Journal of Hazardous Materials 321 (2017) 47–53

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

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

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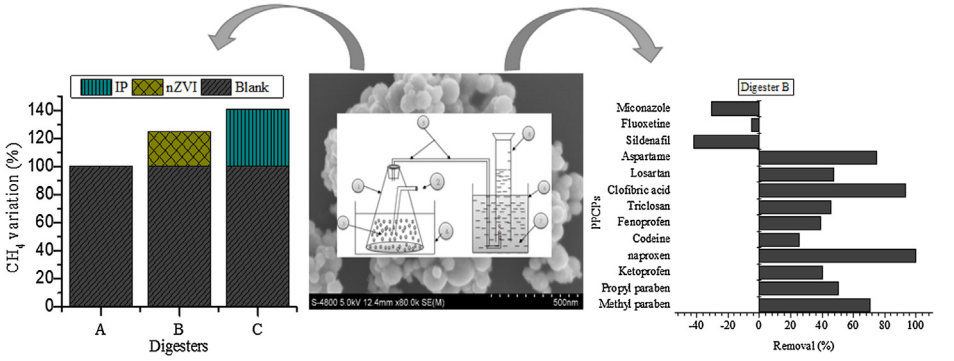
HIGHLIGHTS

- 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



ARTICLE INFO

Article history:
Received 6 June 2016
Received in revised form 2 August 2016
Accepted 31 August 2016
Available online 31 August 2016

Keywords:
Anaerobic digestion
Sewage sludge
Nanoscale zero valent iron (nZVI)
Iron powder (IP)
Pharmaceutical and personal care products (PPCPs)

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.

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http://dx.doi.org/10.1016/j.jhazmat.2016.08.076
0304-3894/

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 μg 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.

Table 2
Physicochemical characterization of the sludge and mixtures before experimentation.

Parameters	Sludge	A[a]	B[a]	C[a]
TS (%)	25.4	15	15	15
pH	8.5	7.2	7.3	7.1
VS (% TS)	49.6	49.6	49.6	49.6
TA (mg L^{-1} $CaCO_3$)	1653.8	800.5	800.5	800.5
COD (mg L^{-1})	6651.0	6651.0	6651.0	6651.0
C/N	7.7	7.7	7.7	7.7

A, B, and C are three different digesters; [a], after pH adjustment.

2.4. Physical and chemical analysis of the sludge

Physicochemical characterizations of the sludge, including pH, water content (Wc), TS, volatile solid (VS), TA, COD, C, N, and S content, are shown in Table 2. Wc, TS, VS and TA were determined according to the standard methods by American Public Health Association [33], and pH was determined using a multi-parameter meter (HACH, HQ40d). Elemental analysis (C, N, S) was performed using a Macro Elemental CNHS/O Analyzer (Vario MAX; Elementar, Germany), and C/N ratio was calculated accordingly. For the determination of COD and TA, samples were centrifuged at 10,000 × *g* for 15 min at 4 °C, and the supernatants were used.

As shown in Table 2, the sludge exhibited remarkable COD concentration, with the value of 6651.0 mg L^{-1}. Sludge solution was basic (pH 8.4). For a better comparison, mixtures were set at the same initial condition with pH at 7.0 ± 0.3. C/N ratio of the raw sludge was low (7.7) for suitable anaerobic digestion [34]. This is why we have assumed that the use of electron donor would improve the digestion process.

2.5. Biogas measurement and composition

The volume of biogas was measured by displacing the tap water which was inside the calibrate glass cylinder (Fig. S3 in SI). Gas samples were taken twice a week for composition analysis using gas chromatography (GC) equipped with flame ionized detector (FID) (GC 9890A-Shanghai Linghua Inc.). Temperatures of injector, detector and column were kept at 100, 250 and 60 °C, respectively. Nitrogen (N_2) was used as the carrier gas at flow rate of 50 mL min^{-1}. The GC column was 2 m × Ø3 mm GDX-103 packed columns. A volume of 0.100 mL of produced biogas was taken using a syringe (with pressure lock) and injected to the column.

2.6. PPCP extraction and analysis

PPCPs in the sludge samples were analyzed in the beginning and at the end of the digestion process. Sludge were dried via lyophilization, grounded in a clean mortar and sieved. The extraction of PPCPs from sludge samples was performed by the ultrasonic assistant extraction, and the clean-up procedure was conducted by the solid phase extraction (SPE) according to the U.S. Environmental Protection Agency [35]. The detection was conducted by liquid chromatography tandem mass spectrometry (LC-QqQ-MS) [36]. The details of the sample preparation and instrument analysis procedure of PPCP are provided in SI.

