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Fate and chemical fraction distribution changes of arsenic and mercury during ultrasonic sludge treatment process

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ABSTRACT

Arsenic and mercury are typical elements with high toxicity found in sewage sludge, and only low content of them could cause severe environmental risks. Therefore, changes of arsenic and mercury during sludge treatment and disposal should be concerned. In this study, ultrasound irradiation was used for sludge treatment. The contents and chemical fraction changes of arsenic and mercury during sludge sonication were investigated in detail. Results showed that arsenic and mercury were released from sewage sludge into the aqueous phase by sonication. The concentrations of arsenic and mercury in the aqueous phase increased steadily during 30 min of sonication. The release of arsenic was higher than that of mercury (58% vs. 26%), since the content of unsteady chemical fractions of arsenic in sludge was high. Sonication enhanced the stability of arsenic and mercury in sludge. For arsenic, the unsteady fraction decreased from 85.0% to 0.0% and transformed into a stable fraction after 30 min of sonication. For mercury, the chemical fractions changed little during sonication due to the high content of stable fractions in mercury. Furthermore, a ‘concentration’ phenomenon of arsenic and mercury in the solid phase occurred during sonication. Additionally, contents of arsenic and mercury in sludge after sonication met Chinese legal standards.

Keywords: Sonication; Arsenic; Mercury; Solubilization; Chemical fractions

1. Introduction

The rapid growth of industrialization and urbanization in the 21st century has resulted in the production of unmanageable quantities of sludge from municipal wastewater treatment plants (WWTPs). Sewage sludge contains pollutants such as trance heavy metals and eggs of parasitic organisms, which have potential environmental risks [1,2]. Therefore, the sludge must undergo a proper treatment before it enters into the environment (e.g. land application). Various technologies for sludge treatments and disposal have been developed, of which ultrasonic irradiation is considered to be one of the most promising technologies for sludge treatment [3–6]. Researchers have done great efforts in investigating the effect and optimization of sonication on physico-chemical characteristics of activated sludge, such as floc particle size distribution, the solubilization of COD, proteins, and polysaccharides [4,7–9].

The presence of heavy metals in sewage sludge is an increasing problem in sludge disposal. Municipal wastewater in China is usually mixed with industrial wastewater before treatment, and therefore concentrations

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of heavy metals in sewage sludge are high [10]. Heavy metals in sludge are of great concern due to their high toxicity to the environment. Unsteady forms of sludge heavy metals penetrated through the soil when sludge was used for land application, resulting in groundwater pollution. Furthermore, unsteady metals were assimilated by plants and then accumulated in the food chain, which could cause serious health problems to humans and animals [11,12]. Researchers found that heavy metals in sludge could be released during sludge treatment processes [13,14]. However, the detailed description of an ultrasonic irradiation of sludge on the changes of heavy metals has not been mentioned.

Arsenic and mercury are two typical elements with high toxicity found in sewage sludge [15], and even low concentrations could cause severe environmental risk. Arsenic and mercury could not be degraded during wastewater treatment process, and might form compounds with higher toxicity when they were combined with other toxic matter in the environment [16]. The mercury combined with organic matter has been considered as the highest toxic Hg-compounds. Arsenic is a kind of metalloid. In reducing environments, arsenic occurs primarily as arsenite, As(III), which is the most soluble and mobile among the As-species [16,17]. Arsenic and mercury probably behave like most transition metals, which tend to be associated with fine suspended particles. Therefore, the fate of arsenic and mercury during sludge sonication should be known clearly. Besides, since toxicity and mobility of heavy metals were determined by their chemical fractions [18], the chemical fraction changes of arsenic and mercury should be investigated.

This study has investigated the detailed fate and chemical fraction changes in the arsenic and mercury contained in the sludge during sonication. The aim of this paper is (1) to understand the detailed changes of mercury and arsenic during sonication, and (2) to evaluate the stability of mercury and arsenic with sonication.

