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Effect of nanoscale zero-valent iron and magnetite (Fe_3O_4) on the fate of metals during anaerobic digestion of sludge

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ABSTRACT

Anaerobic digestion (AD) is one of the most widely used processes to stabilize waste sewage sludge and produce biogas renewable energy. In this study, two different iron nanoparticles [nanoscale zero-valent iron (nZVI) and magnetite (Fe_3O_4)] were used in the mesophilic AD processes (37 ± 1 °C) to improve biogas production. In addition, changes of heavy metal (Cd, Co, Cu, Zn, Ni and Cr) speciation during AD of sludge with and without iron nanoparticles have been investigated. Concentrations of metals in the initial sludge were as follows: 63.1, 73.4, 1102.2, 2060.3, 483.9 and 604.1 mg kg^{-1} (dry sludge basis) for Cd, Co, Cu, Zn, Ni and Cr, respectively. Sequential fractionation showed that metals were predominantly bonded to organic matter and carbonates in the initial sludge. Compared with AD without iron nanoparticles, the application of iron nanoparticles (at dose of 0.5% in this study) showed positive impact not only on biogas production, but also on improvement of metals stabilization in the digestate. Metals were found concentrated in Fe–Mn bound and residual fractions and little was accumulated in the liquid digestate and most mobile fractions of solid digestate (water soluble, exchangeable and carbonates bound). Therefore, iron nanoparticles when properly used, could improve not only biogas yield, but also regulate and control the mobilization of metals during AD process. However, our study also observed that iron nanoparticles could promote the immobilization of phosphorus within the sludge during AD, and more research is needed to fully address the mechanism behind this phenomenon and the impact on future phosphorus reuse.

1. Introduction

Industrialization and urbanization are among the words that characterized our new society as a consequence of population growth and development. It goes without saying that the development often has substantial impacts on the environment. Indeed, population growth has led to the generation of huge and various amounts of wastes that cause the environmental problems, especially in big cities. Sewage sludge is one of the most important municipal wastes, and its management has received particular concern for the governments and scientific community all over the world. As reported by Chu et al. (2009) in China, over 11.2 million tons of dry sludge was generated each year, and over 80% was disposed by improper dumping (Yang et al., 2015). Sewage sludge is well known as fertilizer and a potential source of organic substances and nutrients (nitrogen and phosphorus) indispensable for plants as it can valuably replace synthetic N and P fertilizers (Kelter et al., 1997; Gao et al., 2008; Roca-Pérez et al., 2009). The reuse of sludge in agriculture or for land application would have been the best way for its disposal if it wasn't contaminated with various organic and inorganic pollutants. Unlike organic pollutants, inorganic pollutants, mainly heavy metals, are non-biodegradable and common sludge treatment such as anaerobic digestion (AD) or composting cannot effectively remove them from sludge (Chipasa, 2003). Some heavy metals like chromium and cadmium are ubiquitous to the environment and harmful to the living organisms due

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to their toxicity and accumulative behavior (Karvelas et al., 2003; Wei and Liu, 2005). Long-term land application of biosolids containing heavy metals can also affect the productivity of soils (McBride, 1995) and food safety. The behaviors of heavy metals are linked to their chemical forms and mobility rather than their total concentration (Filgueiras et al., 2004; Amir et al., 2005). In another words, the quantification of the chemical forms of heavy metals in the sludge is essential for better assessment of their toxicological risk in the environment. Therefore, for safe application of sewage sludge, stabilization of metals to reduce their mobility would be highly essential.

AD is one of the most widely used processes to destroy and stabilize waste sludge through converting part of its organic matter into the biogas renewable energy. Nanoparticles have also been found to accelerate AD hydrolysis, improve methane yield and produce more stabilized sludge (Liu et al., 2012; Feng et al., 2014; Li et al., 2015). Iron nanoparticles are inexpensive and known as pollutant absorbents and strong reductants (Nasiri et al., 2013). They have been used in environmental remediation, mainly for hazardous material treatments in water and ground water, owing to their superior reactivity (Karn et al., 2011; Tratnyek and Johnson, 2006). Stabilization of sludge with nanoscale zero-valent iron (nZVI) by sequestrating sulfur compounds, degrading and stabilizing organic pollutants present in sludge has been reported (Li et al., 2007). More recently, addition of nZVI in AD has been shown to improve methane yield due to the release of hydrogen during nZVI corrosion/oxidation, which can serve as the electron-donor for methanogens (Hu et al., 2015). In addition, Fe_3O_4 nanoparticles have also been documented to promote methanogenesis through facilitating direct interspecies electron transfer in syntrophic methane production (Li et al., 2015).

