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Magnetite enhances anaerobic digestion and methanogenesis of fresh leachate from a municipal solid waste incineration plant

Yuqing Lei[a,b], Lianxue Wei[a], Tianyuan Liu[a], Yangyi Xiao[a], Yan Dang[a,*], Dezhi Sun[b,*], Dawn E. Holmes[c]

[a] College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, China
[b] Beijing Key Laboratory for Source Control Technology of Water Pollution, Engineering Research Center for Water Pollution Source Control and Eco-remediation, Beijing Forestry University, Beijing 100083, China
[c] Department of Physical and Biological Sciences, Western New England University, 1215 Wilbraham Rd, Springfield, MA 01119, United States

HIGHLIGHTS

- Magnetite dosing enhanced methane production and treatment efficiencies.
- Magnetite may help stimulate DIET between bacteria and acetoclastic methanogens.
- Magnetite may enhance the formation of protective interspecies biofilms.
- Magnetite may adsorb toxic compounds from leachate.
- Magnetite stimulated the growth of acetate-producing bacteria.

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ABSTRACT

Anaerobic digestion of municipal solid waste (MSW) incineration leachate is limited by high organic loading rates, high concentrations of complex organic matter, and the presence of compounds like ammonia, heavy metals, and salts that can inhibit microbial activity. The purpose of this study was to investigate whether the addition of magnetite could help reactors treating MSW incineration leachate overcome these limitations and promote efficient conversion of complex organic matter to methane. These studies showed that magnetite amendments improved chemical oxygen demand (COD) removal efficiencies (78.8% vs 89.0%) and methane production rates (3.7 $m^3_{STP}/(m^3 \cdot d)$ vs 4.8 $m^3_{STP}/(m^3 \cdot d)$) at an organic loading rate (OLR) of 18.2 kg COD/$(m^3 \cdot d)$. Significant differences in microbial community structures were also observed between non-amended and magnetite-amended reactors. The majority of sequences from the magnetite-amended reactor clustered with acetogenic and mixed acid fermentative bacteria. Sequences from bacteria capable of extracellular electron transfer and methanogens from the genera *Methanosarcina* and *Methanosaeta* were also more abundant in magnetite-amended reactors. It is possible that these species were participating in direct interspecies electron transfer (DIET) facilitated by magnetite amendments. In addition, ammonia nitrogen, calcium, and heavy metals were lower in effluent collected from magnetite-amended reactors than non-amended controls, suggesting that magnetite adsorbed these inhibitory compounds and created an environment more amenable to microbial growth. These results are significant and should be used to develop strategies designed to optimize bio-methanogenic treatment of complex waste with elevated contaminant concentrations.

1. Introduction

It is difficult to operate bio-methanogenic reactors treating fresh leachate collected from municipal solid waste (MSW) incineration plants for a number of reasons. Not only is treatment limited by extremely high organic loading rates (OLRs), high ammonia, calcium and heavy metal concentrations also significantly impair treatment efficiencies [1]. These limitations result in an accumulation of volatile fatty acids (VFAs) and acidification which can cause reactor souring [2,3].

The main goal of bio-methanogenic reactors is to convert as much complex organic matter in the influent to methane that can be used as a renewable energy source. This process relies on syntrophic partnerships

* Corresponding authors.
E-mail addresses: yandang@bjfu.edu.cn (Y. Dang), sdzlab@126.com (D. Sun).

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between a variety of bacteria and archaea. High concentrations of VFAs, low pH, high salinity, and high heavy metal and ammonia content in reactors treating MSW incineration leachate inhibit microbial activity and disrupt this synergistic food chain. Studies have shown that addition of non-biological conductive materials treating MSW incineration leachate such as carbon cloth [4] and graphite rods [5], can help microorganisms overcome some of these limitations. Not only do these materials provide surface area for microorganisms to form protective biofilms, they also likely adsorb inhibitory compounds (i.e. ammonia, Ca^{2+}, H_2S and heavy metals) and remove them from the reactor environment [6–8]. In addition, they have been shown to promote direct interspecies electron transfer (DIET) between bacteria and methanogens [9,10], which is less energetically expensive than indirect interspecies electron transfer (IIT) which is the other major syntrophic metabolism present in biomethanogenic reactors [11–13]. During IIT, methanogens accept electrons from diffusible compounds formed by fermentative bacteria such as hydrogen and formate [14]. In the case of DIET, electrons available from oxidation of a compound by a bacterium can be directly accepted by a methanogen, thus eliminating dispersive loss of electrons into the environment [15].

Magnetite is a conductive material that has not yet been tested in reactors treating MSW incineration leachate. It is known to stimulate DIET in co-cultures of *Geobacter metallireducens* and *Methanosarcina barkeri* [10], *G. sulfurreducens* and *Thiobacillus denitrificans* [16], and *G. sulfurreducens* and *G. metallireducens* [9]. Magnetite was also shown to enhance methanogenesis in enrichment cultures initiated with rice paddy soil, and could stimulate the complete oxidation of propionate and butyrate to methane via DIET [14]. Some recent studies have also shown that magnetite enhanced anaerobic digestion of wastewater sludge [17] and synthetic wastewater [12]. However, all of these studies were conducted on reactors treating relatively simple substrates under mild conditions.