3. Results and discussion

3.1. pH and TA

Value of pH is an important factor which influences the fermentation process. According to Ogejo et al. [37], the most favorable pH for bacteria growth and to achieve maximal methane yield during anaerobic digestion was in the range of 6.8–7.2. In the current study, the initial pH was adjusted to 7.0 ± 0.3 in all digesters. As shown in Fig. 1a, pH increased at the beginning of the digestion, then decreased but did not go under 7.0 till the end of the process. The highest pH values were all recorded on Day 7, with the values of 7.8, 7.6, and 8.5 in digesters A–C, respectively (Fig. 1a). The drastically increase of pH in the digester C at the beginning of the digestion might be due the Fe^0 hydrolysis since the IP content was 1.6% of the sludge solution. Indeed, in anoxic conditions, where the amount of dissolved oxygen is not sufficient for iron oxidation,

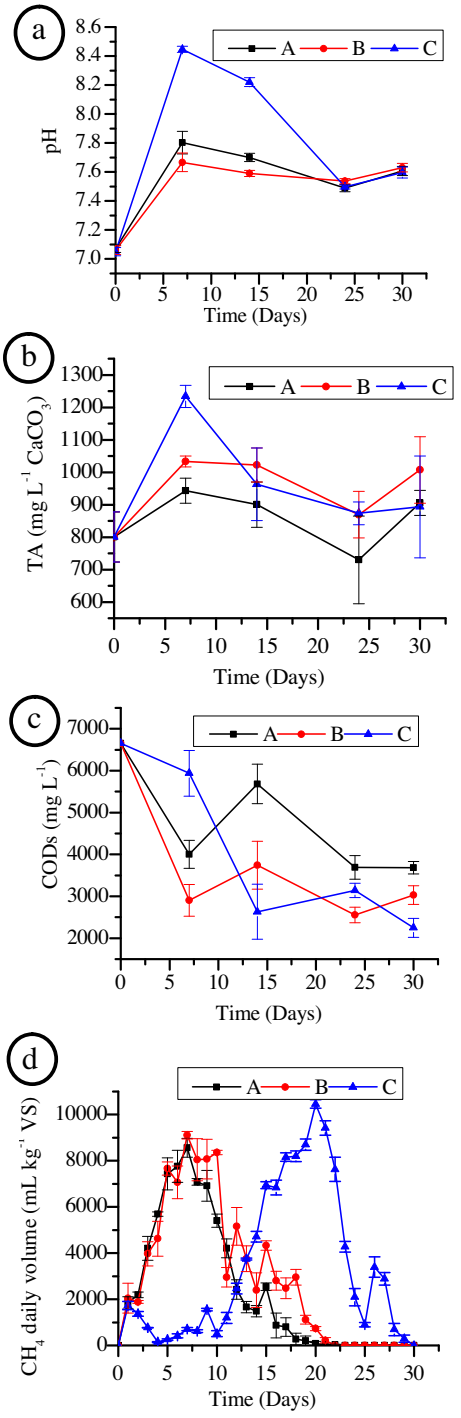

Fig. 1. Profile of studied parameters during anaerobic digestion process (a)-pH, (b) Total alkalinity (TA), (c)-Chemical oxygen demand (COD), (d)-Daily volume of methane, (e)-Cumulative volume of methane, (f)-effect of additive materials (nZVI and IP) and methane production and (g)-Total carbon dioxide production.

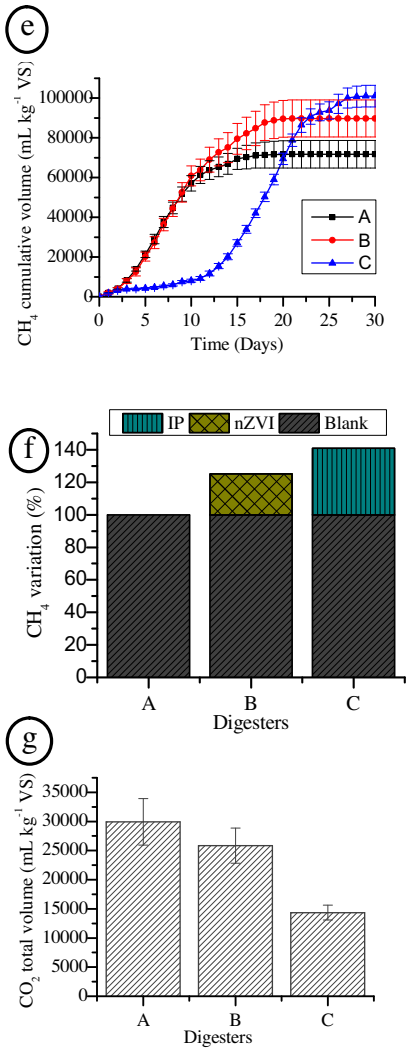

Fig. 1. (*Continued*)