Limited efforts have been made for understanding the behaviors of metals and changes of heavy metals speciation during AD of sewage sludge (Dong et al., 2013). In addition, to our knowledge, none has focused on the effect of nanoparticles on distribution of sludge's metal forms during AD process. Therefore, the main objective of the current study was to evaluate the effect of nanoparticles including nZVI and magnetite (Fe_3O_4) nanoparticles on fractionation and stabilization of heavy metals including chromium (Cr), cadmium (Cd), nickel (Ni), copper (Cu), zinc (Zn) and Cobalt (Co) during AD. To this end, sewage sludge was spiked with nanoparticles and passed through AD process. Different physical and chemical parameters including pH, total solid (TS), moisture content (Mc), volatile solids (VS), total alkalinity (TA), total phosphorus (TP), elemental analysis (C, N, and S), soluble chemical oxygen demand (sCOD) and methane (CH_4) production have been determined. The stabilization of heavy metals was assessed based on the changes of their species distribution in the end product of AD compared to the initial sludge. In the end, our goal is to understand the effect of iron nanoparticles on AD process and metal speciation.

2. Materials and methods

2.1. Sludge and nanoparticles

Dewatered excess sludge collected from a municipal wastewater treatment plant in Xiamen, China was used for the anaerobic digestion, and some anaerobic sludge from the same plant was also collected as the inoculum. After collecting the sludge, part of it was dried under oven at 105 °C until constant weight, ground and sieved through a mesh size <0.15 mm for physicochemical characterization (Table 1). The rest sludge was used for AD process after it was spiked with nanoparticles. The nanoparticles used involved nZVI (diameter of 50 nm, purity 99.9%) and (Fe_3O_4 nanoparticles, diameter of 20 nm, purity > 99.5%) as reported by the manufacturer (Fig. S1 in Supporting Information (SI)). Both were purchased from Aladdin Industrial Corporation, Shanghai, China. Further characterization of the two iron nanoparticles including scanning electron microscopy (SEM) images and size distribution analysis are shown in the Figs. S2 and S3 in SI.

Table 1
Physicochemical characterization of initial sludge and solid digestates after AD.

Parameters	pH	EC	VS	sCOD	TA	TP	N	S	C/N
Initial sludge	7.8	3.6	47.6	7072	533.3	0.82	3.3	1.8	10.8
A	6.8	7.6	24.2	3468.9	1333	0.57	2.6	0.4	7.5
B1	7.1	6.5	15.4	2221	1083	0.76	2.1	0.3	7.5
B2	6.8	7.1	32.4	4503.2	1033	0.62	2.8	0.4	8.6
C1	6.9	6.4	20.4	2760.6	1136	0.71	2.3	0.3	7.4
C2	7.2	6.3	27.6	3632.2	1233	0.63	2.9	0.6	7.6

Where VS in % of TS, C, N, S and TP in % dry weight basis, EC in mS cm^{-1}, sCOD in mg L^{-1} and TA in mg L^{-1} $CaCO_3$.

2.2. AD and experimental design

Lab scale AD was adopted in this study. Reactors were made of 500 mL amber glass bottles. Five sets of batch experiments were set up: Blank (A), with nZVI [B1 (0.5%) and B2 (1%)] and with Fe_3O_4 nanoparticles [C1 (0.5%) and C2 (1%)]. The same sludge was used for all experimental setup (moisture content 75%; physicochemical properties in Table 1). The design is as follows: (A): 150 g of sludge without any nanoparticles, (B1): 150 g of sludge + 0.75 g of nZVI, (B2): 150 g of sludge + 1.5 g of nZVI, (C1): 150 g of sludge + 0.75 g of Fe_3O_4 nanoparticles and (C2): 150 g of sludge + 1.5 g of Fe_3O_4 nanoparticles. Mixtures were well homogenized and diluted to 15% of total solid with distilled water and then sonicated for 10 min. Each set of experiments was in duplicate. After feeding the reactors, each bottle was flushed with nitrogen gas for about 5 min to assure anaerobic condition before starting the experiment. Reactors were then kept in the water bath under mesophilic condition (37 ± 1 °C). Biogas volume was daily recorded by reading water displacement inside the calibrate glass cylinder which was fitted to the reactor. After the digestion was completed (after 12 d), collected digestate samples were centrifuged and filtered through Millipore filter (0.45 μm). After acidifying with concentrated HNO_3, samples were kept at 4 °C prior to metal analysis. The solid residues were dried at 105 °C, ground and sieved through a mesh size <0.15 mm. The obtained powder was used for physicochemical characterizations and metal forms determination via chemical fractionation.

