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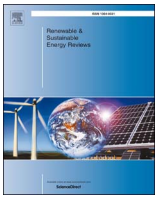

Feasibility analysis of anaerobic digestion of excess sludge enhanced by iron: A review

Jing Wei[a], Xiaodi Hao[a,*], Mark C.M. van Loosdrecht[a,b], Ji Li[a]

[a] *Sino-Dutch R&D Centre for Future Wastewater Treatment Technologies/Key Laboratory of Urban Stormwater System and Water Environment, Beijing University of Civil Engineering & Architecture, Beijing 100044, PR China*
[b] *Dept. of Biotechnology, Delft University of Technology, van der Maasweg 9, 2629 HZ Delft, The Netherlands*

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ABSTRACT

The Paris Climate Treaty implies the coming of a new era towards carbon-neutral operation in wastewater treatment plants (WWTPs), and thus energy self-sufficiency from biosolids and/or heat in the form of wastewater temperature has to be considered. In this regard, anaerobic digestion (AD) of sludge should be paid renewed attention to resolve a low conversion efficiency of biosolids. As a potential way to energy positive operation, exogenous iron has been proposed to enhance methane production in recent years. In this review, the authors provided a deep insight into the feasibility of iron-enhanced AD system. Hydrogen evolution from iron corrosion and its effects on CH_4 production is firstly reviewed; then the roles of iron in reducing ORP was illustrated with regard to its impact on fermentation type; serving as an essential element and potential electron donor, the stimulating effects of iron on microorganisms and enzyme activities were also elaborated, and thus the technical feasibility of iron-based AD could be evaluated. In regards of the environmental and economic impacts of iron-based AD, life cycle assessment (LCA) was employed to calculate its economic feasibility, and the results revealed that iron-based AD system could reduce both operational costs and carbon emissions. Conclusion was drawn that iron-based anaerobic digestion is promising on technical level as well as economic perspective, and is expected to contribute to carbon-neutral operation of WWTPs. Iron-based anaerobic digestion is such a promising and sustainable strategy towards circular economy that it could be applied to many cross-disciplinary fields.

1. Introduction

After the Paris Climate Treaty was signed and started up, some roadmaps of low-carbon operation and even carbon neutrality for wastewater treatment plants (WWTPs) are gradually emerging all over the world [1–3]. At this point, energy self-sufficient operation is often used as a specific definition, implying that WWTPs operate without inputting external energy. Although energy contained in wastewater mainly comes from heat (up to 90%) [4,5], organic energy from wastewater and/or excess sludge can also contribute to energy recovery via anaerobic digestion (AD) for methane production. AD is not only a traditional technology for stabling sludge, but also a developing technology to be regained in energy self-sufficient operation. In recent years, much more attention has been paid to enhancing the conversion from organics to CH_4.

In practice, stable bacterial cell walls and refractory organics such as lignocellulosic materials and humic acids severely inhibit the decomposition of excess sludge and consequent organic conversion efficiency [6,7]. For this reason, some pretreatment techniques like thermal, ultrasonic and acidic/alkaline pretreatments have been developed to enhance AD [8–10]. Indeed, significant biogas production can be obtained by these pretreatment techniques, but the high input energy and the corresponding costs are always keeping these techniques from being applied to WWTPs.

Under the circumstance, other approaches beyond the pretreatment techniques are also put into practice to enhance CH_4 production. For instance, exogenous exhaust hydrogen and scrap iron were applied in some studies [11–15], and the results indicated that scrap iron had great potentials in enhancing CH_4 production effectively and economically. Ruan et al. found that a 1.5-fold COD removal ratio and 1.4-fold of methane yield were achieved when scrap iron was loaded to AD reactors [16]; in Suanon's study, methane yield increased by 40.8% in the presence of iron powder [17]; Kong et al. also confirmed the positive role of iron in enhancing methane production, and an increase of 41.7% of CH_4 yield was achieved [18]. An overview of iron-enhanced AD is summarized in Table 1. Since the positive role of iron in promoting AD has been found in quite a few studies recently, the function of iron in enhancing CH_4 production deserves in-depth study.

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* Corresponding author.
E-mail address: xdhao@hotmail.com (X. Hao).

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Table 1
Summary of anaerobic digestion enhanced by iron.

Substrate	Type of iron	Dosage of iron (g/L)	Temperature (°C)	Increment in CH_4 yield (%)	Increment in COD/VSS removal (%)	Reference
Excess sludge	Scrap iron	10	35	10.1^{a} 21.4^{b}	83.3^{c}	[19]
Excess sludge	Scrap iron	4	35	43.5	33.6^{c}	[20]
Swine wastewater	ZVI powder	25	30	145.5	56.2^{d}	[21]
Excess sludge	nZVI	1	37	25.2	22.0^{d}	[17]
	ZVI powder	16.7	37	40.8	48.4^{d}	
Excess sludge	mZVI	10	35	131.6	NA	[22]
	nZVI	10	35	46.1	NA	
Pig manure	mZVI	20	35	20	NA	[23]
Manure	nZVI	0.02	37	159	NA	[24]
OFMSW	mZVI	12	35	41.7	105.9 ^{c}	[18]
Excess sludge	Scrap iron	2.385	35	38.3	NA	[25]
Excess sludge	nZVI	16.6	35	1304	NA	[11]
	Scrap iron	33.3	35	25.3	NA	

ZVI-Zero-valent iron; nZVI-nanoscale zero-valent iron; mZVI-microscale zero-valent iron; NA-not available; OFMSW-Organic fraction of municipal solid waste; ^{a}acidogenesis phase; ^{b}methanogenesis phase; ^{c}VSS; ^{d} COD.

