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Application of nanoscale zero valent iron and iron powder during sludge anaerobic digestion: Impact on methane yield and pharmaceutical and personal care products degradation

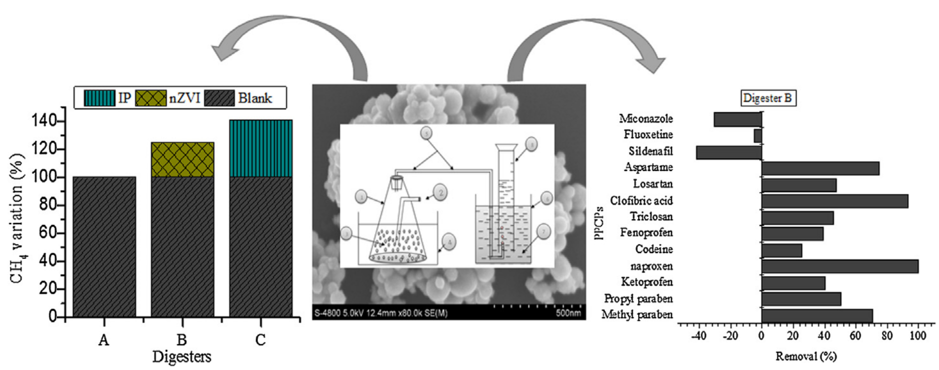
Fidèle Suanon [a,b,c], Qian Sun [a,*], Mingyue Li [a,b], Xiang Cai [a], Youchi Zhang [a], Yijun Yan [a], Chang-Ping Yu [a,d,*]

[a] CAS Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China
[c] Laboratory of Physical Chemistry, University of Abomey-Calavi, BP 4521 Cotonou, Republic of Benin
[d] Graduate Institute of Environmental Engineering, National Taiwan University, Taipei 106, Taiwan

HIGHLIGHTS

- nZVI and IP in anaerobic bioreactor enhanced methane yield up to 25% and 40%.
- Removal efficiencies of COD increased in the presence of nZVI and IP.
- nZVI and IP selectively enhanced chlorinated PPCP removal in anaerobic digestion.
- nZVI and IP in anaerobic bioreactor showed minor effect on most PPCP removal.

GRAPHICAL ABSTRACT



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ABSTRACT

Lab scale and single stage high solid anaerobic digestion of sewage sludge spiked with freshly synthesized nanoscale zero valent iron (nZVI) and commercial iron powder (IP) under mesophilic condition (37 ± 1 °C) was performed. The effects of both additives on methane yield, and pharmaceutical and personal care product (PPCP) removal were investigated. Results showed that methane yield was increased by 25.2% and 40.8% in the presence of nZVI (0.1%) and IP (1.6%), respectively. Removal efficiencies of chemical oxygen demand were 54.4% and 66.2% in the presence of nZVI and IP, respectively, which were higher compared to the control group (44.6%). In addition, most PPCPs could be partly or completely removed during the anaerobic digestion process. The application of nZVI and IP showed positive impact on the removal of chlorinated PPCPs ($p < 0.05$), but did not show significant impact on other PPCPs ($p > 0.05$). Our finding suggests that the application of nZVI and IP in anaerobic digestion could be a promising way to enhance methane yield but had less improvement on PPCP degradation.

* Corresponding authors at: CAS Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China.
E-mail addresses: qsun@iue.ac.cn (Q. Sun), cpyu@iue.ac.cn (C.-P. Yu).

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1. Introduction

The rapid increase in the waste production as a result of economic development and population growth is one of the environmental crises [1]. According to Chu (2009), over 11.2 million tons of dry sludge was produced annually in China, of which over 80% is improperly dumped [2]. The organic waste generates from cites in India is nearly 700 million tons annually [1], while in the U.S., approximately 6×10^6 metric tons of biosolids are produced each year, of which about 60% is land applied [3]. The disposal of sewage sludge is a great challenge all over the world due to its huge production and the occurrence of various inorganic and organic pollutants.

Among the organic pollutants, pharmaceuticals and personal care products (PPCPs) have received particular attention. PPCPs include a diverse collection of chemical substances, including human and veterinary drugs used to prevent or treat human and animal diseases, disinfectants and fragrances used in personal care products, and household chemicals to improve the quality of daily life [4]. Large number of studies investigated PPCP occurrence and fate during the wastewater treatment plants [5,6]. Results showed that PPCPs were widely detected in the wastewater and sewage sludge, with a concentration range from $pg\,L^{-1}$ to $\mu g\,L^{-1}$ [7–9] for wastewater and $ng\,kg^{-1}$ to $mg\,kg^{-1}$ [9,10] for sewage sludge, depending on the type of PPCPs and wastewater or sludge in different regions. Due to the continuous input of PPCPs, they are referred to as "pseudo-persistent" contaminants [11]. Previous studies indicated that PPCPs might spread through water cycle via land application or agricultural use of sewage sludge [4,12–14]. Considering PPCPs might pose adverse effects on the ecological safety and human health due to their biologically activity and bioaccumulation [15], the proper treatment of PPCPs in the sludge is necessary.