2.3. Metal contents and sequential fractionation

The target heavy metal stock solutions (1000 mg L^{-1}) were prepared by dissolving a well weighted amount of their corresponding salts into Milli-Q water, and stored at 4 °C. Dissolved salts involved $K_2Cr_2O_7$, $(CdCl_2)_2 \cdot 5H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, and $ZnCl_2$ $CoCl_2 \cdot 6H_2O$. Working standard solutions (0, 2, 4, 10, 25, 50, 75 and 100 mg L^{-1}) were prepared by appropriate dilution with Milli-Q water. Total metal concentration was determined by digesting sludge sample according to Chen and Ma, 2001, and chemical fractionation was performed according to the modified Tessier et al. (1979) procedure as reported by Aikpokpodion et al. (2013) (Table S1 in SI). A total of six fractions were extracted including: Water soluble (F1), Exchangeable (F2), Carbonate-bound (F3), Fe–Mn oxides-bound (F4), Organic and sulfide-bound (F5) and Residual (F6). Sequential fractionation efficiency [SFE (%)] was evaluated by calculating the ratio between the sum of the six fractions (F1, F2, F3, F4, F5 and F6) and the total concentration. In addition, parallel digestion of the same amount (1 g) of a standard sediment reference material (GBW07309, General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China) was performed using the same acid digestion procedure (Chen and Ma, 2001). Recovery [R (%)] was calculated as the ratio between extracted and standard concentration in the standard sediment reference material.

2.4. Analytical methods

Physicochemical characterizations including (pH, EC, Mc, TS, VS, TA, C, N, S, TP and sCOD) were performed. EC and pH were determined using a multi-parameter meter (HACH, HQ40d) on the sludge with milli-Q water [ratio 1:10 (w:v)]. Elemental analysis (C, N, S) was done using a macro elemental CNHS/O analyzer (Vario MAX, Elementar). C/N ratio was calculated as the ratio of the percentage of carbon over the percentage of nitrogen. TP was determined by aqua regia digestion according to ISO 11464, EN 12880 and quantification was made by flow injection analyzer (Lachat QC8500, USA). Mc, TS, VS and TA were determined according to the standard methods (APHA, 1995). For determining sCOD and TA, AD samples were centrifuged at 10,000 g for 15 min at 4 °C, and the supernatant was then filtered through a Millipore membrane filter with size of 0.45 μm and the filtrate was used for analysis. Biogas methane content was determined by gas chromatography (GC 9890A-Shanghai Linghua Inc.) equipped with flame ionization detector (FID). Temperatures of injector, detector and column were kept at 100, 250 and 60 °C. Nitrogen was used as the carrier gas at flow rate of 50 mL min^{-1}. The column was 2 m × Ø3 mm GDX-103 packed columns. A volume of 0.1 mL of produced biogas was injected to the GC. Sludge morphology and structure was analyzed via SEM (HITACHI S-4800) with energy dispersive X-ray (EDX) spectroscopy (Genesis XM2). Metals were analyzed using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, PerkinElmer Optima 7000 DV, USA).

3. Results and discussion

3.1. Physicochemical characterization

Physiochemical characterizations of the sludge before and after digestion are shown in Table 1. The pH of initial sludge was close to the neutrality (7.8), and thus we did not make pH adjustment. By the end of the digestion, EC remarkably increased from 3.6 mS cm^{-1} to 7.6, 6.5, 7, 6.4 and 6.4 mS cm^{-1} in the digesters A, B1, B2, C1 and C2, respectively. These changes might be explained by the release of organic and inorganic ions such as Cl^-, Na^+, K^+, NH_4^+, NO_3^-, SO_4^{2-}, HCO_3^- (Wong et al., 2001). The concentration of sCOD considerably decreased from 7072 mg L^{-1} to 3468.9, 2221, 4503.2, 2760.6 and 3632.2 mg L^{-1} corresponding to 50.9, 68.6, 36.3, 60.9 and 48.6% removal in digesters A, B1, B2, C1 and C2, respectively. The highest sCOD removal efficiency was noted in digesters B1 and C1, which might be attributed to the improved methane production in the AD process; in contrast, the low sCOD removal efficiency agreed with the inhibition of methane production in digesters B2 and C2 (discussed below).

