{2+}, CO_3^{2-})	Biochar performance varies with feedstock; excessive Ca^{2+} release may cause scaling	[39,49]
Ammonia adsorption	Zeolite (ion exchange, 60–80% removal efficiency); biochar (10–50 mg NH_3-N/g capacity)	Competitive adsorption with VFAs can reduce capacity by 20–40%; regeneration required for long-term use	[39,51,52]
Heavy metal/inhibitor removal	Biochar (high surface area, surface complexation); activated carbon (porous structure, hydrophobic interactions)	Adsorption capacity limited by available surface sites; potential secondary pollution from spent materials	[4,54]
Potential toxicity concerns	-	Graphene oxide exhibits cytotoxicity at >50 μg/mL; excessive metal-based materials may cause metal ion accumulation	[57,58]

4. Performance Evaluation of Various Exogenous Materials

To better reflect the transition from conventional non-recyclable additives to recyclable material systems, the performance of exogenous materials is discussed below not only in terms of AD enhancement, but also, where applicable, in terms of recoverability and reuse potential.

4.1. Carbon-Based Materials

Carbon-based materials, including activated carbon, biochar, graphite, and graphene, have been widely investigated as exogenous additives for sludge AD because of their large specific surface area, porous structure, adsorption capacity, and electrical conductivity [7]. These properties allow them to function as microbial carriers, adsorb inhibitory intermediates, and facilitate extracellular electron transfer, particularly DIET [7,59]. In addition, their porous frameworks provide favorable attachment sites for syntrophic consortia and may shorten the lag phase of methanogenesis [59]. Table 2 summarizes the typical studies on the effects of adding common carbon-based materials on AD performance.

Table 2. Effects of conventional carbon-based materials on AD of sludge.

Carbon-Based Material	Size	Dosage (g/g VS)	Temp. (°C)	HRT (d)	Inoculum	Methane Increase	Lag Phase Change	VFAs Effect	Hydrolysis Effect	Key Mechanism	References
GAC	8–12 mm/ 1.70 mm	0.27–0.33	35–37	28–30	WAS	+13.1–17.4%	Reduced by up to 2.1 d or not reported	Enhanced consumption	No significant effect to +6.1% VS reduction	GAC as conductive carrier; enriched *Geobacter* and *Methanosaeta*; promoted DIET	[60,61]
PAC/Powdered biochar	0.075–0.08 mm/ <0.1 mm	0.05–0.72	37	20–30	WAS	+28–146%	Reduced by 2.3–4.1 d	Enhanced conversion	Not reported to +18–32%	Enriched DIET-associated microbes; surface functional groups mediate electron transfer	[62,63]
Digestate-derived biochar	-	0.15	37	21	WAS	+48%	Reduced from 6.76 to 4.89 d	Promoted transforma-tion	Accelerated bioconversion	Electron transfer via surface functional groups; quinone moieties act as electron shuttles	[39]
Biomass-derived biochar (corn stover, rice husk)	–/0.1–0.5 mm	0.10–1.0	35	24–28	WAS	+31.2–47.0%	Reduced by up to 3.2 d	Enhanced conversion	+25.3% to no significant effect	Redox-active moieties; enriched *Geobacter*, *Methanosaeta*, and *Syntrophomonas*; DIET establishment	[64,65]
Crayfish shell-derived biochar	-	0.10–0.25	35	28	WAS	No significant increase	Not reported	No enhancement	+10.6–34.0% (hydrolysis)	Accelerated solubilization and hydrolysis only; limited DIET promotion	[64]
Walnut shell-dervied biochar	-	0.05	35	16	WAS	+23.5%	Not reported	Enhanced conversion	+16.6% carbon release	Enriched *Clostridia* and *Methanosarcina*; DIET establishment	[66]
Graphite	38 μm/150 μm	0.10–0.15	35–37	20–25	WAS	+12.3–18.7%	Reduced by up to 1.8 d	Promoted production and degradation	+15.2–39.1% VSS reduction	Enhanced pilus-associated genes; conductive particles facilitate interspecies electron transfer; DIET	[67]
Graphene/Reduced graphene oxide	0.5–2 μm/ 0.5–5 μm	0.0012–0.005	35–37	14–20	WAS	+38.7–51.4%	Reduced by up to 2.5 d	Enhanced acetate conversion	+22.3%	DIET between *Methanosaeta* and *Geobacter*; high conductivity; enriched electroactive biofilm	[59,68]

Notes: Temp = temperature; WAS = waste activated sludge; VS = volatile solids; HRT = hydraulic retention time; VFAs = volatile fatty acids; DIET = direct interspecies electron transfer. Dosages are normalized to g/g VS based on sludge VS concentrations reported in the original studies.

Activated carbon is among the most extensively studied carbon-based additives for sludge AD. Representative studies have shown that granular activated carbon (GAC) can accelerate VFAs consumption and moderately increase methane production, although its influence on sludge hydrolysis is often limited [60,61]. Mechanistically, GAC mainly acts as a conductive microbial carrier, enriching electroactive bacteria and methanogens on its surface and thereby strengthening syntrophic interactions [69,70]. The enrichment of genera such as *Geobacter* and *Methanosaeta*/*Methanosarcina* suggests that activated carbon can promote DIET between fermentative bacteria and methanogens [61]. Powdered activated carbon (PAC), owing to its smaller particle size and larger accessible surface area, may further improve VFAs conversion and early-stage methane production under suitable conditions, although its performance remains system-dependent [62,71].