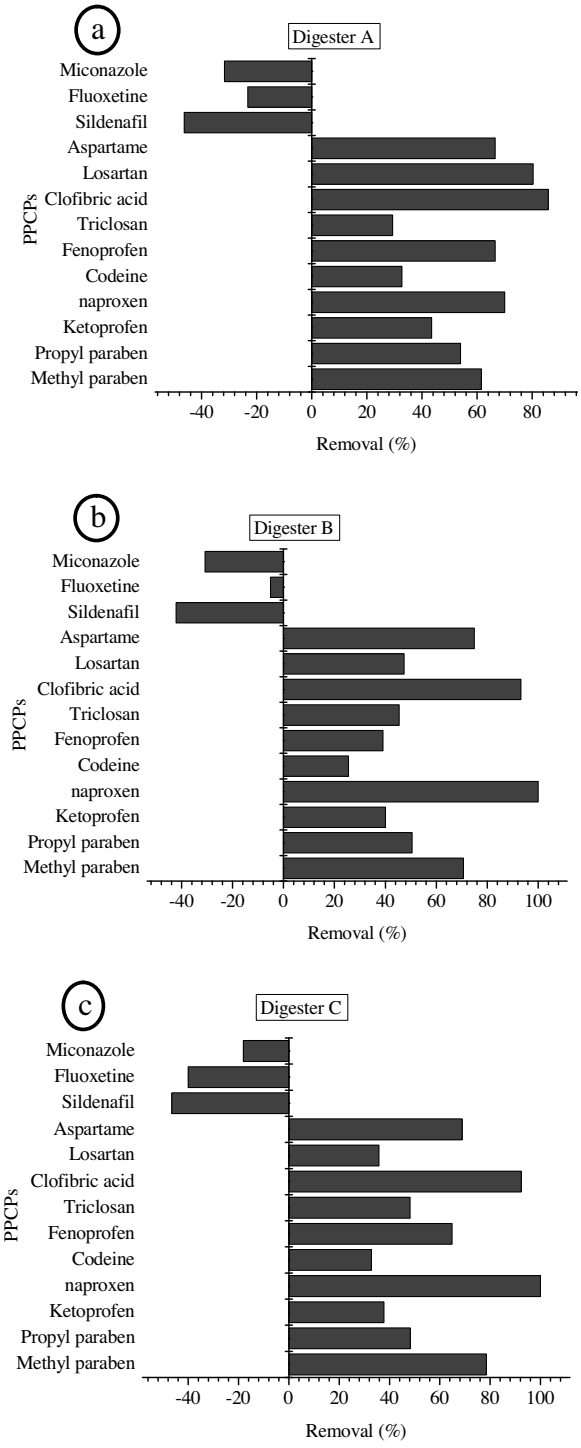

Fig. 2. PPCP removal during AD process. (a)-digester A (control), (b)-digester (B + 0.1% nZVI), (c)-digester (C + 1.6% IP).

water can serve as an oxidant and Fe^0 was oxidized to Fe^{2+} as shown in equation (Eq. (1)) [38,39], which might lead to an increased pH in the weakly-buffered systems [27,40]. The oxidization is also possible via the reaction of Fe^0 with some organic compounds in the medium [41]. The decrease of pH after Day 7 might be due to the formation of volatile fatty acid (VFAs) [42].

$$Fe^0(s) + 2H_2O(aq) \rightarrow Fe^{2+}(aq) + H_2(g) + 2OH^-(aq) \quad (1)$$

The alkalinity showed a similar profile as pH, reaching the highest level of 943.3, 1033.3, and 1234.0 mg L^{-1} $CaCO_3$ on Day 7 in the digesters A–C, respectively (Fig. 2b). The minimum level of 730.0, 669.1 and 573.3 mg L^{-1} $CaCO_3$ was observed on Day 25. The decrease of TA could also be explained by the production and accumulation of VFAs [43]. The slight increase of alkalinity in the final stage (Day 25–30) might be due to the consumption of the remaining VFAs by the methanogens or other microbes [43].

3.2. COD

The microbial activity is responsible for the release of soluble COD compounds to the medium, followed by their consumption as carbon source. Generally, COD showed a decreasing trend in all digesters during the anaerobic digestion process (Fig. 1c). COD dropped from 6651 mg L^{-1} in digesters A–C at the beginning of digestion to 3683 mg L^{-1} (digesters A), 3032.1 mg L^{-1} (digester B) and 2247.5 mg L^{-1} (digester C) in the end. In term of the percentage, COD removal efficiencies were about 44.6%, 54.4%, and 66.2% in digester A–C, respectively. The decrease of COD was the consequence of the activity of microbes which consumed and degraded organic matters [44]. The fluctuation of COD (decrease and timely increase) during the digestion process could be explained by the fact that after digestion of most available compounds (resulting in COD decreasing), the solid particulate materials that was not yet acclimatized at first by the microorganisms or accessible to the microorganisms were converted into soluble organic compounds

such as acetic acid, propionic acid, and butyric acid, which led into an increase of COD concentration in the solution [44]. To be noticed, in digester B and C, the addition of nZVI and IP showed a positive impact on COD removal. The increments in COD removal efficiency in the presence of IP and nZVI were estimated at 21.6% and 7.8%, respectively.

3.3. Methane production

Methane is a precious and important product during anaerobic digestion. Methane content in biogas is an important index to assess the performance of anaerobic digestion process. The average methane contents of the produced biogas were estimated at 70 ± 3.9% (digester A), 73.4 ± 2.3% (digester B), and 81.9 ± 2.1% (digester C). The addition of nZVI and IP in bioreactor B and C enhanced the methane content by 3.1% and 11.6%.

Daily volumes of methane production are shown in Fig. 1d. It was noted that methane generation began on Day 1 in digesters A and B. This was predictable since the sewage sludge was freshly collected and rich in anaerobic bacteria, as methane production rate in batch conditions is directly related to the activity of methanogenic bacteria [45]. Daily methane production increased and reached the maximum with an average volume of 8563.9 and 9108.2 mL kg^{-1} VS in digester A and B on the day 7. In digester C, the daily methane production was inhibited during the first 10 days. It drastically increased from the day 10, and reached a maximum with the average volume of 10461.5 mL kg^{-1} VS on the day 20, following by a decrease until the end of the process. This observation was strongly linked to the pH profile. As shown in Fig. 1a, pH drastically increases from 7.1 on the day 0 to 8.4 on the day 7 in digester C, the high pH would affect microbial activity and reduce the methane production [46]. It can be noted that as pH decreased in the following days due to the formation of VFAs [42,47], the microbes were able to adapt the conditions and get a better activity, and consequently, the daily methane volume increased.

