



## Sequential extraction of anaerobic digestate sludge for the determination of partitioning of heavy metals

Neng-min Zhu<sup>a,b,\*</sup>, Qiang-Li<sup>a,b</sup>, Xu-jing Guo<sup>a,b</sup>, Hui-Zhang<sup>a,b</sup>, Yu-Deng<sup>a,b</sup>

<sup>a</sup> Biogas Institute of Ministry of Agriculture, 13 4th Section Renmin South Road, Chengdu Sichuan Province 610041, China

<sup>b</sup> Key Laboratory of Development and Application of Rural Renewable Energy, Ministry of Agriculture, 13 4th Section Renmin South Road, Chengdu Sichuan Province 610041, China

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### ABSTRACT

In China, agricultural use of anaerobic digestate sludge is considered a concern due to high heavy metal content of the sludge. In this study, sequential extraction procedure (SEP) was conducted to determine metal speciation which affects release and mobility of metal significantly. The results of SEP showed that each heavy metal possessed different distribution characteristics. Cu mainly reacted with carboxyl functional group to form the fraction bound to organic matter. Zn and Mn were dominated in the fraction bound to Fe–Mn oxides and carbonates, respectively. Pb, Ni, Cr, Cd and As were present as the residual fraction. Examination of mobility factors (MFs) indicated that Zn, Pb, Ni, Mn and Cd were more mobile whereas Cr and As were immobilized in anaerobic digestate. Based on the results, it can be stated that Cu, Zn, Mn, Ni and Cd may be grouped as toxic and active components in sludge and should be regarded as the priority pollutants for elimination. Pb should be monitored in terms of its high mobility factors (MF). Cr and As, nevertheless, were the most stable components in sludge.

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### 1. Introduction

In the past decade, a large number of household digester and large-scale biogas plants were constructed across the country in China (Chen et al., 2012). Consequently, a great deal of by-products named as anaerobic digestate was generated. According to traditional farming practice in China, the anaerobic digestate is commonly used as organic fertilizer to amend agricultural soil. Heavy metals are extensively used as feeding additive for stimulating poultry growth in China, however, their contents are found to be increased in poultry slurry which is used as main substrate materials for anaerobic digestion (Jiang et al., 2011). These additive metals mainly consist of macroelements Zn, Cu, Mn, and microelements Ni, Pb, Cr, Cd, As (Gosens et al., 2013). As a consequence, the resulting anaerobic digestate contains large amounts of heavy metals whose concentrations may be several times higher than their background concentrations in arable soil (Zhang et al., 2012). Therefore the use of anaerobic digestate as organic fertilizer has been criticized considerably in recent years.

Recently, some studies have been carried out to investigate the phytotoxicity and ecotoxicity of these heavy metals after they were introduced into agricultural soil along with anaerobic digestate. However, their toxic effects on plants and living beings were usually concluded on the basis of their total contents in previous reports

\* Corresponding author at: Biogas Institute of Ministry of Agriculture, 13 4th Section Renmin South Road, Chengdu Sichuan Province 610041, China. Tel./Fax: +86 28 85215106.

E-mail address: [zhunengmin2004@163.com](mailto:zhunengmin2004@163.com) (N.-m. Zhu).

(Auda et al., 2011; Demirel et al., 2013; Mantovi et al., 2003; Singh et al., 2008). According to Tessier et al. (1979), the speciation of particulate heavy metal was divided into five fractions and each fraction possessed distinctive characteristics and migration behavior in environmental matrix. This means that each fraction might play a different role considering its phytotoxicity and toxicity to plants and living beings. In fact, it has been proved that metal only in the form of free ionic or exchangeable fraction could migrate in soil and accumulate in plant tissues and therefore cause direct toxicity to the ecosystem (Li et al., 2010a; Salazar et al., 2012; Walter et al., 2006; Yang et al., 2010). Consequently, it is untenable to assess the toxic effect of heavy metal in anaerobic digestate only in view of its *pseudo*-total content, which supposes that all fractions of a given metal have an equal impact on ecosystem.

To our best knowledge, there are limited reports aimed at the partitioning of heavy metal in anaerobic digestate. In this study, speciation distribution characterization as well as the total content of heavy metals in anaerobic digestate was investigated extensively. FTIR, XRD and ICP–OES were performed to assist in illuminating metals distribution characteristic. Meanwhile, a cost-effective and practical method used for feasibility assessment of anaerobic digestate for land use was also proposed in terms of obtained results.