Biochar differs from activated carbon in that its performance is strongly influenced by feedstock type and thermochemical preparation conditions [49]. In sludge AD, biochar can simultaneously serve as a microbial carrier, a pH-buffering adsorbent, a conductive bridge for DIET, and a redox-active electron reservoir through quinone-/phenazine-like moieties [39,55,64]. Representative studies have shown that digestate- or biomass-derived biochar can accelerate the bioconversion of organics, promote VFAs transformation, shorten the lag phase of methane production, and enhance methane yield [39,64]. However, the enhancement pattern of biochar is not universal. Some biochars mainly promote the acetogenic-methanogenic phase [64], whereas others preferentially improve solubilization, hydrolysis, or acidification [66,72]. This variability indicates that biochar selection should be tailored to specific treatment objectives rather than generalized across different sludge systems.

Graphite and graphene are highly conductive carbon materials with strong potential to stimulate DIET [73,74]. Graphite has been reported to enrich pilus-associated and electroactive microorganisms and strengthen electron exchange between syntrophic fermenters and methanogens, thereby improving substrate conversion and methane formation [67]. Graphene may further enhance methane production because of its exceptional conductivity and nanoscale structure [59]. However, its practical application should be evaluated cautiously, since oxidized derivatives may exhibit reduced conductivity and potential cytotoxicity [57,75,76]. Overall, the enhancement effect of carbon-based materials is primarily attributed to microbial enrichment, DIET facilitation, and adsorption-mediated stabilization rather than direct stimulation of sludge hydrolysis alone.

Carbon-based materials face several critical limitations. For activated carbon, dose-dependent effects must be considered: while moderate PAC dosages (2–4 g/L) markedly enhance methane yields, excessive addition (>10 g/L) may impair mass transfer within the sludge matrix, highlighting the importance of dosage optimization [62]. For biochar, performance variability arises from feedstock type and pyrolysis conditions, leading to inconsistent enhancement effects across studies [63,69]. Notably, conflicting results have been reported: for instance, crayfish shell-derived biochar accelerated sludge hydrolysis and acidification by 10.6–34.0% and 16.3–22.4%, respectively, yet produced no significant improvement in methane yield [66], likely due to insufficient electrical conductivity to support downstream DIET. Furthermore, batch-to-batch inconsistency in biochar properties presents a practical challenge for standardized full-scale implementation. For graphene and its derivatives, dose-dependent cytotoxicity has been demonstrated; concentrations above 50 μg/mL inhibit key methanogenic enzymes such as coenzyme F_{420}, potentially offsetting conductivity benefits [74]. The high production cost of graphene (estimated at 50–200 USD/kg for high-purity grades) and the lack of long-term stability data under AD conditions substantially constrain its large-scale applicability. From a life cycle perspective, the energy-intensive production of graphene and the pyrolysis process for biochar

generation incur measurable carbon footprints that partially offset methane yield gains. Finally, most conventional carbon-based materials lack recoverability, resulting in material loss with effluent and increasing operational costs and secondary pollution risks [5].

Despite their promising enhancement performance, most conventional carbon-based materials are evaluated primarily from the perspective of process improvement rather than material recovery. Their separation from digestate is often difficult, and their recyclability is generally limited or insufficiently documented. Therefore, recovery-oriented carbonaceous systems are discussed separately in Section 4.5.

4.2. Metal-Based Materials

Metal-based materials are another important class of exogenous additives for sludge AD. In addition to acting as conductive media that facilitate interspecies electron transfer, some metal-based materials can regulate redox conditions, release catalytically active ions, or promote interspecies proton/hydrogen transfer. The effects of metal-based materials on AD of sludge are shown in Table 3.

Table 3. Effects of metal-based materials on AD of sludge.

Carbon-Based Material	Size	Dosage (g/g VS)	Temp. (°C)	HRT (d)	Inoculum	Methane Increase	Lag Phase Change	VFAs Effect	Hydrolysis Effect	Key Mechanism	References
Magnetite	50 μm/ 45 ± 12 nm/ 8–12 mm	0.02–0.27	35–37	20–30	WAS	+7.3–75.6%	Not reported or reduced	Enhanced consumption to +12.0% VFAs	Increased protease activity accelerates decomposition	Stimulated DIET; enriched electroactive bacteria; enriched Fe (III)-reducing bacteria	[60,77,78]
Zero-valent iron (ZVI)	0.2 mm/50 nm	0.04–0.10	35	12–30	WAS	+21.2–43.5%	Not reported or reduced	+37.3% VFAs (0.2 mm) to not reported (nZVI)	+21.9% protein degradation to stimulated hydrolysis/acidification	Promoted hydrogenotrophic methanogenesis; H_2 supply; Fe^{2+} release; enhanced reducing environment	[58,79,80]
Red mud	75–100 μm	0.10	35	30	WAS	+24.0%	Not reported	Not reported	Improved solubilization, hydrolysis, acidification	Fe (III) reduction; dissimilatory iron reduction	[81]
Nano MnO_2	-	0.40	35	30	WAS	+42.0%	Not reported	Promoted consumption	Not reported	Mn^{4+}/Mn^{2+} redox cycle; stimulated key methanogenic enzymes	[82]

Notes: Temp = temperature; WAS = waste activated sludge; VS = volatile solids; HRT = hydraulic retention time; VFAs = volatile fatty acids; DIET = direct interspecies electron transfer. Dosages are normalized to g/g VS based on sludge VS concentrations reported in the original studies.