2. Materials and methods

2.1. Abbreviations and indices definition

S_{COD}: sludge solubilization degree, an index to represent the amount of the organic compounds that is released. According to Gonze et al. [9], this index can be calculated by Eq. (1).

$$S_{\mathrm{COD}}(\%) = (\mathrm{COD_s} - \mathrm{COD_{s0}}) / \mathrm{COD_{p0}} \times 100 \tag{1}$$

where $\mathrm{COD_S}$ is the soluble chemical oxygen demand (SCOD) concentration in the supernatant after sludge sonication; $\mathrm{COD_{S0}}$ is the initial soluble COD concentration in the supernatant of untreated sludge; $\mathrm{COD_{p0}}$ is the initial particulate COD concentration in sludge.

S_{TSS}: solubilization degree of solid mass [4,7,9], an index to represent how much sludge solid mass is reduced during sonication, which can be calculated by Eq. (2)

$$S_{\mathrm{TSS}}(\%) = (\mathrm{TSS_0} - \mathrm{TSS}) / \mathrm{TSS_0} \times 100 \tag{2}$$

where $\mathrm{TSS_0}$ is the total sludge solid mass of untreated sludge and TSS the total sludge solid mass after sludge sonication.

- F1: exchangeable fraction,
- F2: carbonated-bound fraction,
- F3: Iron-Manganese (Fe/Mn) oxides-bound fraction,
- F4: organically-bound fraction,
- F5: residual fraction.

2.2. Sludge and reagents

The sludge was collected from the secondary sedimentation tank of a wastewater treatment plant in Harbin, China, which employed an anaerobic–anoxic–aerobic wastewater treatment process. The characteristics of the sludge were: (a) the water content of sludge was 99.83%, (b) the total suspended solid content (TSS) was 4050 mg $\mathrm{L^{-1}}$, (c) the volatile suspended solid content (VSS) was 2969.2 mg $\mathrm{L^{-1}}$, and (d) the SCOD was 210 mg $\mathrm{L^{-1}}$. The content of arsenic and mercury in sludge was 2.43 mg $\mathrm{kg^{-1}}$ DS and 3.55 mg $\mathrm{kg^{-1}}$ DS, respectively.

Ultra-pure water was used for all experiments and analyses. It was generated in the lab using a Millipore ultra-pure water generator. All reagents were of analytical reagent grade or higher.

2.3. Operations

The sonication equipment was a horn-system (JY90-II, Ningbo Haishu Kesheng Ultrasonic Equipment Co., China) that emitted 20 kHz ultrasound waves through a tip with a surface area of 2.12 $\mathrm{cm^2}$. The range of ultrasonic power was from 0 to 250 W. Each time 100 mL sludge was put in a 150 mL beaker for sonication and the probe was dipped 1 cm below the sludge surface in the center of the beaker. The ultrasonic intensity was 1.2 W $\mathrm{mL^{-1}}$, which was chosen according to previous study [7].

The untreated sludge and sonicated sludge were both centrifuged at 4000 rpm for 30 min (TCL-16G, Anting Sci., China) to separate the solid phase and liquid phase (supernatant). Supernatant was used to measure the SCOD and aqueous heavy metal concentrations. The solid phase was used for the analysis of the changes of heavy metal content and chemical fraction distributions in the solid sludge, and floc surface functional groups.

2.4. Analysis

The SCOD, TSS, and VSS were measured according to APHA standard methods [19].

The elements in both liquid and solid phase of the sludge were measured by a Perkin–Elmer Optima 5300 DV ICP (Perkin–Elmer Inc., America) [20]. The operational parameters of the ICP-OES were: (1) observation mode was horizontal; (2) temperature of the ray room was 34.8 °C; (3) radio-frequency power was 1.1 kW; (4) argon gas pressure was 248 kPa; (5) cooled gas flow was 20 L min^{-1} and auxiliary gas flow was 2 L min^{-1}; (6) lifting speed of pump was 1.2 mL min^{-1}; and (7) exposure time was 25 s.