### 2. Materials and methods

#### 2.1. Chemicals and anaerobic digestate

Analytical or higher grade chemical reagents involved in this study were used without any pretreatment, including nitric acid, hydrogen peroxide, hydrochloric

acid, perchloric acid, hydrofluoric acid, acetic acid, hydroxylamine hydrochloride, anhydrous sodium acetate and ammonium acetate. Milli-Q ultrapure water ( $18.2 \text{ M}\Omega \text{ cm}^{-1}$ ) was used for all the experiments.

Anaerobic digestate was obtained from a biogas plant with  $800 \text{ m}^3$  of space volume which is located in a large-scale intensive pig farm. The pig slurry in this farm was introduced into biogas plant as main substrate for anaerobic digestion. After one stabilization period, 50 kg of anaerobic digestate were sampled and stored in refrigerator at  $4^\circ \text{C}$  for subsequent analysis.

## 2.2. Sequential extraction procedure

For sequential extraction, 1 kg of raw anaerobic digestate was centrifuged at 10,000 rpm to achieve liquid–solid separation. The resultant liquid phase was digested with aqua regia for ICP-OES analysis and defined as water-soluble fraction. The solid phase was dried at  $105^\circ \text{C}$  in a forced air oven for 24 h. Dry solid phase was ground in an agate mortar, homogenized and stored at  $4^\circ \text{C}$  for subsequent extraction procedures.

A four-step extraction procedure was performed sequentially to determine the metal speciation according to previous literatures (Mahan et al., 1987; Tessier et al., 1979), and the details are listed in Supporting Information (Table S1). In brief, 2 g of dry sample (at  $105^\circ \text{C}$ ) was mixed with extractant in 100 ml Teflon bottles and subjected to extraction in sequence. After one extraction step, the extract was filtrated using  $0.45 \mu\text{m}$  pore water-phase filter paper. Subsequently, the solid residue from pervious extraction step was subjected to the next extraction step. Each aqueous extract sample was digested with aqua regia at  $120^\circ \text{C}$  in order to destroy organic materials completely for ICP-OES analysis. Extraction step 1–2 and sub-step 3 in step 4 were conducted with continuous shaking at 163 rpm and the other steps were carried out with occasional shaking. Batch experiments were performed in triplicate to ensure the reproducibility and each data point reported in all figures and tables represents the mean of triplicates with standard deviation.

## 2.3. Analytical methods

X-ray diffraction (XRD) analysis was carried out using PANalytical X'Pert Powder X-ray diffractometer (Netherlands). Fourier transform infrared spectroscopy (FTIR) was performed using ThermoFisher Nicolet 6700 spectrometer (USA). Inductively coupled plasma–optical emission spectrometry (ICP-OES) was conducted using Perkin Elmer OPTIMA 2000 spectrometer (USA).

## 3. Results and discussion

### 3.1. Normal physicochemical properties of anaerobic digestate

Table 1 shows the normal physicochemical characteristics of the anaerobic digestate involved in this study. As can be seen, its moisture content is higher than 95% corresponding to its low dry matter content below 5%. In this intensive pig farm, the pig slurry consisting of excrement and urine was not subjected to solid–liquid phase separation but put into the biogas digester directly. Accordingly, the moisture content in digester was much higher and subsequently resulted in the water content in anaerobic digestate being beyond 90% in present study. In this atmosphere, the substrates were present as fluid state and therefore a slight turbulence appeared occasionally during digestion process, which might affect the distribution of metals among different phases (Bollon et al., 2013; Dąbrowska and Rosińska, 2012). In terms of high water content, COD ( $844 \text{ mg/kg DM}$ ) and TOC ( $241 \text{ mg/kg DM}$ ) shown in Table 1, this type of anaerobic digestate can be regarded as “organic waste water” and should be subjected to

some pretreatment before use as fertilizer, such as dilution with fresh water. Oxidation–reduction potential (ORP) and pH are considered as important factors which can affect metabolism activity of microorganism remarkably (Tanwar et al., 2008; Watling et al., 2012). Hence, the necessary adjustment of ORP and pH should be conducted in order to alleviate their impact on microbe community in soil. In fact, items in Table 1 can be adjusted easily via simple physical treatment in order to meet the requirement for land application. Therefore, characteristic indexes in Table 1 need not be paid special attention to in terms of agricultural use of anaerobic digestate. As for heavy metal, however, both its concentration and speciation should be given more special attention due to its accumulation in plant tissues, which would pose potential risk to living beings via the food chain.