Magnetite is widely recognized as an effective conductive mineral for stimulating DIET in anaerobic systems [77,83,84]. Representative studies have shown that magnetite addition can significantly increase sludge conductivity, enrich electroactive bacteria and hydrogenotrophic methanogens, and enhance methane production [60,77,78]. It can function as an extracellular electron conductor between syntrophic microorganisms and may also enrich Fe (III)-reducing bacteria, thereby accelerating the decomposition of complex organic matter and indirectly supporting downstream acidification and methanogenesis [83,84]. In this respect, magnetite contributes not only to electron transfer but also to microbial community restructuring.

Zero-valent iron (ZVI) enhances sludge AD through a different mechanism [58,79]. Because of its strong reducing capacity, ZVI lowers the redox potential and creates a more favorable environment for strict anaerobes [85,86]. During corrosion, ZVI releases Fe^{2+} and H_2, which can support hydrogenotrophic methanogenesis and improve the activity of Fe-containing enzymes involved in acidification and methanogenesis [86,87]. Representative studies have reported that ZVI can stimulate protein degradation, increase VFA formation, and promote hydrogen-dependent methane production [58,79,80]. Thus, compared with magnetite, which primarily enhances extracellular electron conduction, ZVI plays a stronger role in redox regulation, iron supplementation, and hydrogen turnover.

Other metal-containing materials, such as red mud and Mn-based oxides, have also shown potential in improving sludge AD. Red mud contains abundant iron oxides and polyvalent metals, which can stimulate dissimilatory iron reduction, improve sludge floc structure, and facilitate extracellular electron transfer, ultimately enhancing methane production [81,88]. Mn oxides participate in Mn^{4+}/Mn^{2+} redox cycling and may stimulate the electron transfer system and key methanogenic enzymes, thereby enhancing methane production and methane content [82,89]. However, compared with carbon-based materials, some metal-based additives may raise concerns regarding residue accumulation, secondary contamination, or dosage sensitivity, all of which should be considered when assessing engineering applicability.

Metal-based materials face distinct challenges that must be addressed. For iron-based materials, significant material loss occurs during continuous operation; one study reported cumulative iron loss of 9.37 ± 0.22 g over 130 days, accounting for 94.51% of total iron added [90], necessitating continuous replenishment and increasing long-term operational costs. Dose-dependent inhibition is particularly critical: while optimal ZVI concentrations (4–10 g/L) enhance methane production, excessive addition may cause over-reduction in the system, leading to H_2 accumulation and potential methanogenesis inhibition [79]. For red mud, the presence of trace heavy metals (e.g., Cr, As, Pb) poses environmental risks for digestate utilization, requiring careful risk assessment before land application [81]. Nano-sized metal materials (e.g., nano-MnO_2) involve high energy consumption during synthesis and potential occupational safety concerns [82]. Furthermore, the long-term stability of metal-based materials under continuous AD conditions remains insufficiently characterized, particularly regarding gradual passivation of reactive surfaces and loss of catalytic activity over multiple cycles.

In this subsection, materials are classified according to their dominant chemical nature rather than their recoverability. Accordingly, magnetically responsive materials such as magnetite are retained here as representative metal-based additives. When magnetic separation and repeated reuse have been explicitly demonstrated, their recyclability is further discussed in Section 4.5.

4.3. Metal-Carbon Composite Materials

Metal-carbon composite materials integrate the conductivity, adsorption capacity, and microbial affinity of carbon matrices with the redox activity, catalytic properties, or ion-release behavior of metal species. Compared with single-component carbon-based or metal-based additives, such composites are generally expected to provide more efficient electron-transfer pathways and broader functional versatility in sludge AD. Their development reflects an effort to overcome the limitations of individual materials and to exploit synergistic effects between conductive carbon frameworks and reactive metal phases. The effects of metal–carbon composite materials on AD of sludge are shown in Table 4.

Among these materials, MnO-modified biochar and metal–organic framework (MOF)-derived or MOF-supported carbon composites have shown notable potential. MnO-modified biochar can reduce the distance between syntrophic bacteria and methanogens, facilitate VFAs conversion, and improve methane production through the combined effects of microbial attachment, redox mediation, and improved interfacial electron transfer [91]. Compared with pristine biochar, metal modification often introduces more active sites and stronger electron-transfer capability, leading to better digestion performance [91,92].

Table 4. Effects of metal–carbon composite materials on AD of sludge.