Cumulative volumes of methane production are shown in Fig. 1e. During the anaerobic digestion process, there were 71720.2, 89773.0 and 101018.0 mL kg^{-1} VS methane produced in the digesters A–C, respectively. The application of nZVI enhanced the methane yield for about 18052.7 mL kg^{-1} VS, corresponding to the increase rate of 25.2%, while the addition of IP enhanced methane yield by 29297.3 mL kg^{-1} VS, corresponding to an improvement rate of 40.8% (Fig. 1f). The present result was in accordance with previous findings [23,28,48] that an increase in methane production was observed when zero valent iron was applied in anaerobic digestion bioreactor. For example, Su et al. [28] reported the enhancement of methane concentration in produced biogas by 5.1–13.2%, and the improvement of biogas and methane production by 30.4% and 40.4%, respectively, after addition of 0.1% nZVI in anaerobic bioreactor during 17 days of digestion. Xu et al. [48] found that the methane yield increased by 8.7% when Fe^0 was added in the anaerobic digestion bioreactor. The causes of the increase in methane production with zero valent iron could be explained by several possible reasons. First, it could be because Fe^0 produced electrons ($Fe^0 \rightarrow Fe^{2+} + 2e^-$) to enrich anaerobic fermentation process and stimulate the metabolism and growth of critical microbes involved in anaerobic process and consequently resulted in the increase of biogas yield [23,27,49,50]. In addition, there was lower CO_2 production in both digesters B and C containing nZVI and IP, respectively (Fig. 1g). It was probably due to the partial conversion of produced CO_2 to methane in the presence of IP or nZVI via the electron transfer [20,25,49,51] as shown in equation (Eq. (2)). As mentioned in Section 3.1, the addition of nZVI could contribute to the production of H_2 via Fe^0 anaerobic corrosion (Eq. (1)) [27], and the produced H_2 could produce methane and thereby improve methane yield. For example, the hydrogenotrophic methanogen could not only form extra CH_4, but also consume part of CO_2 and convert it into CH_4 (Eq. (3)) by using produced H_2 as energy source [25,27]. Likewise, homoacetogenic bacteria, could also fix CO_2/H_2 as sole energy source for the formation of methanogenic precursor acetate (Eq. (4)) [25], which would be further converted into methane (Eq. (5)). Therefore, the methane yield in both digesters B and C was improved. In addition, Fe^0 could also remove toxic and harmful compounds to bacteria such as H_2S via $Fe^0 + H_2S \rightarrow FeS + H_2$ [20], which would stabilize the sludge and lead to a more stable methane production.

$$8H^+ + 4Fe^0 + CO_2 \rightarrow CH_4 + 4Fe^{2+} + 2H_2O, \quad \Delta G^0 = -150.5 kJmol^{-1} CH_4 \tag{2}$$

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O; \Delta G^0 = -131\ K/Jmol \tag{3}$$

$$4H_2 + 2CO_2 \rightarrow CH_3COO^- + H^+ + 2H_2O; \Delta GO = -95\ K/Jmol \tag{4}$$

$$CH_3COO^- + H^+ \rightarrow CH_4 + CO_2, \quad \Delta G^0 = -75.7\ K/J\ mol \tag{5}$$

3.4. PPCP occurrence and fate during anaerobic digestion

A total of 19 PPCPs (Table S1) were investigated in the sewage sludge at the beginning and the end of the digestion. PPCP concentrations are displayed in Table 3. Among the investigated PPCPs, 13 were detected in the sludge, while 6 compounds, including benzyl paraben, atenolol, sulfadiazine, clenbuterol, pirenzepine, and carbamazepine, were below the method detection limits (Table S2, SI). In the raw sludge, triclosan concentration nearly reached the order of mg kg^{-1} (979.0 μg kg^{-1}). The high concentration of triclosan in sewage sludge was in accordingly to the previous reports [52]. Ketoprofen and miconazole were 110.7 and 120.2 μg kg^{-1}, respectively. The average concentrations of fluoxetine, sildenafil, fenoprofen, aspartame, methyl paraben, and codeine concentrations were 14.9, 16.2, 17.2, 22.5, 30.3 and 34.6 μg kg^{-1}, respectively. All others compounds, including naproxen, clofibric acid, losartan and propyl paraben, showed a lower concentration in the sludge, with the range of 1.1 μg kg^{-1} (losartan) to 6.5 μg kg^{-1} (propyl paraben).

After 30 days of anaerobic digestion, PPCP concentrations were determined in digesters A–C, and the results are shown in Table 3. The removal efficiencies (RE) (Fig. 2) were calculated as follows: $RE(\%) = \frac{mi-mf}{mi} \times 100$, where mi and mf are the average concentrations of a given PPCP in the sludge before and after anaerobic

Table 3
PPCP concentrations (μg kg^{-1}, dry weight) in the raw sludge and digestates.