Anaerobic digestion is a process under controlled conditions where free oxygen is absent and temperatures are suitable for naturally occurring mesophilic or thermophilic anaerobic and facultative bacteria and archaea species, which convert the inputs to biogas and whole digestate [16]. Anaerobic digestion allows the stabilization of sewage sludge. It has been reported that providing of electron donor in the anaerobic digestion reactor can improve the digestion process and biogas yield. Regarding the capability of nanoscale zero valent iron (nZVI) on the pollutant removal due to its superior reactivity and very strong reducing character [17–19], it has been used to reduce chlorinated benzenes, hexa-valent chromium [20] and many other pollutants in different environment compartments [21,22]. In addition, nZVI, iron powder (IP), and iron scrap have been successfully used for the enhancement of methane yield [23–27], elimination and diminution of odors (such as H_2S), and better sludge stabilization [20,28] during anaerobic digestion process. However, Yang et al. reported the negative effect of nZVI in anaerobic digestion bioreactors where the inhibition of methane production was observed [29]. The contradictory results indicated that further investigations are still needed to access the impact of ZVI on methane production during anaerobic digestion process. In addition, the effect on PPCP removal during sludge anaerobic digestion with the addition of nZVI or IP is still not yet well documented.

Therefore, the objectives of the current study were: (1) to investigate the impact of both nZVI and IP on the anaerobic digestion of sludge. To this end, the biogas composition, methane production, chemical oxygen demand (COD), total alkalinity (TA), and pH were determined during the anaerobic digestion process. (2) To investigate the impact of nZVI and IP on PPCP removal during the anaerobic digestion process. To our knowledge, this is the first report on the effect of IP and nZVI on PPCP removal during anaerobic digestion of sewage sludge.

Table 1
Experimental design.

Materials	Sludge (g)	IP (g)	nZVI (g)
A	300.0	–	–
B	300.0	–	0.300 (~0.1% sludge)
C	300.0	5.000 (~1.6% sludge)	–

Note: Sludge was weighted basing on wet weight.

2. Materials and methods

2.1. Sludge and additive materials

Sewage sludge was collected from a municipal wastewater treatment plant (Xiamen, China). IP (purity > 98%) with the diameter of 0.2 mm and BET surface area of $2.48\,m^2\,g^{-1}$ was purchased from Sinopharm Chemical Reagent Co. Ltd. The nZVI was freshly prepared according to Yuvakkumar's method [30] (Fig. S1 in the Supplemental information (SI)). Scanning electron microscopy coupled with an energy dispersive X-ray microanalysis system (SEM/EDX) (HITACHI S-4800) was used to characterize the synthesized nZVI and Quantachrome Instrument v2.0 was used for the BET surface area determination. As shown in SI Fig. S2, the average diameter of nZVI is 160 nm (Fig. S2a and d) and BET surface area is $23.3\,m^2\,g^{-1}$ (Fig. S2c). In addition, XRD patterns of both nZVI and IP indicate that the particles have a face center cubic structure. The peaks could be attributed to 011, 002, and 112 crystallographic planes (Fig. S2e in SI).

2.2. PPCPs

A total of 19 PPCPs (Table S1) were selected and investigated mainly based on their high detection frequencies and high concentrations reported in the previous studies [9]. All analytical standards were of high purity (mostly > 98%) and purchased from Sigma-Aldrich (St. Louis, MO, USA), Fluka (St. Louis, MO, USA), Dr. Ehrenstorfer GmbH (Augsburg, Germany), AccuStandard (New Haven, CT, USA) or Cambridge Isotope Laboratories (Andover, MA, USA). Methanol and acetone (HPLC grade) were provided by Tedia (Fairfield, OH, USA). The reagent water was prepared with a Milli-Q water purification system (Millipore, USA). Stock solutions of individual PPCP were prepared in methanol and stored at −20 °C in the dark.

2.3. Bioreactor and experimental design

The schematic diagram of anaerobic digestion is shown in Fig. S3 in SI. Sludge digestion was performed in a 500 mL conical flask capped with rubber stoppers. An outlet was perforated on the stoppers, and connected to a water displacement system consisting of calibrate glass cylinder (500 mL) to measure the volume of biogas. A second orifice was perforated on the body of the conical flask which allows the weekly collection of sludge samples after mechanical shaking. Before digestion, the sludge substrate was diluted with distilled water to get total solid (TS) 15%. As shown in Table 1, three batch experiments were setup. Digester A was control group with 300.0 g sludge (wet weight) in the anaerobic digestion bioreactor, while digester B and C were 300.0 g sludge with addition of nZVI, and IP, respectively. The pH of each flask was adjusted to 7.0 ± 0.3 using 1.0 M HCl or 1.0 M NaOH as recommended by Xie et al. [31]. The sludge solution was flushed with nitrogen gas for 5 min to assure the anaerobic condition in the bioreactor at the beginning [32]. Bottles were then kept within a water bath under mesophilic condition (37 ± 1 °C), and the digesters were manually shaken twice a day for one min. All experiments were conducted in triplicate.