Carbon-Based Material	Size	Dosage (g/g VS)	Temp. (° C)	HRT (d)	Inoculum	Methane Increase	Lag Phase Change	VFAs Effect	Hydrolysis Effect	Key Mechanism	References
Fe_3O_4/GAC	200–450 μm	0.10	35	30	WAS	+17.1% (vs. GAC)	Not reported	Promoted consumption	Not reported	Larger specific surface area; abundant Fe^{2+}/Fe^{3+} species	[77]
Magnetic biochar	0.2–1.0 mm/ ~1 μm/ 10–20 nm/ ~20 μm	0.01–0.30	35–37	20	WAS	+10.6–55.9% (vs. control); up to +22.1% (vs. biochar)	Not reported or reduced	Enhanced conversion	Promoted hydrolysis, acidification, methanogenesis	Combined conductivity of carbon and redox activity of metal oxides; promoted DIET; enriched electroactive microbes	[10,78,91]
MnO-modified biochar	~0.15 mm	0.12	35	30	WAS	+59.9–76.6% (vs. control)	Not reported	Enhanced conversion	Not reported	Reduced distance between syntrophs; improved interfacial electron transfer	[92]
MOF-808	-	0.15	35	30	WAS	+26.7%	Not reported	Accelerated bioconversion	Enhanced biological and abiotic hydrolysis	Proton conductivity; promoted H^+ transfer	[93]
Biochar@ MIL-88A(Fe)	-	0.25	35	30	WAS	+113%	Not reported	Accelerated consumption	Improved solubilization and hydrolysis	Fe^{3+}/Fe^{2+} redox pairs; DIET and IHT synergism	[94]

Notes: Temp = temperature; WAS = waste activated sludge; VS = volatile solids; HRT = hydraulic retention time; VFAs = volatile fatty acids; DIET = direct interspecies electron transfer. Dosages are normalized to g/g VS based on sludge VS concentrations reported in the original studies.

Another representative group is MOF-related composites. Materials such as MOF-808 and biochar-supported MIL-88A(Fe) can introduce proton-transfer capability, Lewis acidic catalytic sites, and metal-centered redox pairs into the anaerobic system [95]. As a result, these materials can simultaneously enhance hydrolysis, stimulate electron/proton transfer, and accelerate the conversion of VFAs into methane [93,94]. For example, MOF-808 has been reported to improve both biological and abiotic hydrolysis of sludge and to accelerate methanogenic conversion of intermediates [93], while biochar-supported iron-based MOFs may combine microbial colonization, conductive carbon structure, and Fe (III)/Fe (II) redox cycling in a single platform [94,96].

Metal–carbon composites face challenges related to synthesis complexity and structural stability. Different synthesis methods (e.g., chemical loading, hydrothermal carbonization, ball milling) produce composites with distinct structures (core–shell vs. surface-loaded), leading to variable performance in AD systems [10,92]. The incorporation of metal nanoparticles does not fully prevent metal ion leaching; long-term stability studies under AD conditions remain lacking for most composites [35]. MOF-based composites, despite their high porosity and proton conductivity, suffer from poor stability in aqueous environments and high synthesis costs [93,94]. Furthermore, the recyclability of many composites has not been systematically evaluated, with recovery efficiency data available only for a few magnetic variants [5,38]. The scalability of these advanced materials remains a significant barrier to engineering applications, as large-scale production methods are often unavailable or economically prohibitive.

Despite their promising performance, the practical applications of many metal–carbon composites are still restricted by synthesis complexity, material cost, and uncertain long-term stability. Therefore, when evaluating their engineering feasibility, enhancement efficiency should be considered together with preparation cost, structural robustness, and the potential for regeneration or reuse. To maintain a clear classification framework, magnetic or explicitly recovery-oriented composites are discussed separately in Section 4.5, where their separation and recycling advantages can be more directly addressed.

4.4. Inorganic Mineral Materials

Inorganic mineral materials represent another group of low-cost additives for sludge AD. Typical examples include natural zeolite, diatomite, and wollastonite, as shown in Table 5. Their enhancement effects are generally associated with porous structure, ion-exchange capacity, cation release, microbial immobilization, and adsorption of inhibitory compounds such as ammonium [97].

Natural zeolite is among the most widely studied mineral additives because of its low cost, ion-exchange capacity, microbial colonization potential, and ammonium adsorption ability [37,52]. Representative studies have shown that zeolite can improve hydrolysis, acidification, methanogenesis, and process stability, particularly under ammonia-stressed conditions [37]. Its surface also supports biofilm formation, which may improve substrate transfer and microbial cooperation within sludge AD systems [37].

Diatomite provides a high-surface-area siliceous matrix and can enhance hydrolysis and biomethanation by improving contact between sludge particles and microbial communities [97]. At the same time, its adsorption properties may help alleviate ammonia inhibition. Wollastonite, another natural inorganic mineral, can also be utilized to enhance sludge anaerobic digestion. Its primary component is calcium silicate ($CaSiO_3$). Protons generated during VFAs fermentation can accelerate the release of cations from silicate minerals ($CaSiO_3 + 2H^+ \rightarrow Ca^{2+} + SiO_2 + H_2O$), such as wollastonite. An optimal concentration of calcium ions (Ca^{2+}) is beneficial for AD [98,99]. These examples indicate that inorganic minerals can contribute to AD enhancement even without strong intrinsic conductivity.

Table 5. Effects of inorganic mineral materials on AD of sludge.