Compounds	Concentration (average ± standard deviation, n = 3)			
	A/B/C (initial)	A (final)	B (final)	C (final)
Methyl paraben	30.3 ± 5.4	10.4 ± 2.1	8.9 ± 1.2	6.5 ± 1.8
Propyl paraben	6.5 ± 1.4	3.1 ± 0.6	3.2 ± 0.2	3.4 ± 0.4
Benzyl paraben	BDL	BDL	BDL	BDL
Ketoprofen	111 ± 7	69.7 ± 13.7	66.3 ± 15.2	67 ± 10
Naproxen	1.9 ± 1.3	0.8 ± 0.4	BDL	BDL
Codeine	34.6 ± 6.2	17.6 ± 5.6	25.8 ± 2.7	23.3 ± 2.3
Fenoprofen	17.7 ± 4.5	6.6 ± 0.7	10.7 ± 0.3	6.2 ± 2.0
Atenolol	BDL	BDL	BDL	BDL
Triclosan	979.0 ± 134	691.6 ± 42.1	535.0 ± 15.3	507.6 ± 13.6
Sulfadiazine	BDL	BDL	BDL	BDL
Clofibric acid	3.2 ± 0.6	0.4 ± 0.1	0.2 ± 0.1	0.2 ± 0.0
Losartan	1.1 ± 0.5	0.2 ± 0.1	0.6 ± 0.2	0.7 ± 0.1
Clenbuterol	BDL	BDL	BDL	BDL
Pirenzepine	BDL	BDL	BDL	BDL
Aspartame	22.5 ± 13.4	2.6 ± 0.5	5.6 ± 0.9	7.0 ± 2.1
Sildenafil	16.2 ± 5.3	8.8 ± 1.0	23.0 ± 0.4	23.7 ± 3.4
Carbamazepine	BDL	BDL	BDL	BDL
Fluoxetine	14.9 ± 7.9	27.5 ± 11.8	15.7 ± 4.5	20.9 ± 5.2
Miconazole	120.2 ± 45.3	116.0 ± 4.0	157.3 ± 13.3	142.0 ± 6.1

BDL means below the method detection limit.

digestion, respectively. Results showed that the RE varies among different PPCP. For example, clofibric acid, lostartan, naproxen, aspartame, methyl paraben, and propyl paraben were labile and readily degraded during the anaerobic digestion process with the average removal efficiencies higher than 50%. Triclosan, fenoprofen, codeine, and ketoprofen were moderate removed with the removal efficiencies of (29.3%, 45.4%, 48.1%), (66.6%, 39.1%, 64.8), (32.7%, 25.5%, 32.8%) and (43.5%, 40.1%, 37.7%), respectively, in the digester (A–C). However, sildenafil, miconazole, and fluoxetine showed negative removal efficiencies (−18% to −47%) in all digesters. The increase of concentrations was probably due to the release of free PPCPs from the conjugated forms during the anaerobic processes [53,54].

One way ANOVA test on PPCP RE during the anaerobic digestion in digester A–C was performed with SPSS 20.0. Generally, nZVI and IP did not show significant improvement on the removal of target PPCP ($p > 0.05$). For example, the RE of propyl paraben was 53.9%, 50.5% and 48.3% in digester A–C, respectively, while the RE of ketoprofen was 43.5%, 40.1%, and 37.7%. However, the difference of removal efficiencies for specific PPCP was observed. Losartan exhibited better degradation rate in the absence of zero valent iron (digester A) compared to the digesters B and C. The RE was 80.4% in digester A, 47.4% in digester B and 35.8% in digester C. In contrast, the RE of naproxen was positively impacted by the addition of both NPs and IP in the anaerobic bioreactor ($p = 0.005$). In addition, the removal efficiencies for the chlorinated PPCPs, including clofibric acid and triclosan, were improved ($p < 0.05$). For example, RE of clofibric acid was 87.5%, 93.7%, and 93.7% in digesters A–C, respectively, while RE of triclosan were 29.3%, 45.4%, and 48.1% in digester A–C, respectively. The RE of triclosan was improved by 16.1% in the presence of nZVI and 18.8% in the presence of IP. Although the applied concentration of nZVI (0.1%) was lower compared to IP (1.6%), its positive impact on triclosan removal was remarkable. Bokare et al. [55] and Murugesan et al. [56] have reported the positive effect of nZVI on triclosan removal in aqueous system; in the presence of nZVI, triclosan degradation process passes through dechlorination via electron transfer between nZVI and triclosan. The capability of ZVI and nZVI for remediating chlorinated or polychlorinated compounds have been widely studied and reported [57–59]. The present study suggested, to some extent, the use of nZVI and IP could improve the removal of chlorinated PPCPs during the anaerobic digestion process.

4. Conclusions

The effect of nZVI and IP on methane production and PPCP removal during sludge anaerobic digestion was investigated. Results showed that the use of nZVI and IP during anaerobic digestion can enhanced methane yield by 25.2% at dose rate of 0.1% wet weight for nZVI and 40.8% at the dose rate of 1.6% wet weight for IP. COD removal was also improved in the presence of nZVI and IP. Despite the improvement of the digestion process with the addition of ZVI in anaerobic digestion bioreactor, there was no significant difference on the removal efficiencies of most PPCPs. The use of nZVI and IP seems to selectively enhance chlorinated PPCP degradation. As a consequence, the use of nZVI or IP was found to be an effective way to increase methane production but showed less improvement on the PPCP removal during anaerobic digestion of sewage sludge.