The concentration of arsenic and mercury in the supernatant was measured directly while for the solid phase, the sludge was first digested with HNO_3–HF–$HClO_4$ before measurement. The detailed procedures are shown in the supporting information. The standard curve method was employed for element measurement. The standard solution of each element with the concentration of 1 mg^{-1} mL was bought from Perkin–Elmer Inc., which was stepwise diluted for standard curve. Standard recovery test with six times' parallel determination was operated for checking the accuracy of the method. The recovery was 89.8–101.2%, and the relative standard deviation was lower than 2.5%. The detection limit of ICP-OES was 0.003 mg L^{-1} for arsenic and mercury. The chemical fraction of arsenic and mercury in the solid phase was analyzed by a five-step sequential extraction procedure [21].

Floc surface functional groups of the sludge were measured by IR spectra, which were obtained by diluting the solid samples with a transparent component, KBr [22]. The signals of CO_2 and aqueous vapor in the air and possible impurities of KBr were subtracted from all the spectra through collecting a background spectrum. Eight scansions between 400 and 4000 cm^{-1} were performed for each spectrum. The IR spectra were recorded using a Perkin–Elmer 1000 infrared spectrometer (America).

All measured values of each index were the average values calculated from duplicate samples.

3. Results and discussion

3.1. Characteristic changes of activated sludge during sonication

Ultrasound has been viewed as an effective method for sludge disintegration. Low-frequency ultrasounds can disrupt the sludge floc, lyze the bacterial cells, and therefore change the characteristics of the sludge.

Sonication could convert the particulate organic matter into soluble organic components. This was achieved by cell lysis and/or by reducing the size of the organic particles [23–25]. Therefore, the organic matters in the supernatant increased and the solid mass decreased correspondingly, as shown in Fig. 1. S_{COD} and S_{TSS} increased steadily with the sonication duration, and reached 36% and 25% after 30 min, respectively. The increased S_{COD} meant that cells or flocs could be lyzed by sonication.

3.2. Changes of heavy metals during sonication

The detailed solubilization process of arsenic and mercury during sonication is depicted in Fig. 2. During the ultrasonic sludge treatment process, both arsenic and mercury were released from the sludge into the aqueous phase by sonication. The released concentration in the aqueous phase was rather low, which might

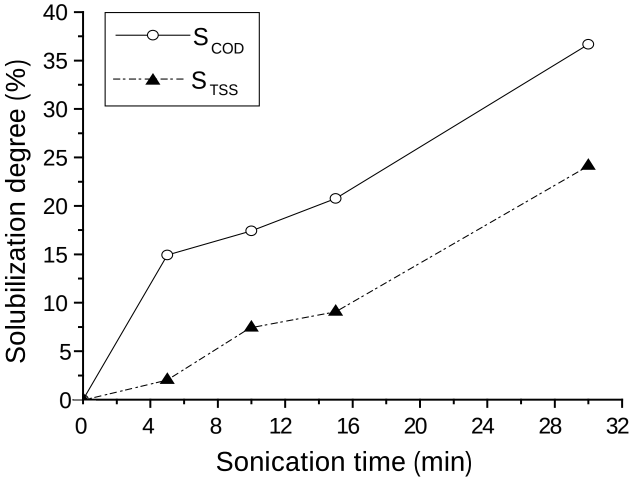


Fig. 1. Sludge solubilization during sonication, 1.2 W mL^{-1}.