Carbon-Based Material	Size	Dosage (g/g VS)	Temp. (° C)	HRT (d)	Inoculum	Methane Increase	Lag Phase Change	VFAs Effect	Hydrolysis Effect	Key Mechanism	References
Natural zeolite	0.5–1.0 mm	0.10	35	20	WAS	+20.1%	Not reported	Enhanced conversion	Improved hydrolysis, acidification	Biofilm formation; NH_4^+ adsorption; ion exchange	[37]
Diatomite	-	2.00	35	20	WAS	+23.3%	Not reported	Not reported	+78.9% hydrolysis rate	High porosity; Al/Fe improve conductivity	[97]
Wollastonite	21.0 μm	0.20	35	24	WAS	+30.8%	Not reported	Enhanced conversion	Enhanced hydrolysis	Ca^{2+} release; CO_2 sequestration	[98]
Magnetite modified zeolite	0.2–0.5 mm	0.012	35	20	WAS	+37.4%	Not reported	Enhanced conversion	Enhanced degradation of refractory organics	Improved electron mediating ability; DIET	[38]

Notes: Temp = temperature; WAS = waste activated sludge; VS = volatile solids; HRT = hydraulic retention time; VFAs = volatile fatty acids; DIET = direct interspecies electron transfer. Dosages are normalized to g/g VS based on sludge VS concentrations reported in the original studies.

Inorganic mineral materials exhibit several inherent limitations. Their enhancement effects are generally moderate, with methane yield increases typically below 40% compared to carbon-based or metal-based materials [37,97]. Performance varies significantly with source and composition, leading to inconsistent results across studies [52]. While cation release (e.g., Ca^{2+}) can be beneficial at optimal concentrations, excessive release may cause scaling or inhibition; for instance, Ca^{2+} concentrations above 1000 mg/L may precipitate as calcium carbonate, reducing system efficiency [98]. The dissolution mechanism of these materials makes them inherently non-recyclable, as their active components are consumed during operation [97]. Furthermore, the long-term stability of magnetically modified mineral materials under continuous operation has not been sufficiently evaluated [38].

However, the effect of inorganic mineral materials is often moderate and highly dependent on sludge characteristics, dosage, and operating conditions. Their engineering attractiveness mainly lies in low cost, availability, and operational simplicity. To avoid overlap with the emerging recyclable-material framework, magnetically modified mineral materials are not discussed in detail here. Once a mineral material is intentionally endowed with magnetic separation capability and evaluated for recovery and reuse, it is more appropriately categorized as a recyclable material and discussed in Section 4.5.

4.5. Recyclable Materials

Recyclable materials constitute an emerging direction for exogenous-material design in sludge AD. Unlike conventional additives that are difficult to separate from digestate, these materials are intentionally developed to combine process enhancement with facile recovery and reuse. Their engineering advantage lies not only in improving methane production, DIET, or process stability, but also in reducing material loss, simplifying post-treatment, and lowering long-term operating costs. Typical examples include magnetic biochar, magnetic activated-carbon composites, magnetically modified mineral carriers, magnetic MOF-based composites, and magnetic porous microspheres. Comparative assessment of recyclable materials for enhanced sludge AD is shown in Table 6.

Natural Magnetic biochar is one of the most representative recyclable materials because it combines the porous carbon framework of biochar with magnetic components such as Fe_3O_4 [10,92]. This design allows magnetic biochar to retain the adsorption capacity, microbial immobilization ability, and redox activity of biochar while also enabling magnetic separation from digestate [78]. Representative studies have shown that magnetic biochar can promote hydrolysis and methanogenesis, enrich electroactive microorganisms, facilitate DIET, and improve VFAs conversion [10,78,92]. Compared with pristine biochar, magnetic biochar is more attractive for long-term operation because the possibility of recovery and reuse directly addresses the practical drawback of biochar loss after one-time addition.

Table 6. Comparative assessment of recyclable materials for enhanced sludge AD.

Material	Methane Yield Increase	Recovery Efficiency	Reuse/Cycling Stability Evidence	Key Advantages	Limitations	References
Magnetic biochar	Increasing methane yield by 20–40% compared with control; increasing methane yield by 22.1% compared with pristine biochar; achieving an additional 5.5% synergistic enhancement	Exceeding 90%	Long-term cycling not systematically evaluated; preliminary reuse feasibility suggested	Low cost, abundant feedstock, dual functionality (conductive and adsorptive), promoting DIET, enriching electroactive microbes, synergistic effect of biochar and magnetite	Performance varying with feedstock and synthesis method; magnetic stability under long-term operation needing further validation	[10,92,100,101]
Magnetic porous microspheres	Increasing methane yield by up to 100%; increasing methane content in biogas by 21.1%	Exceeding 90%	Cycling stability demonstrated in preliminary studies; quantitative retention data limited	High stability, minimal ion leaching, excellent electron/proton transfer, promoting PCET and metabolic cooperation	Higher synthesis cost, complex fabrication, requiring specialized magnetic separation equipment	[5,34]
Fe_3O_4/GAC	Increasing methane yield by 17.1% compared with GAC alone	Exceeding 90% (estimated from material design)	Not reported	Improved conductivity, enhanced microbial attachment, larger specific surface area, abundant Fe^{2+}/Fe^{3+} species	Additional synthesis step required; long-term magnetic stability and recovery efficiency needing systematic evaluation	[102]
Magnetic MOF composites	Increasing methane yield by 26.7–55.9%; increasing VFAs concentration by 1.68 times	Exceeding 85% (estimated)	Not reported; structural stability under aqueous conditions requiring further validation	High porosity, tunable structure, proton conductivity, highly defective structure with unsaturated metal sites, Fe^{3+}/Fe^{2+} redox pairs facilitating electron transfer	High cost, potential stability issues in aqueous environments; scalability remaining challenging	[35]
Magnetite modified zeolite	Increasing methane yield by 37.4%	Not explicitly reported (magnetic separation applicable)	Not reported	Low-cost natural mineral, improved electron mediating ability, enhanced VFAs conversion, enriching electroactive genera (*Methanobacterium*, *Methanosaeta*); cytochrome c and F_{420} activities increased by 33.3% and 29.8%, respectively	Recovery efficiency needing systematic evaluation; long-term stability in continuous systems requiring further study	[38]