Acknowledgments

This work was funded by Hundred Talents Program of Fujian Province, China, National Natural Science Foundation of China (31370503, 41573102), the Young Talent Foundation of IUE CAS (IUEQN201505), Xiamen Southern Oceanographic Center Project (14GNY022NF22), Youth Innovation Promotion Association CAS (2016280), and Chinese Academy of Sciences-The World Academy of Sciences (CAS-TWAS) president's fellowship program for developing countries. We appreciate Mr. Lifeng Lin for the maintenance of HPLC–MS/MS and Ms Jiani Wang for XRD analysis.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2016.08.076.

References

[1] T.T. Mane, S.S. Raskar, Management of agriculture waste from market yard, Res. J. Recent Sci. 1 (2012) 289–296.
[2] G. Yang, G. Zhang, H. Wang, Current state of sludge production management, treatment and disposal in China. A Review, Water Res. 78 (2015) 60–73.
[3] J. Peccia, T. Paez-Rubio, Quantification of airborne biological contaminants associated with land applied biosolids, Water Environ. Res. (2006) 169.
[4] A.B.A. Boxall, M.A. Rudd, B.W. Brooks, D.J. Caldwell, K. Choi, S. Hickmann, E. Innes, K. Ostapyk, J.P. Staveley, T. Verslycke, G.T. Ankley, K.F. Beazley, S.E. Belanger, J.P. Berninger, P. Carriquiriborde, A. Coors, P.C. DeLeo, S.D. Dyer, J.F. Ericson, F. Gagné, J.P. Giesy, T. Gouin, L. Hallstrom, M.V. Karlsson, D.G.J. Larsson, J.M. Lazorchak, F. Mastrocco, A. McLaughlin, M.E. McMaster, R.D. Meyerhoff, R. Moore, J.L. Parrott, J.R. Snape, R. Murray-Smith, M.R. Servos, P.K. Sibley, J.O. Straub, N.D. Szabo, E. Topp, G.R. Tetreault, V.L. Trudeau, G. VanDer Kraak, Pharmaceuticals and personal care products in the environment: what are the big questions? Environ. Health Perspect. 120 (2012) 1221–1229.
[5] J. Radjenovic, M. Petrovic, D. Barceló, Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment, Water Res. 43 (2009) 831–841.
[6] A. Jelic, M. Gros, A. Ginebreda, R. Cespedes-Sanchez, F. Ventura, M. Petrovic, D. Barcelo, Occurrence, partition and removal of pharmaceuticals in sewage water and sludge during wastewater treatment, Water Res. 45 (2011) 1165–1176.
[7] N. Ratola, A. Cincinelli, A. Alves, A. Katsoyiannis, Occurrence of organic microcontaminants in the wastewater treatment process. A mini review, J. Hazard. Mater. 239 (2012) 1–18.
[8] Q. Sun, M. Lv, A. Hu, X. Yang, C.-P. Yu, Seasonal variation in the occurrence and removal of pharmaceuticalsand personal care products in a wastewater treatment plant in Xiamen, China, J. Hazard. Mater. 277 (2014) 69–75.
[9] Q. Sun, M. Li, C. Ma, X. Chen, X. Xie, C.-P. Yu, Seasonal and spatial variations of PPCP occurrence, removal and mass loading in three wastewater treatment plants located in different urbanization areas in Xiamen, China, Environ. Pollut. (2015), http://dx.doi.org/10.1016/j.envpol.2015.10.003.
[10] J.L. Liu, M.H. Wong, Pharmaceuticals and personal care products (PPCP): a review on environmental contamination in China, Environ. Int. 59 (2013) 208–224.
[11] J.B. Ellis, Pharmaceutical and personal care products (PPCP) in urban receiving waters, Environ. Pollut. 144 (2006) 184–189.
[12] A.B.A. Boxall, The environmental side effects of medication, EMBO Rep. 5 (2004) 1110–1116.
[13] O. Bergersen, K.Ø. Hanssen, T. Vasskog, Anaerobic treatment of sewage sludge containing selective serotonin reuptake inhibitors, Bioresour. Technol. 117 (2012) 325–332.
[14] A.B.M. Lajeunesse, B. Barbeau, S. Sauve, C. Gagnon, Ozone oxidation of antidepressants in wastewater e treatment evaluation and characterization of new by-products by LC-QToFMS, Chem. Cent. J. 7 (2013) 1–11.
[15] L.H.M.L.M. Santos, A.N. Araújo, A. Fachini, A. Pena, C. Delerue-Matos, M.C.B.S.M. Montenegro, Ecotoxicological aspects related to the presence of pharmaceuticals in the aquatic environment, J. Hazard. Mater. 175 (2010) 45–95.
[16] A. Gashaw, Anaerobic co-digestion of biodegradable municipal solid waste with human excreta for biogas production: a review, Am. J. Appl. Chem. 2 (2014) 55–62.
[17] P.G. Tratnyek, R.L. Johnson, Nanotechnologies for environmental cleanup, Nano Today 1 (2006) 44–48.
[18] B. Karn, T. Kuiken, M. Otto, Nanotechnology and in situ remediation: a review of the benefits and potential risks, Cienc. Saude Coletiva 16 (2011) 165–178.
[19] J. Nasiri, A. Gholami, E. Panahpour, Removal of cadmium from soil resources using stabilized zero-valent iron nanoparticles, J. Civil Eng. Urban. 3 (2013) 338–341.
[20] X.Q. Li, D.G. Brown, W.X. Zhang, Stabilization of biosolids with nanoscale zero-valent iron (nZVI), J. Nanopart. Res. 9 (2007) 233–243.
[21] C. Miege, J.M. Choubert, L. Ribeiro, M. Eusebe, M. Coquery, Fate of pharmaceuticals and personal care products in wastewater treatment plants-conception of a database and first results, Environ. Pollut. 157 (2009) 1721–1726.