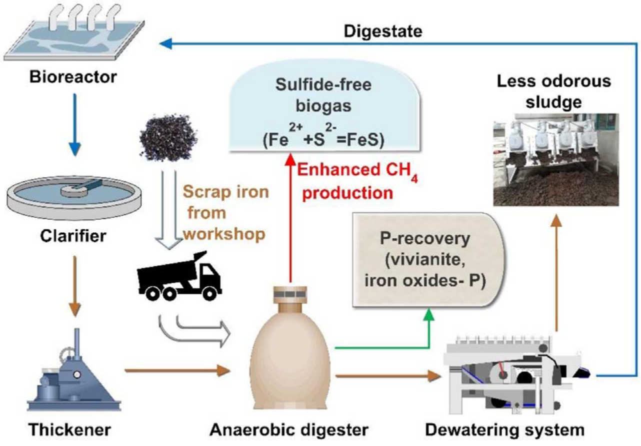

Fig. 1. Schematic process of anaerobic digestion of excess sludge enhanced by iron.

A schematic process of AD enhanced by iron is proposed in Fig. 1. Apart from enhancing biogas production in AD, iron could also help to prevent emission of hydrogen sulfide (H_2S) via iron-sulfide (FeS) precipitation [16,26–28]. In this way, both quantity and quality of biogas could be significantly improved. Furthermore, phosphate recovery is another interesting topic when iron is added in AD. The compounds of iron and phosphate existing in AD are often in the forms of either phosphate minerals (e.g. vivianite, much easier to be formed in AD) [29–32] or adsorbed complexes due to the high affinity of iron oxides on orthophosphate [33–35]. Phosphate recovery in the form of vivianite could be achieved by applying external magnetic field in AD, due to the magnetic nature of vivianite and iron oxides [36–38]. Moreover, desulfurization with iron is an efficient method for less odorant sludge by removing smelly volatile organic sulfur compounds via FeS precipitation, so that the unfavorable environmental impacts of biosolids could be minimized [39–42]. Research also found that the dewaterability of digested sludge could be improved as with the crystallization of phosphorus [43], indicating the Fe-P precipitation may also help to reduce the sludge disposal costs. In the future, perhaps, dosing scrap iron into AD would become an ordinary way to upgrade WWTPs towards the goal of energy and resource recovery. As a potential direction, an increasing interest in iron-based AD system is arising among researchers, and there is a recognized need for the systematic analysis of the feasibility of this approach to provide a comprehensive theoretical support for the application of iron-based AD system. Under the circumstance, this review was initiated, which tries to analyze the feasibility of iron-based AD system in all aspects, including chemistry, physiology, microbiology, as well as the feasibility in economy. The surface reaction of iron, i.e. hydrogen evolved from iron corrosion was firstly analyzed for its multiple impacts on AD; then the influence of oxidation-reduction potential (ORP) change on methane yield was also taken into consideration; moreover, the potential of iron in stimulating the activity of anaerobic microorganisms was evaluated as well; finally, the economic feasibility was calculated using life cycle assessment (LCA).

2. Anaerobic iron corrosion

Iron corrosion mainly proceeds in three ways: simple chemical corrosion, electrochemical corrosion and physical corrosion. When iron is in the anaerobic aquatic environment, both chemical (reacting with water, see Eq. (1)) and electrochemical corrosions (normally caused by the products of microbial metabolisms like sulfate reducing bacteria-SRB in AD, see Eq. (2)) prevail [44]. Chemical corrosion (hydrogen-evolution corrosion) results in a direct impact on hydrogen production. The hydrogen evolved from iron corrosion was proposed to be associated with AD: slowly evolved hydrogen could serve as the substrate of hydrogenotrophic methanogens (HMs) and homoacetogens (HAs) to enhance CH_4 production [21,45]. In terms of ORP, iron corrosion would reduce ORP as well and thus facilitate AD. In addition, electrons released from iron could participate in anaerobic processes which might contribute to the biodegradation of refractory organics [46–48].

Microbial corrosion is related to microbes and will be discussed in Section 4.

2.1. Hydrogen evolution from iron corrosion

Hydrogen evolution from iron corrosion can simply be expressed by Eq. (1), and the associated kinetics have been generalized [49,50]. However, further studies have been continuing for more detailed mechanisms like metal protection against corrosion and electrolytic hydrogen production problems [51–55]. In fact, hydrogen evolution is so complicated a process which requires the coexistence of electrons and protons, as expressed by Eq. (3); electrons are firstly transferred to protons and then hydrogen atoms which are adsorbed onto the surface of iron are formed; two hydrogen atoms are further combined and finally form H_2. Since $k_2 \gg k_1$, forming hydrogen atoms on iron is a rate-limiting step in hydrogen-evolution corrosion [56,57]. $Fe(OH)_2$ is not stable enough in the anaerobic environment and is liable to be transformed to Fe_3O_4 (Eq. (4)) at $T > 80\,^{\circ}C$ [58]. Although Eq. (4) hardly proceeds in room temperature, the presence of iron can catalyze the reaction (Eq. (4)) [59]. Thus, both Eqs. 1 and 4 are relatively significant in the anaerobic iron corrosion.

$$Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2 \qquad (1)$$