SEM was used to observe the morphology of sludge (Fig. 1). The sludge showed an intact and smooth structure before AD. Smaller particles were observed and clumped together to form a cluster of granules after AD. Visibly, it is hard to tell the morphological difference between digested sludge with and without iron nanoparticles, except that there seemed more numbers of nanoscale particles adsorbed on the surface of sludge. EDX analysis revealed the increase of iron contents in the sludge samples with the addition of iron nanoparticles. Element composition profiles from EDX analysis also indicated that some other elements, such as Ca, Al, Mg, K, P, etc. coexisted in the digested sludge samples.

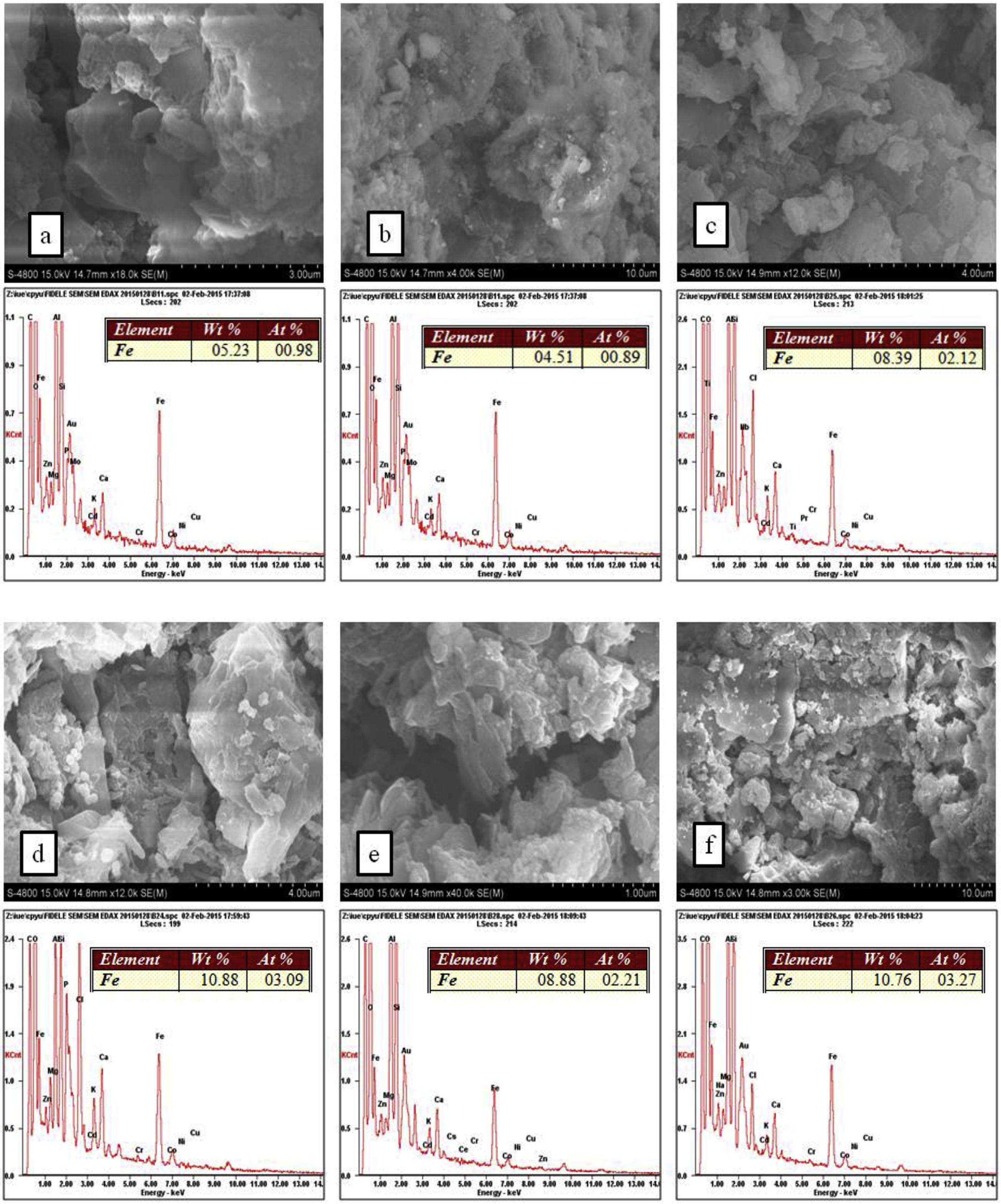
3.2. Methane gas production

As a key parameter for evaluating the AD process, biogas, mainly methane gas production was followed twice a week during the process. The average values (n = 4 measurements) of methane content in wet produced biogas was calculated for about 58.9 ± 2.5, 64 ± 7.5, 61.2 ± 3.6, 64.4 ± 5.7 and 67.6 ± 3.8% in digesters A, B1, B2, C1 and C2, respectively. Daily and cumulative volume of produced methane can be seen in Fig. 2. The total volumes of produced methane were 67,091.4, 97,804.1, 47,185.8, 84,274.7 and 59,366.8 mL kg^{-1} VS added in the digesters A, B1, B2, C1 and C2, respectively. Results showed that methane contents were improved with the addition of nZVI and Fe_3O_4 nanoparticles. The higher methane production could be due to the improved activity of hydrolysis and autotrophic methanogenesis in the presence of ZVI (Feng et al., 2014) and direct interspecies electron transfer in the presence of Fe_3O_4 nanoparticles (Li et al., 2015). However, the volume of methane gas was not improved in all digesters with iron nanoparticles and it seemed to be dependent on the dose of nanoparticles. Indeed, the volumes of produced methane was remarkably improved at the dose of 0.5% of nZVI or Fe_3O_4 nanoparticles (digesters B1 and C1), while it was strongly inhibited at the dose of 1% (digesters B2 and C2). Therefore, it could then be stated that high concentration of iron nanoparticles exhibited toxicity effect on AD and led to the inhibition of the process as previously mentioned by Yang et al. (2013). When comparing methane production in digesters B2 and C2, it can be implied that under higher concentrations, nZVI exhibited stronger inhibitory effect on the AD process than Fe_3O_4 nanoparticles.

3.3. Heavy metal contents and fractionation in the initial sludge