[22] N. Le-Minh, S.J. Khan, J.E. Drewes, R.M. Stuetz, Fate of antibiotics during municipal water recycling treatment processes, Water Res. 44 (2010) 4295–4323.
[23] Y. Liu, Y. Zhang, X. Quan, Y. Li, Z. Zhao, X. Meng, S. Chen, Optimization of anaerobic acidogenesis by adding Fe^0 powder to enhance anaerobic wastewater treatment, Chem. Eng. J. 192 (2012) 179–185.
[24] X. Meng, Y. Zhang, Q. Li, X. Quan, Adding Fe^0 powder to enhance the anaerobic conversion of propionate to acetate, Biochem. Eng. J. 73 (2013) 80–85.
[25] Y. Feng, Y. Zhang, X. Quan, S. Chen, Enhanced anaerobic digestion of waste activated sludge digestion by the addition of zero valent iron, Water Res. 52 (2014) 242–250.
[26] Y. Zhang, Y. Feng, Q. Yu, Z. Xu, Xie. Quan, Enhanced high-solids anaerobic digestion of waste activated sludge by the addition of scrap iron, Bioresour. Technol. 159 (2014) 297–304.
[27] G. Zhen, X. Lu, Y.-Y. Li, Y. Liu, Y. Zhao, Influence of zero valent scrap iron (ZVSI) supply on methane production from waste activated sludge, Chem. Eng. J. 263 (2015) 461–470.
[28] L. Su, X. Shi, G. Guo, A. Zhao, Y. Zhao, Stabilization of sewage sludge in the presence of nanoscale zero-valent iron (nZVI): abatement of odor and improvement of biogas production, J. Mater. Cycles Waste Manage. 15 (2013) 461–468.
[29] Y. Yang, J. Guo, Z. Hu, Impact of nano zero valent iron (NZVI) on methanogenic activity and population dynamics in anaerobic digestion, Water Res. 47 (2013) 6790–6800.
[30] R. Yuvakkumar, V. Elango, V. Rajendran, N. Kannan, Preparation and characterization of zero valent iron nanoparticles, Dig. J. Nanomater. Biostruct. 6 (2011) 1771–1776.
[31] S. Xie, P. Lawlor, J. Frost, Z. Hu, X. Zhan, Effect of pig manure to grass silage ratio on methane production in batch anaerobic co-digestion of concentrated pig manure and grass silage, Bioresour. Technol. 102 (2011) 5728–5733.
[32] G.K. Kafle, S.H. Kim, K.I. Sung, Ensiling of fish industry waste for biogas production: a lab scale evaluation of biochemical methane potential (BMP) and kinetics, Bioresour. Technol. 127 (2013) 326–336.
[33] APHA (American Public Health Association), Standard Methods for the Examination of Water and Wastewater, 19th ed., APHA, Washington, DC, USA, 1995.
[34] T. Forster-Carneiro, M. Perez, L.I. Romero, Composting potential of different inoculum sources in the modified SEBAC system treatment of municipal solid wastes, Bioresour. Technol. 98 (2007) 3354–3366.
[35] EPA, Method 1694: Pharmaceuticals and Personal Care Products in Water, Soil, Sediment, and Biosolids by HPLC/MS/MS, 2007 http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2008_01_03_methods_method_1694.pdf.
[36] M. Lv, Q. Sun, A. Hua, L. Hou, J. Li, X. Cai, C.-P. Yu, Pharmaceuticals and personal care products in a mesoscale subtropical watershed and their application as sewage markers, J. Hazard. Mater. 280 (2014) 696–705.
[37] J.A. Ogejo, Z. Wen, J. Ignosh, E. Bendfeldt, E.R. Collins, Biomethane Technology, Virginia Cooperative Extension. Publication, 2009, pp. 442–881 http://pubs.ext.vt.edu/442/442-881/442-881_pdf.pdf.
[38] H. Chen, H. Luo, Y. Lan, T. Dong, B. Hu, Y. Wang, Removal of tetracycline from aqueous solutions using polyvinylpyrrolidone (PVP-K30) modified nanoscale zero valent iron, J. Hazard. Mater. 192 (2011) 44–53.
[39] P.D. Mackenzie, D.P. Horney, T.M. Sivavec, Mineral precipitation and porosity losses in granular iron columns, J. Hazard. Mater. 68 (1999) 1–17.
[40] Y. Liu, T. Phenrat, G.V. Lowry, Effect of TCE concentration and dissolved groundwater solutes on NZVI-promoted TCE dechlorination and H2 evolution, Environ. Sci. Technol. 41 (2007) 7881–7887.
[41] Y. Liu, G.V. Lowry, Effect of particle age (Fe^0 content) and solution pHon NZVI reactivity: H2 evolution and TCE dechlorination, Environ. Sci. Technol. 40 (2006) 6085–6090.