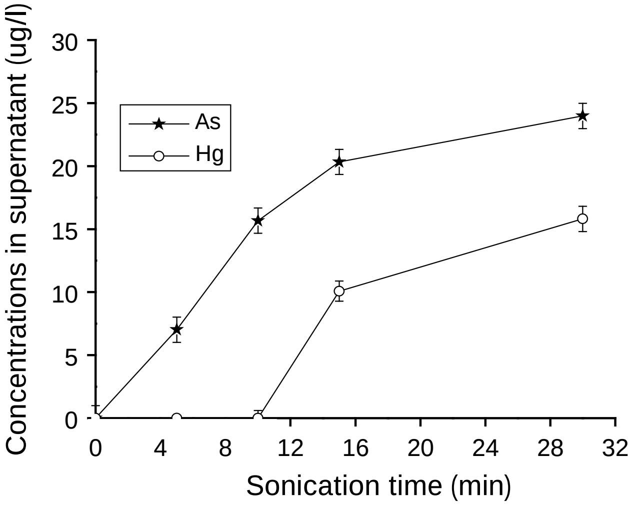


Fig. 2. The concentration changes of arsenic and mercury in supernatant during sonication, 1.2 W mL^{-1}.

not have potential risks when the sonicated sludge was used as a carbon source in bioreactors [26]. The concentrations in the supernatant increased steadily up to a treatment duration of 15 min, and then increased more slowly with longer sonication duration.

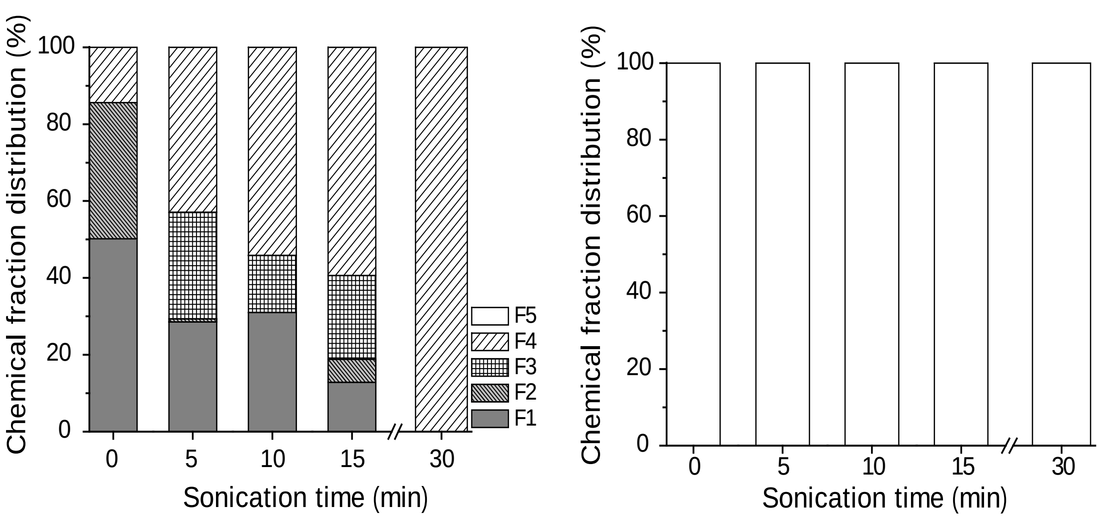
The solubilization patterns were different for arsenic and mercury. Arsenic was easier released by sonication than mercury. The content of arsenic in the untreated sludge was lower than that of mercury (2.43 mg kg^{-1} DS vs. 3.55 mg kg^{-1} DS); however, the concentration of arsenic in the supernatant was higher than that of mercury for 30 min of sonication. Furthermore, the release of arsenic began earlier than that of mercury. The release of arsenic occurred at the beginning of sludge sonication; however, the release of mercury began after 10 min of sonication. A possible explanation might be that the chemical binding forces between heavy metals and sludge were different, and arsenic was more unsteady than mercury in sewage sludge. Therefore, the chemical fraction distributions of arsenic and mercury were investigated (Fig. 3).