The total concentrations of target heavy metals in sludge (TC) are as follows: 63.1, 73.4, 1102.1, 2058.3, 483.5 and 603.5 mg kg^{-1} (dry sludge basis) for Cd, Co, Cu, Zn, Ni and Cr, respectively. The sequential extraction gave the total concentrations as follows: 58.8, 68.9, 929.6, 1974.2, 449.4 and 595.6 mg kg^{-1} (dry sludge basis). As a consequence, SFE was estimated at 93.3, 94, 84.3, 95.9, 92.9 and 98.7% for Cd, Co, Cu, Zn, Ni and Cr, respectively. Besides, the recovery of analysis reached 96.7, 105.4, 94.1, 94.5, 95.2 and 100.2% for Cd, Co, Cu, Zn, Ni and Cr, respectively. The results of chemical fractionation of metals in initial sludge (Fig. 3) showed that target metals were strongly bonded to organic matter and sulfide (F5) ($25\% \leq F5 \leq 52\%$) followed by carbonate (F3) ($10\% \leq F3 \leq 49\%$), while they were less bonded to Fe–Mn oxides (F4) ($6\% \leq F4 \leq 16\%$) and residual (F6) ($6\% \leq F6 \leq 25\%$). Unlike other metals, exchangeable Cr (F2) was relatively higher (>15%). Water soluble fraction (F1) was ≤5% for all metals. It is widely said that organic-bound metals are relatively stable; however, under certain conditions which lead to the degradation of organic maters, metals can easily be released (Tessier et al., 1979). With carbonates-bound fraction, mobilization process is quicker due the sensitivity of this fraction to the environmental conditions (Mingot et al., 1995). Otherwise, Fe–Mn oxides-bound fraction known as reducible fraction (Álvarez-Valero et al., 2009) can be reduced and converted to exchangeable fraction especially in anaerobic conditions.

According to Liu et al. (2007), the first five fractions (F1 to F5) of heavy metals are considered as mobile. In the current study, the sum of the five fractions could be up to 91.1, 86.8, 74.9, 85.1, 85.8 and 93.5% for Cd, Co, Cu, Zn, Ni and Cr, respectively. More specifically, the sum of (F1 + F2 + F3) is considered as the minimum available heavy metals that can easily be taken in by plants (Mingot et al.,



Element	Wt %	At %
Fe	05.23	00.98

Element	Wt %	At %
Fe	04.51	00.89

Element	Wt %	At %
Fe	08.39	02.12

Element	Wt %	At %
Fe	10.88	03.09

Element	Wt %	At %
Fe	08.88	02.21

Element	Wt %	At %
Fe	10.76	03.27

Fig. 1. SEM/EDX images of sludge exposed to nZVI and Fe_3O_4 nanoparticles. (a) Initial sludge, (b) Digester A (blank), (c) Digester B1 (0.75 g nZVI), (d) Digester B2 (1.5 g nZVI), (e) Digester C1 (0.75 g Fe_3O_4 nanoparticles) and (f) Digester C2 (1.5 g Fe_3O_4 nanoparticles).