Other recyclable magnetic composites further illustrate the transition from purely performance-oriented materials to recovery-oriented materials. Fe_3O_4/GAC [102], magnetite-containing biochar [10], $MnFe_2O_4$-biochar [92], Fe-Mn-modified biochar [92], and magnetically modified zeolite all combine surface functionality with magnetic responsiveness [38]. In these systems, the carbon or mineral matrix provides surface area, porosity, and microbial attachment sites, whereas the magnetic or metal-containing phase contributes conductivity, redox activity, and external separability. Such materials are therefore not only active enhancers of AD but also more practical candidates for repeated use.

Magnetic MOF-based composites and magnetic porous microspheres represent a further step toward multifunctional and recyclable material systems. Magnetic porous microspheres, for example, can provide a stable microbial carrier, facilitate electron/proton transfer, and be rapidly recovered from digestion residues under an external magnetic field [5,34]. Their ordered structure, high surface area, and controllable surface chemistry make them particularly attractive for future recovery-oriented AD systems. More broadly, these materials embody the concept of being designed for recycling, in which easy separation, regenerability, and structural stability are treated as core material-design criteria rather than secondary benefits.

To facilitate cross-comparison and guide material selection, Table 5 summarizes the key performance indicators of representative recyclable materials discussed above, including methane yield enhancement, recovery efficiency, reuse/cycling stability evidence, key advantages and main limitations. Among the materials reviewed, magnetic biochar and magnetic porous microspheres demonstrate the most promising recyclability potential due to their magnetic responsiveness and preliminary reuse evidence, although quantitative recovery efficiency and long-term cycling stability data remain limited in current sludge AD studies. Fe_3O_4/GAC composites and magnetite-modified zeolite also show effective methane enhancement and magnetic separability, but their recovery efficiency and multi-cycle performance require further systematic evaluation. Magnetic MOF composites exhibit high porosity and tunable structure favorable for electron/proton transfer, yet their stability in aqueous anaerobic environments and scalability remain challenging. Overall, while these materials represent a transition toward recyclable systems, standardized evaluation protocols for recovery efficiency, cycling stability, and regeneration performance are still lacking, which limits cross-study comparison and engineering translation.

Despite their promising potential, recyclable material systems face several challenges that must be addressed. The synthesis costs of engineered recyclable materials (e.g., magnetic porous microspheres, magnetic MOF composites) are substantially higher than those of conventional additives, requiring life cycle assessment to justify economic feasibility [5,35]. Long-term stability of magnetic components under AD conditions remains a concern; although core–shell structures mitigate iron leaching, gradual degradation over multiple cycles has not been systematically quantified [38]. Recovery efficiency depends on the strength of the applied magnetic field and the design of separation equipment, which may not be readily available in existing sludge treatment facilities [90]. Standardized protocols for evaluating recovery efficiency, regeneration methods, and cycling stability are lacking, hindering cross-study comparison and technology benchmarking [5]. Finally, the potential environmental impacts of residual magnetic particles in digestate (e.g., effects on soil microbiota or plant growth) require further investigation before large-scale implementation.

5. Challenges and Future Perspectives: From Non-Recyclable to Recyclable Materials

5.1. Limitations and Challenges of Current Exogenous Materials

In summary, exogenous materials can enhance AD of sludge through mechanisms such as facilitating electron and proton transfer, providing microbial carriers, adsorbing inhibitory substances, supplementing trace elements, and improving microbial community structure. However, existing exogenous materials all possess inherent limitations that restrict their widespread application.

Carbon-based conductive materials often exhibit a limited number of surface electron transfer sites. Furthermore, the ubiquitous presence of extracellular polymeric substances around cells makes the issue of electron capture between the cell surface and the carbon material surface non-negligible. Additionally, even in the presence of carbon materials, complex organic substances cannot be directly degraded via the DIET pathway; that is, these carbon-material-mediated DIET pathways demonstrate high substrate selectivity. Biochar, in particular, suffers from significant performance variability depending on feedstock type and pyrolysis conditions, leading to inconsistent enhancement effects across studies [62,68]. The high cost of engineered carbon materials (e.g., graphene, carbon nanotubes) further limits their economic feasibility for large-scale applications [66].

Metal-based materials, particularly iron-based ones, face challenges such as small particle sizes and the tendency for iron ions to leach. The necessity for continuous replenishment of iron-based materials presents a significant bottleneck for long-term operation, leading to high cost. One study utilizing magnetite to enhance AD reported a cumulative iron loss of 9.37 ± 0.22 g via the effluent over 130 days of continuous reactor operation, accounting for 94.51% of the total iron added [90]. Therefore, the loss of iron limited the application of iron-based materials, although iron-based materials are advantageous for improving AD performance. Dose-dependent inhibition is another critical concern: while optimal ZVI concentrations (4–10 g/L) enhance methane production, excessive addition may cause over-reduction in the system, leading to H_2 accumulation and potential methanogenesis inhibition [79]. For red mud, the presence of trace heavy metals (e.g., Cr, As, Pb) poses environmental risks for digestate utilization [82]. Nano-sized metal materials involve high energy consumption during synthesis and potential occupational safety concerns [83].