The chemical fractions of metal and metalloid elements determined their behaviors in the environment. According to the extraction produces [21], the exchangeable fraction (F1) is likely to be affected by changes in water ionic composition and sorption–desorption process. Carbonated-bound fraction (F2) is susceptible to changes in pH. Therefore, F1 and F2 present a low stability of the associated metals [18]. The Fe/Mn oxide-bound fraction (F3) also represents a low stability of the metals, since metals associated with this fraction are thermodynamically unstable under anoxic conditions [27]. Organically-bound fraction (F4) is susceptible to oxidizing conditions. The elements bound to the residual fraction (F5) contain mainly primary and secondary minerals, which may hold metals within their crystalline structure, therefore F5 is identified as a stable fraction [21,27]. Also, the unsteady fractions of the heavy metals were considered to be available forms since they were easily assimilated by plants when the sludge was for land application [11].

Clearly, the unsteady fractions (F1 and F2) accounted for about 85% of the total concentration of arsenic in the sludge, which contributed to the quick release by sonication. Mercury in the sludge was mainly formed by the residual fraction, which was a kind of stable combination between metals and sludge. Therefore, the release of mercury was much slower than that of arsenic by sonication.

Chemical fraction distributions of arsenic and mercury changed differently during 30 min of sonication. For arsenic, F1 and F2 decreased from 85% to 0% and the stable fraction F4 increased substantially from 15% to 100%. Partial arsenic fractions transformed from F1 and F2 to F3, and then transformed to F4, and finally there is no arsenic in F1, F2 and F3. The reason of the changes might be that the unsteady forms of arsenic were continuously released by sonication and combined with organic matters. After 30 min of sonication, the arsenic in the sludge was almost entirely composed of organically bound-arsenic. The methylation of arsenic might be the major contribution [17].

Since the functionality of the sludge floc might be altered qualitatively and quantitatively by sonication



(a) Arsenic

(b) Mercury

Fig. 3. Chemical fraction distributions of arsenic and mercury during sludge sonication, 1.2 W mL^{-1}.

[22,28], floc IR spectra were employed to investigate the functional groups before and after 30 min of sonication (Fig. 4). For the untreated sludge, the high peak at 3650–3200 cm^{-1} was attributed to methyl. Protein and polysaccharide functional groups (carboxyl, amine, and hydroxyl) appeared at 1700–1000 cm^{-1} in the fingerprint-area spectrum. Clearly, sonication modified the IR spectra of sludge flocs, and the changes of IR spectra focused on the peaks of 1600–800 cm^{-1} and 3650–3200 cm^{-1}. The changes of methyl group in the FTIR spectra spectrum after sonication might reflect that the high content of organically-bound arsenic (Fig. 3). The chemical fraction distribution changes of arsenic showed that the unstable arsenic was stabilized by sonication, and the stability of arsenic increased with sonication time.

For mercury, little change was obtained after 30 min of sonication, which also contributed to the low concentration of mercury in the supernatant (Fig. 1). The mercury in the sludge consisted mainly of the most stable form (F5); however, it could be released by sonication when the sludge was sonicated for a certain time. An explanation might be that a low concentration of elemental mercury existed in the sludge, and longer sonication times heated up the sludge temperature and caused the volatilization of mercury.

In summary, sonication assisted in breaking up the unsteady fractions (F1, F2 and F3) and increasing the stable fractions (F4 and F5) of heavy metals in sludge. The stability of arsenic and mercury in sludge was enhanced by sonication.

Sonication released only a small amount of metals from the sludge to the supernatant (Fig. 2), therefore there was still a relatively large amount of metals left in the sludge solid phase, as depicted in Fig. 5. Obviously, sonication had a 'concentration' effect on the sludge heavy metal, and the concentration of arsenic and mercury in the sludge was actually increased (Fig. 5). The heavy metal content in the sludge was equal to the weight of heavy metals in the sludge/total sludge solid mass. Significant loss of the total sludge solid mass was observed during sonication (Fig. 1) while the solubilization of heavy metals was less effective (Fig. 2). Therefore, the contents of arsenic and mercury in the solid phase were increased in spite of a little release by sonication.