1995). In other words, the total fractions of (F1 + F2 + F3) are used to calculate the mobility factor (MF) (Achiba et al., 2010). Herein, the MFs are 50.5, 25.9, 33.6, 24.2, 27.9 and 30.3% for Cd, Co, Cu, Zn, Ni and Cr, respectively. It can be seen that all metals have a MF > 20 with Cd on top of all. This indicates high mobility and migration possibility of metals within the sludge. It also indicates potential hazard or risk on ecosystem especially with repeated disposal of such sludge in agricultural soils. As a consequence, particular

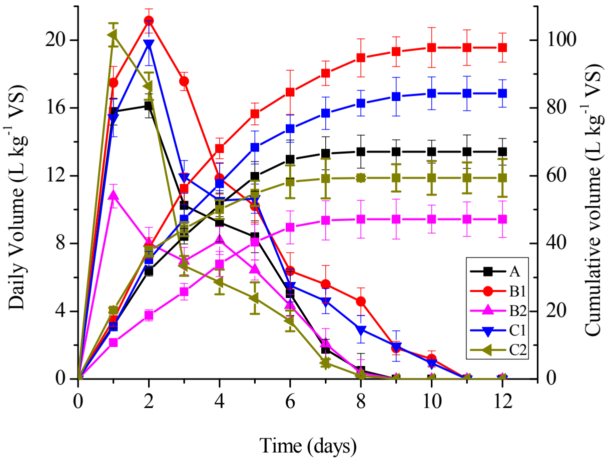


Fig. 2. Daily and cumulative volume of produced methane during AD.

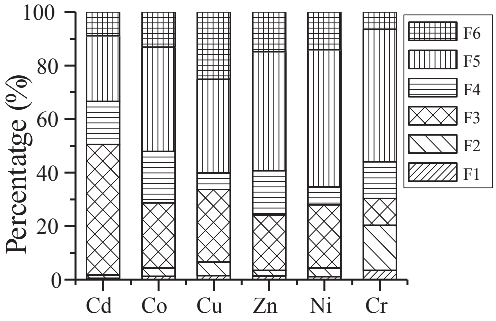


Fig. 3. Chemical fractionation of heavy metals in the initial sludge.

attention should be given to metal mobilization and stabilization in the sludge to evaluate its use in agriculture as fertilizer and reduce its negative impacts on plants and crops.

3.4. *Metals contents and fractionation in the digestate*

By the end of the digestion, metal contents were determined in both liquid and solid phase in order to understand the metal mobilization in the AD. Otherwise, to highlight and better understand the effect of nanoparticles on the changes of metal distribution and evaluate the level of their stabilization, the fractionation of metals in the solid residue of AD was performed.

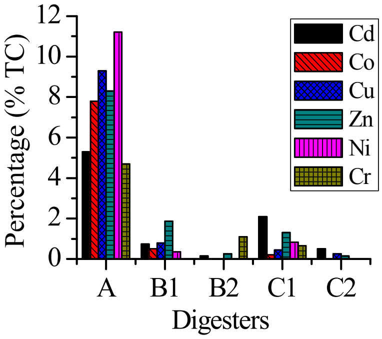


Fig. 4. Metals contents in the liquid phase of AD digestate.

3.4.1. *Metal contents in the liquid phase of digestate*

Data revealed that during AD of the sludge, some metals were released into the liquid phase (Fig. 4). A concentration of 0.30, 0.51, 9.22, 15.37, 4.88 and 1.68 mg L^{-1} equivalent to 5.3, 7.8, 9.3, 8.3, 11.2 and 3.1% of TC for Cd, Co, Cu, Zn, Ni and Cr, respectively were released within the solution in digester A, which meant that up to 90% of each metal stayed within the solid phase. Ni exhibited highest release followed by Cu and Zn. The observation was in accordance with Kangala (2003). The release of metals within the solution could be related to the decomposition of organic matters and associated compounds in sludge (Appels et al., 2008; Dong et al., 2013; Zhu et al., 2014). Unlike the digester A, metals seemed to be immobilized within the sludge in the digesters B1, B2, C1 and C2, since only very low concentrations of metals were detected in the liquid phase (Fig. 4). This could be mainly explained by the presence of iron nanoparticles within the digesters which reduced or adsorbed the released metals and diminished their concentration in the liquid phase (Xu et al., 2012; Tang and Lo, 2013). Heavy metals were reported to have inhibitory effects on the anaerobic digestion. The concentrations of Cd and Cr exceeding 20 and 5 mg L^{-1}, respectively have been shown to cause inhibition on the anaerobic acidogenesis (Yu and Fang, 2001). Fifty percent inhibition of methanogenesis was observed when the concentrations of $CuCl_2$, $ZnCl_2$ and $NiCl_2$ were over 10, 40, and 60 mg L^{-1}, respectively (Zayed and Winter, 2000). Higher concentrations of iron nanoparticles within the digesters seemed to more significantly reduce metal release and therefore, lower the potential inhibitory effects of heavy metals on the microbial activity during anaerobic digestion.