### 3.2. FTIR and XRD properties of anaerobic digestate

As shown in Fig. S1, the FTIR spectrum reveals a number of absorption peaks indicating the complex nature of the anaerobic digestate. A strong-broad peak at  $3307 \text{ cm}^{-1}$  was ascribed to the hydroxyl group break in cellulose to form diols during the fermentation process (Zhao et al., 2012). Both a sharp peak at  $2926 \text{ cm}^{-1}$  and a weak intense peak at  $2854 \text{ cm}^{-1}$  were the characteristics of C–H asymmetrical and symmetrical stretching vibration of alkyl chains, respectively (Abidi et al., 2014). In some cases, the peak at  $1656 \text{ cm}^{-1}$  was regarded as a chelated form of the carbonyl on the carboxyl group or a C=O stretching mode of amide I band (Sawalha et al., 2007; Majumdar et al., 2008). The appearance of a weak intensive peak at  $1544 \text{ cm}^{-1}$  was ascribed to the combination of N–H bending and C–N stretching vibrations of amide II band (Majumdar et al., 2008). A medium strong peak at  $1418 \text{ cm}^{-1}$  showed the presence of the COO– in carboxylate group, implying that these reactive functional groups might react with some metal ions to form chelate (Pagnanelli et al., 2009). Some previous studies indicated that the weak and broad peak at  $1240 \text{ cm}^{-1}$  might be ascribed to both the overlapping of symmetric carboxyl stretching vibrations from un-ionized carboxylates and C–O–C stretching vibrations from esters (Gardea-Torresdey et al., 2002). The intense and broad peak at  $1056 \text{ cm}^{-1}$  was attributed to the C–O stretching vibration mode (Majumdar et al., 2008). The peak at  $873 \text{ cm}^{-1}$  and  $696 \text{ cm}^{-1}$  were assigned to the  $\beta$ -linkage of cellulose and C–H rocking in crystalline cellulose, respectively (Alonso-Simon et al., 2011). The corresponding spectra assignments were presented in Table 2. As mentioned above, the FTIR spectra in Fig. S1 confirms the presence of amide, hydroxyl, and carboxyl groups in this anaerobic digestate.

In terms of chemical reactivity to metal ions, carboxyl and  $\text{NH}_2$  groups were much more reactive than other functional groups such as hydroxyl and carbonyl group (Pagnanelli et al., 2009; Zhao et al., 2012). It is hard to identify the chemical bond between functional groups and metal ions definitely but some changes of the peak position in FTIR spectra could be ascribed to the interaction of metal ions with functional groups. Pagnanelli et al. (2009) reported that the enhancement of peak intensity at  $1418 \text{ cm}^{-1}$  was ascribed to the interaction of metals with carboxylic adsorbent sites. Meanwhile, Majumdar et al. (2008) also suggested that the shift of peak position from  $1544.9 \text{ cm}^{-1}$  and  $1407.9 \text{ cm}^{-1}$  to  $1523.2 \text{ cm}^{-1}$  and  $1399.8 \text{ cm}^{-1}$ , respectively, resulted from the interaction of copper ions with the amine and carboxyl groups. In the present study, the weak peak at  $1516 \text{ cm}^{-1}$  in Fig. 1 might be assigned to the vibration of carboxyl groups in chelated form of the (COO–)Cu(COO–) according to the FTIR characteristic described by Majumdar et al. (2008). Sawalha et al. (2007) also pointed out that the weak peak at  $1656 \text{ cm}^{-1}$  was mainly ascribed to the binding Cd(II) and Cr(III) with carboxyl functional group, which is consistent with that in Fig. S1. As mentioned above, some metal ions interact with reactive functional group during anaerobic digestion process to form metal–organic

**Table 1**  
Normal physical and chemical characteristics of anaerobic digestate.

Density ( $\text{g mL}^{-1}$ )	0.96	pH	7.38
Dry matter (DM %)	4.77	COD ( $\text{g kg}^{-1} \text{ DM}$ )	844
Moisture content (%)	95.22	TOC ( $\text{g kg}^{-1} \text{ DM}$ )	241
Total N ( $\text{g kg}^{-1} \text{ DM}$ )	64.43	Electrical conductivity (EC $\text{mS cm}^{-1}$ )	12.32
Total C ( $\text{g kg}^{-1} \text{ DM}$ )	258	Total dissolved solids (TDS $\text{g kg}^{-1} \text{ DM}$ )	132
Total P ( $\text{g kg}^{-1} \text{ DM}$ )	14.01	Oxidation–reduction potential (ORP mv)	–145

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