For common metal-carbon composite materials, different synthesis methods (e.g., chemical loading, shear carbonization, hydrothermal carbonization, and ball-milling carbonization) produce composites with distinct structures, such as core–shell or surface-loaded configurations, which subsequently influence their performance in AD. MOFs are usually at the nanoscale, which are prone to loss. The incorporation of metal nanoparticles does not fully prevent metal ion leaching; long-term stability studies under AD conditions remain lacking for most composites [35]. MOF-based composites, despite their high porosity and proton conductivity, suffer from poor stability in aqueous environments and high synthesis costs [94,95]. The scalability of these advanced materials remains a significant barrier to engineering applications.

Inorganic mineral materials, including zeolite, diatomite, and wollastonite, are attractive for their low cost and availability, but they exhibit several inherent limitations. Their enhancement effects are generally moderate, with methane yield increases typically below 40% [97]. The performance of natural minerals varies significantly with source and composition, leading to inconsistent results across studies [53]. Many inorganic minerals function by releasing cations (e.g., Ca^{2+}) or adsorbing inhibitors, but excessive cation release can cause scaling or inhibition; for example, Ca^{2+} concentrations above 1000 mg/L may precipitate as calcium carbonate, reducing system efficiency [99]. The dissolution mechanism of these materials makes them inherently non-recyclable, as their active components

are consumed during operation [94]. Furthermore, the long-term stability of magnetically modified mineral materials under continuous operation has not been sufficiently evaluated [38].

Different from MOFs, the diameter of MPMs is about 100 μm and the magnetism of MPMs remains stable during AD. This imparts controllability to the MPMs, thereby making them less susceptible to loss with the sludge. In addition, MPMs can be recyclable because their core–shell structure prevents the iron inside from being released. Therefore, it can be reasonably considered that MPMs have great potential in the field of the enhancement of AD of sludge. However, the synthesis costs of engineered recyclable materials (e.g., magnetic porous microspheres, magnetic MOF composites) are substantially higher than those of conventional additives, requiring life cycle assessment to justify economic feasibility [5,35]. Recovery efficiency depends on the strength of the applied magnetic field and the design of separation equipment, which may not be readily available in existing sludge treatment facilities [100]. Standardized protocols for evaluating recovery efficiency, regeneration methods, and cycling stability are lacking, hindering cross-study comparison and technology benchmarking [5].

5.2. Future Research Directions

Although various exogenous materials have demonstrated significant potential in enhancing AD of sludge, there are still systematic challenges in terms of their sustainability, recyclability, and engineering applicability. Future research should focus on promoting a paradigm shift from the sole emphasis on efficiency improvement to a balance between efficiency and sustainability (Figure 4), in order to drive the sludge AD technology towards greater efficiency, lower carbon emissions, and greater sustainability.

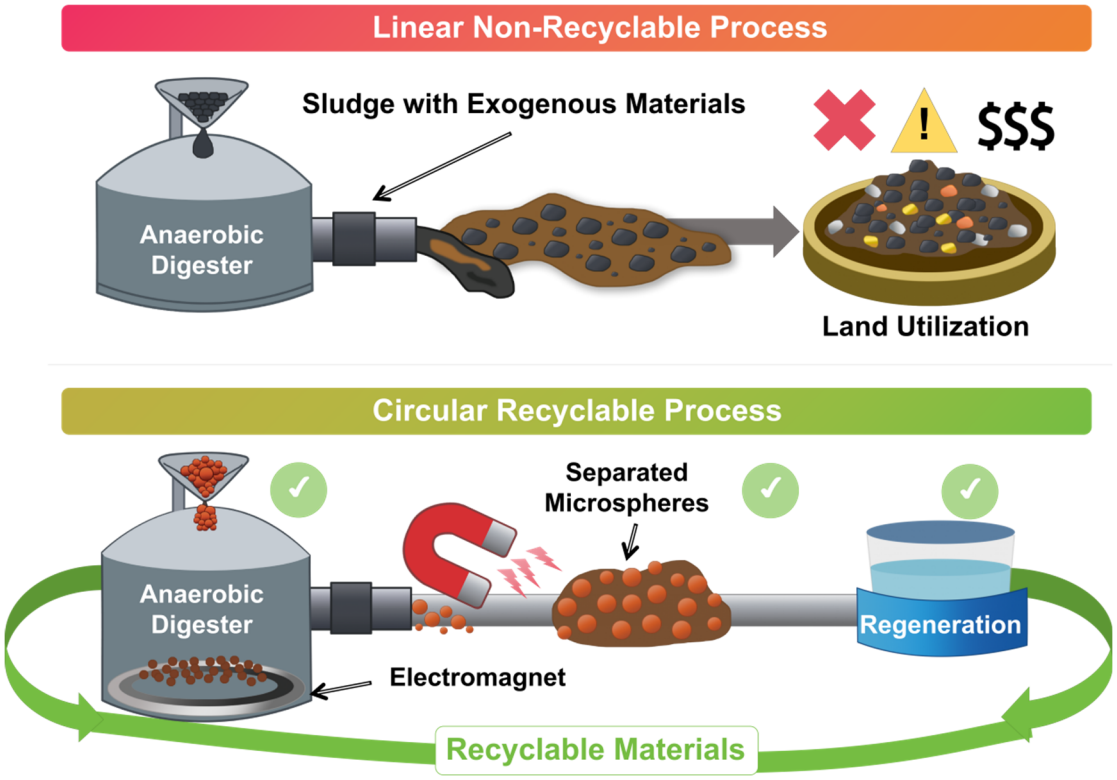

Figure 4. The ideal future sludge anaerobic digestion technology based on exogenous material reinforcement: a paradigm shift from non-recyclable to recyclable.