3.4.2. *Metal fractionation in the solid phase of digestate*

On the basis of Fig. 5, significant changes on distribution of metal forms in the solid digestate can be noted. Indeed, in the absence of iron nanoparticles (digester A), the AD of sludge seemed to mobilize metals from the more stable to the less stable states (mainly exchangeable fraction). Exchangeable fraction changed from 1.2, 0.3, 5.1, 2.1, 3.2 and 16.8% of TC to 18.2, 13.5, 9.1, 21.2, 17.6 and 21.7% of TC for Cd, Co, Cu, Zn, Ni and Cr, respectively. In the presence of iron nanoparticles (digesters B1, B2, C1 and C2), metals were better stabilized within the solid digestate, and water soluble and exchangeable fractions were limited. Metals were dominant in Fe–Mn oxides-bound fraction, from ($6\% \leq F4 \leq 16\%$) in the initial sludge to ($29\% \leq F4 \leq 70\%$) after AD, while carbonate-bound and organic and sulfide-bound fractions remarkably decreased. As reported previously, nZVI was able to remove heavy metals via redox reaction and/or adsorption process (Crane et al., 2011). It has been demonstrated that nZVI could react with water and quickly form a layer of oxyhydroxide on the particle surface, and the formed oxide shell provided sites for sorption and co-precipitation of heavy metals (Tang and Lo, 2013). Previous study also has shown that for Fe_3O_4 nanoparticles, both physical and chemical adsorptions contributed to the removal of heavy metals (Tang and Lo, 2013). Therefore, our results suggested that released metals were likely adsorbed by iron oxide nanoparticles under the aforementioned mechanisms and were concentrated in Fe–Mn oxides-bound fraction, which led to the diminution of their concentrations in the liquid phase and the three most mobile fractions of the solid phase.

Besides, different dose of iron nanoparticles could also considerably change the metal fraction within the solid digestate. For example, higher Fe–Mn oxides-bound metals and lower organic and sulfide-bound fraction were noticed in digesters B1 and C1 (at dose rate of 0.5%). This could be explained by the enhanced methane production in these two digesters, which favored the release of more metals from organic-bound metals