MSW incineration leachate, on the other hand, contains high concentrations of complex organics and a number of compounds known to inhibit anaerobic digestion including ammonium, calcium, humic substances, heavy metals and sulfate. For example, concentrations of sulfate, humic substances, calcium, and heavy metals (zinc, lead, and nickel) were all 1.8–11.2 times higher in the MSW incineration leachate used for these studies than in young landfill leachate from most other bio-methanogenic reactors [18,19] (Table 1).

Detailed studies still need to be done to evaluate the effect of magnetite on bio-methanogenic treatment of complex organic compounds under the extreme conditions associated with reactors being fed MSW incineration leachate.

Therefore, in this study, a group of laboratory-scale up-flow anaerobic sludge bed (UASB) reactors were set up to treat raw MSW incineration leachate, with extremely high concentrations of organic matter and other inhibitory agents. The purpose of this study was to investigate whether incorporation of magnetite into bioreactors could stimulate methanogenesis, resist high organic loading shock, alter microbial community structure, and reduce factors inhibiting microbial activity.

Table 1
Comparison of MSW incineration leachate to young landfill leachate from other reactors.

Item	MSW incineration leachate (mg/L)	Young landfill leachate treated by methanogenic bioreactors (mg/L) [26–29]
COD	42,435 ± 11,377	23,236 ± 11,243
BOD_5	24,404 ± 5733	10,487 ± 723
NH_4^+-N	1218 ± 250	1336 ± 1016
TN	1754 ± 600	1922 ± 664
Cl^-	4358 ± 525	3400 ± 1131
SO_4^{2-}	2370 ± 759	212 ± 125
Ca	4551 ± 1804	1729 ± 1703
Zn	25.2 ± 16.0	3.17 ± 2.64
Pb	4.36 ± 4.60	0.58 ± 0.53
Ni	1.61 ± 0.98	0.51 ± 0.51
Humic substances	6405 ± 3107	3477
pH	4.58–6.42	5.8–7.8

2. Materials and methods

2.1. Inoculated sludge and fresh leachate

Sludge used as an inoculum source was collected from a full-scale anaerobic digester treating food wastewater in Beijing, China. The VSS/TSS ratio of the inoculated sludge was 0.66. Fresh leachate with an extremely high chemical oxygen demand (COD) and biological oxygen demand (BOD) was collected from a MSW-energy incineration plant in Beijing, China and stored at 4 °C until use. Characteristics of the leachate are provided in Table 1.

2.2. Reactor design

Two identical continuous-flow UASB reactors operated at 35 ± 1 °C with a working volume of 1.2 L were inoculated with 360 ml of sludge. Nano-sized magnetite was synthesized by slowly adding an acidic solution of Fe(II)/Fe(III) (0.8 M $FeCl_3$ and 0.4 M $FeCl_2$ in 0.4 M HCl) to a 1.5 M NaOH solution as previously described [20]. This magnetite (12 g) was added to one of the reactors (the experimental reactor). Fresh leachate with a COD of ~40,000 mg/L was provided as influent for both reactors. The OLR was gradually increased from 4.4 to 28.6 kgCOD/(m^3·d) by shortening the hydraulic retention time (HRT) from 9.3 to 1.4 d. A gas–liquid–solid separator was installed at the top of the reactor and a 10 L gas-sampling bag was used to collect biogas from the gas outlet every 24 h.

2.3. Analytical methods

Chemical oxygen demands (COD), total suspended solids (TSS) and volatile suspended solids (VSS) were measured according to standard methods [21]. Acetate, propionate and butyrate concentrations were monitored by high-performance liquid chromatography (Agilent 1260, USA) with 0.8 mM H_2SO_4 as an eluent [4]. Methane concentrations were measured with a gas chromatograph (Agilent 7890A, USA) equipped with a flame ionization detector and a Porapak Q column. Temperatures of detector and injection ports were maintained at 260 °C and 60 °C, respectively [22]. Heavy metal concentrations were determined with an inductively coupled plasma mass spectrometer (Agilent ICP-MS 7900, USA).

2.4. High-throughput sequencing

Sludge samples (0.2 g) were collected from both the experimental and control reactors at the end of the experiment. 1 ml phosphate-buffered saline (PBS; 0.13 M NaCl and 10 mM Na_2HPO_4 pH 7.2) was added to each sample, and samples were pelleted by centrifugation at 4000 × *g*. The pellet was then resuspended in 1 ml PBS with 1% sodium dodecyl sulfate (SDS), Lysing Matrix E (QBIOgene) was added, and cells were lysed in a beadbeater (Biospec, USA) set at 5.5 m/s for 1 min. Lysates were centrifuged for 15 min at 13,000 rpm, and DNA was extracted with the FastDNA kit for soil (QBIOgene, CA) according to the manufacturer's instructions. The quality and purity of extracted DNA was assessed with a micro volume spectrophotometer (NanoDrop 2000, USA).

Archaeal and bacterial 16S rRNA gene fragments were amplified by the polymerase chain reaction (PCR) using the following primer sets: (Arch519F/Arch915R) and (515F/806R) [4]. High-throughput sequencing was done on an Illumina Hiseq 2000 platform (Illumia, San