[42] Y. Chen, J.J. Cheng, K.S. Creamer, Inhibition of anaerobic digestion process: a review, Bioresour. Technol. 99 (2008) 4044–4064.
[43] H. Ahn, M. Smith, S. Kondrad, J. White, Evaluation of biogas production potential by dry anaerobic digestion of switchgrass-animal manure mixtures, Appl. Biochem. Biotechnol. 160 (2010) 965–975.
[44] S. Wan, Lei. Sun, Y. Douieb, J. Sun, W. Luo, Anaerobic digestion of municipal solid waste composed of food waste, wastepaper, and plastic in a single-stage system: performance and microbial community structure characterization, Bioresour. Technol. 146 (2013) 619–627.
[45] A. Nopharatana, P.C. Pullammanappallil, W.P. Clarke, Kinetic and dynamic modelling of batch anaerobic digestion of municipal solid waste in a stirred reactor, Waste Manage. 27 (2007) 595–603.
[46] D.H. Lee, S.K. Behera, J.W. Kim, H.-S. Park, Methane production potential of leachate generated from Korean food waste recycling facilities: a lab scale study, Waste Manage. 29 (2009) 876–882.
[47] N. Zhai, T. Zhang, D. Yin, G. Yang, X. Wang, G. Ren, Y. Feng, Effect of initial pH on anaerobic co-digestion of kitchen waste and cow manure, Waste Manage. 38 (2015) 126–131.
[48] H. Xu, S. Aiyuk, Y. Zhang, G. Chen, J. Pieters, W. Verstraete, Stimulation of methanogenesis in a laboratory scale UASB reactor treating domestic sewage by Fe^0 application, Environ. Technol. 25 (2004) 613–619.
[49] S. Karri, R. Sierra-Alvarez, J.A. Field, Zero valent iron as an electron-donor for methanogenesis and sulfate reduction in anaerobic sludge, Biotechnol. Bioeng. 92 (2005) 810–819.
[50] H. Li, J. Chang, P. Liu, L. Fu, D. Ding, Y. Lu, Direct interspecies electron transfer accelerates syntrophic oxidation of butyrate in paddy soil enrichments, Environ. Microbiol. 17 (2015) 1533–1547.
[51] F. Suanon, Q. Sun, D. Mama, J. Li, B. Dimon, C.-P. Yu, Effect of nanoscale zero-valent iron and magnetite (Fe_3O_4) on the fate of metals during anaerobic digestion of sludge, Water Res. 88 (2016) 897–903.
[52] M. Narumiya, N. Nakada, N. Yamashita, H. Tanaka, Phase distribution and removal of pharmaceuticals and personal care products during anaerobic sludge digestion, J. Hazard. Mater. 260 (2013) 305–312.
[53] B. Blair, A. Nikolaus, C. Hedman, R. Klaper, T. Grundl, Evaluating the degradation, sorption, and negative mass balances of pharmaceuticals and personal care products during wastewater treatment, Chemosphere 134 (2015) 395–401.
[54] A. Jelic, S. Rodriguez-Mozaz, D. Barceló, O. Gutierrez, Impact of in-sewer transformation on 43 pharmaceuticals in a pressurized sewer under anaerobic conditions, Water Res. 68 (2015) 98–108.
[55] V. Bokare, K. Murugesan, Y.-M. Kim, J.-R. Jeon, E.-J. Kim, Y.S. Chang, Degradation of triclosan by an integrated nano-bio redox process, Bioresour. Technol. 101 (2010) 6354–6360.
[56] K. Murugesan, V. Bokare, J.-R. Jeon, E.-J. Kim, J.-H. Kim, Y.-S. Chang, Effect of Fe-Pd bimetallic nanoparticles on *phingomonas* sp. PH-07 and a nano-bio hybrid process for triclosan degradation, Bioresour. Technol. 102 (2011) 6019–6025.
[57] H. Jia, C. Wang, Adsorption and dechlorination of 2,4-dichlorophenol (2,4-DCP) on a multi-functional organo-smectite templated zero-valent iron composite, Chem. Eng. J. 191 (2012) 202–209.
[58] T.T. Le, K.-H. Nguyen, J.-R. Jeon, J.A. Francis, Y.-S. Chang, Nano/bio treatment of polychlorinated biphenyls with evaluation of comparative toxicity, J. Hazard. Mater. 287 (2015) 335–341.
[59] J. Xin, X. Zheng, J. Han, H. Shao, O. Kolditz, Remediation of trichloroethylene by xanthan gum-coated microscale zero valent iron (XG-mZVI) in groundwater: effects of geochemical constituents, Chem. Eng. J. 271 (2015) 164–172.