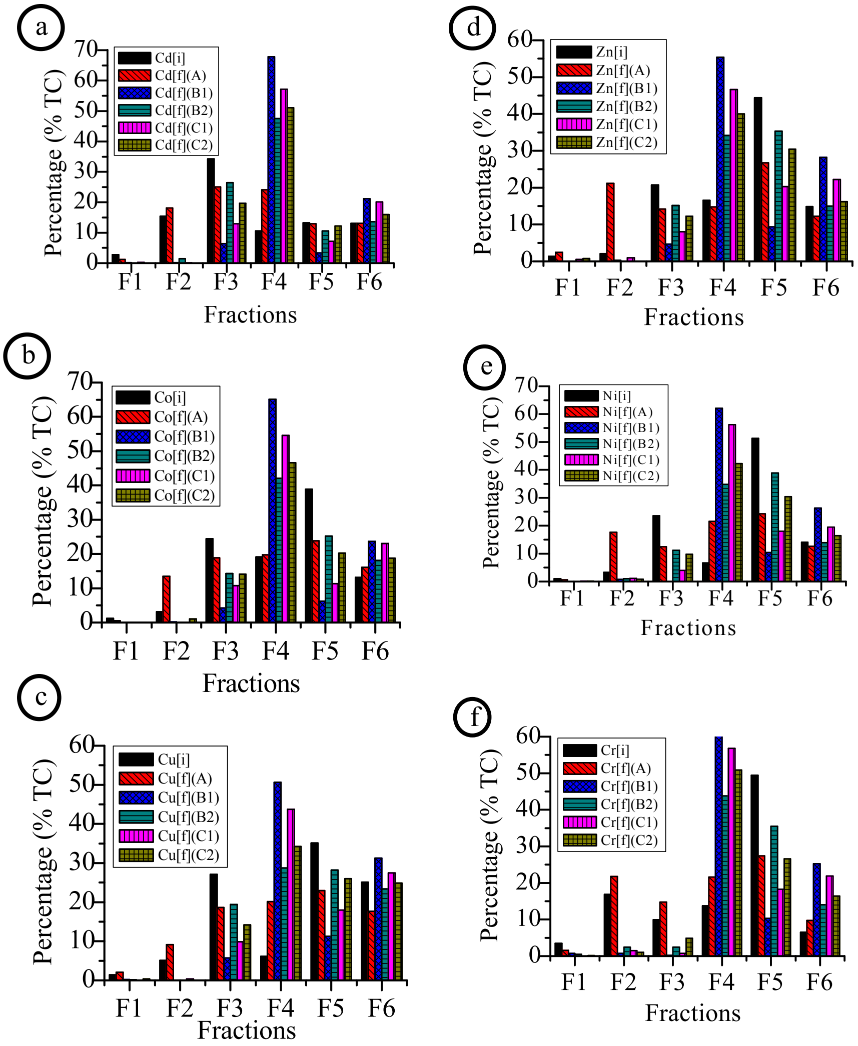


Fig. 5. Metals speciation in sludge after AD. [i] = initial concentration in the sludge, [f] = final concentration in the digestate, A, B1, B2, C1 and C2 represent the digesters.

comparing to B2 and C2, where the AD process was inhibited due to the overdosing of iron nanoparticles. Therefore, based on the data, it can be stated that iron nanoparticles when efficiently used, can improve not only biogas yield, but also regulate and control the mobilization of metals during AD process. To better evaluate the mobility of metals, the comparison of their MFs in sludge before and after digestion is shown in Table 2. The table highlights the risk of metal mobilization during AD in the absence of nanoparticles (digester A), and the better stabilization in the presence of iron nanoparticles.

3.4.3. *Phosphorus release in AD*

Sludge's TP content was estimated for about 0.8% (on dry sludge basis) (Table 1). Previous study has reported that during AD, part of the organically bound phosphorus could be released due to the degradation of organic matters (Latif et al., 2015). In our study, the observation was that by the end of 12 d of AD, up to 28.4, 4.4, 23, 10.6 and 22% of TP was released in the liquid phase in the digester A, B1, B2, C1 and C2, respectively. As a consequence, about 71.6, 95.6, 77.1, 89.4 and 79% was retained within the sludge, respectively (Table 1). Compared with the digester A without iron nanoparticles,

Table 2
Comparison of mobility factors (MFs) of metals in solid digestates (with and without iron nanoparticles) and initial sludge.

Before digestion		After digestion				
Digesters	Initial sludge	A (blank)	B1 (0.5% NPs)	B2 (1% NPs)	C1 (0.5% NPs)	C2 (1% NPs)
Metals	MF	MF	MF	MF	MF	MF
Cd	50.5	44.4	6.8	27.9	13.3	19.8
Co	25.9	32.9	4.4	14.4	10.7	15.1
Cu	33.6	29.8	6.0	19.5	10.2	14.5
Zn	24.1	37.8	5.1	15.1	9.5	13.0
Ni	27.9	30.7	0.7	12.2	5.3	10.7
Cr	30.3	38.1	1.7	5.5	2.2	6.1

released phosphorus was lower in the digesters with the addition of iron nanoparticles. It suggested that the presence of nanoparticles in the AD promoted phosphorus immobilization within the sludge. This could be explained by the fact that the soluble phosphorus like orthophosphate could bind with ferrous ions from nZVI ($Fe^0 + 2H^+ = Fe^{2+} + H_2$), which promoted the formation of precipitates, such as vivianite [$Fe_3(PO_4)_2 \cdot 8H_2O$] (Cheng et al., 2015) or could be adsorbed by Fe_3O_4 nanoparticles (Pan et al., 2010). However, more research is needed to fully address the mechanism behind this phenomenon and the impact on phosphorus reuse for future land application.

4. Conclusion

Change of heavy metals distribution during AD of sewage sludge in the presence of iron nanoparticles has been investigated and the main conclusions are as follows:

i. Iron nanoparticles when properly used, would improve biogas production, but overdosing could inhibit biogas production;
ii. The use of iron nanoparticles would control the mobilization of metals during AD process and tended to concentrate sludge's metals within the Fe–Mn bound fraction;
iii. Phosphorus could be released into the liquid phase of digestate during AD, but adding iron nanoparticles would promote the immobilization of phosphorus within the solid digestate.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2015.11.014.

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