Firstly, it is necessary to deepen the analysis of the multi-dimensional collaborative strengthening mechanism of materials, laying a foundation for the targeted design and

precise application of materials. Current research predominantly focuses on the strengthening effects of single attributes of materials, while the actual reinforcing effects are often the result of the synergistic action of multiple factors. For example, the study of Sun et al. attributed the enhanced DIET during the high-solid AD of sewage sludge to the addition of AC mediator [62], thereby solving the e the acidification issue and then improving the efficiency of methane production. In the future, technologies such as metagenomics, metabolomics, and in situ microscopic electrochemistry should be employed to precisely analyze the dynamic regulatory mechanisms of the physicochemical properties of materials in real sludge matrices on DIET, PCET, the directional enrichment of functional microorganisms, and the interfacial migration and transformation of inhibitors. Through the establishment of a quantitative correlation model based on material properties, microbial functions, and metabolic fluxes, the targeted design and functional integration of materials for specific application scenarios, such as high-solid sludge treatment, ammonia inhibition mitigation, and degradation of refractory organic compounds, can be achieved.

Secondly, material design should adhere to the concept of being designed for recycling. In the future, materials will not only be required to meet the demand of effectively improving AD performance, but also need to incorporate easy separation, recyclability, and regenerability as core design indicators. Priority will be given to the development of composite materials with stable structures and easy separability (e.g., magnetic responsiveness) to ensure that they maintain their key performance after long-term operation and multiple cycles. For instance, by optimizing the composition and structure of MPMs, they can not only efficiently mediate electron and proton transfer and immobilize functional microorganisms but also be rapidly recovered from the discharged sludge or digestion residues through physical methods such as magnetic separation and sieving. In addition, the in situ regeneration and functional restoration of materials are also key means to enhance the recyclability of materials. For example, for adsorption-saturated biochar and partially oxidized ZVI and other recyclable materials, in situ regeneration technologies such as mild pyrolysis, chemical washing, and electrochemical activation are employed to restore their activity.

Thirdly, the transition toward recyclable exogenous materials is still in its early stages, and the lack of standardized evaluation criteria for material recovery and regeneration performance hinders cross-comparison among different studies. Future research should focus on establishing design criteria and application validation frameworks for recyclable materials. Quantitative targets are proposed from dimensions such as recovery efficiency and economic cost. Specifically, recyclable materials should maintain their performance after multiple cycles. A recovery efficiency target of >90% is suggested, with methane enhancement remaining above 80% of the initial level after no fewer than 5 cycles. Furthermore, standardized protocols for evaluating recovery efficiency are needed to enable cross-comparison among different materials.

Finally, to bridge the gap between laboratory research and large-scale engineering applications of exogenous materials, it is imperative to systematically address key issues such as economic feasibility, environmental sustainability, long-term operational stability, and standardized support. This encompasses conducting comprehensive techno-economic analysis and life cycle assessment (LCA) to quantify the comprehensive benefits and economic feasibility of new material systems. LCA studies are particularly critical for recyclable materials, as their higher initial synthesis costs (e.g., magnetic porous microspheres, magnetic MOF composites) may be offset by reduced material replacement frequency and minimized secondary pollution over the operational lifetime [5,35]. Such assessments should evaluate the trade-offs between enhancement efficiency, material cost, recovery efficiency, and long-term environmental impacts, providing a holistic basis for material

selection and process design. For example, in the field of material, by integrating Safe-and-Sustainable-by-Design principles and artificial intelligence/machine learning into life cycle assessment framework, the researchers achieved predictive, data-driven design for material sustainability [103]. This demonstrates the importance of conducting life cycle assessments for materials. Through long-term pilot-scale tests, the performance degradation patterns and failure modes of materials in actual anaerobic environments should be investigated, and the potential environmental risks of their residues in the resource utilization of biogas residues should be evaluated. Meanwhile, a technical standard system covering material classification, quality specifications, dosing methods, recycling processes, and performance evaluations should be gradually established. Additionally, reactor configurations and process coupling modes suitable for the efficient retention and recycling of recyclable materials should be explored to provide support for the standardized and large-scale application of the technology.

6. Conclusions

This review systematically summarizes the mechanisms and application effects of exogenous materials in enhancing sludge AD. The main conclusions are: (1) Exogenous materials enhance methane yield and system stability through synergistic mechanisms including electron/proton transfer, microbial immobilization, and adsorption/buffering; (2) Conventional materials suffer from non-recyclability, material loss, and high costs-iron-based materials show up to 94.5% iron loss during continuous operation, severely limiting engineering applications; (3) A paradigm shift from "efficiency-first" to "efficiency-sustainability balance" is underway; design standards for recyclable mate-rials are recommended. From a policy perspective, it is proposed to incorporate performance indicators of recyclable materials into the technical evaluation system for sludge treatment, and establish material access standards, so as to support the green and low-carbon transformation of sludge treatment systems.

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