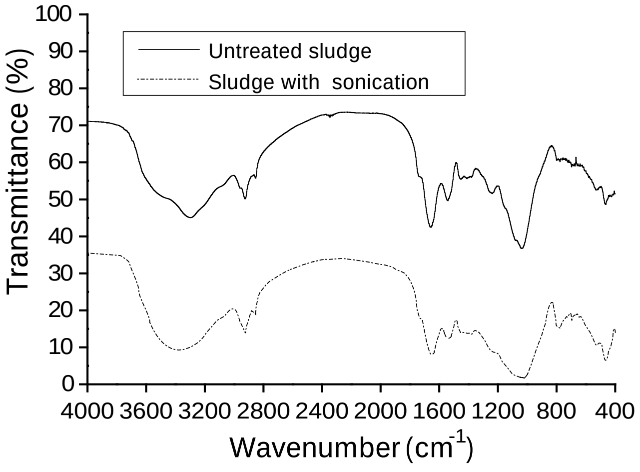


Fig. 4. FTIR spectra of sludge before and after sonication.

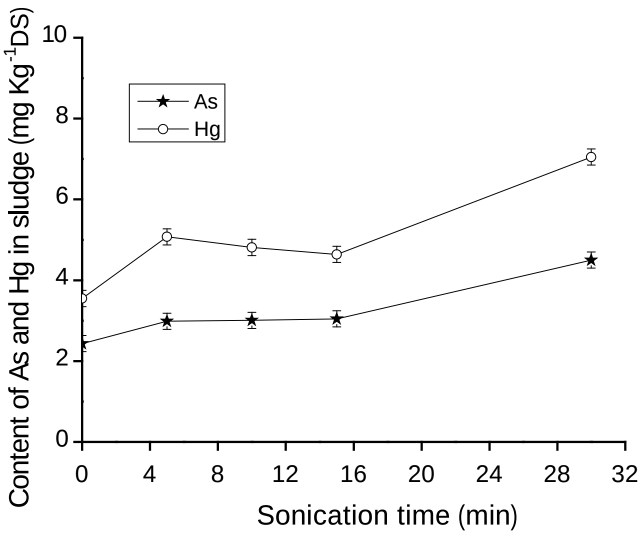


Fig. 5. The solid phase content of arsenic and mercury during sonication, 1.2 W mL^{-1}

The concentration of mercury in the sludge solid phase was higher than that of arsenic, since its solubilization was lower by sonication (Fig. 2). For arsenic, the concentration in the solid phase increased steadily, but insignificantly. For mercury, the content in the solid was fluctuating during sludge sonication. The content of mercury increased in the first 5 min of sonication, because that the release of mercury by sonication had not happened yet in that time.

The concentrations of arsenic and mercury increased in the sludge after sonication, however, they were not beyond the control standards for pollutants in sludge dedicated to land application of China. The available fractions of arsenic and mercury were rather low after sonication (Fig. 3), which again illustrated that sonication could weaken the potential risks of arsenic and mercury in sewage sludge.

4. Conclusions

This paper investigated the changes of arsenic and mercury in sewage sludge during sonication. Several conclusions were as follows.

- Arsenic and mercury were released by sonication, but the concentrations in aqueous phase were low during 30 min of sonication. The concentration of arsenic and mercury in the aqueous phase increased steadily with sonication. Solubilization of arsenic was higher than that of mercury since arsenic was more unsteady in sludge than mercury.

- Sonication enhanced the stability of arsenic and mercury in sewage sludge, and the potential environmental risks of both metals in sludge could be weakened.
- A 'concentration' phenomenon of arsenic and mercury occurred during sludge sonication. The reason was that the total sludge solid mass decreased significantly by sonication.

Acknowledgment

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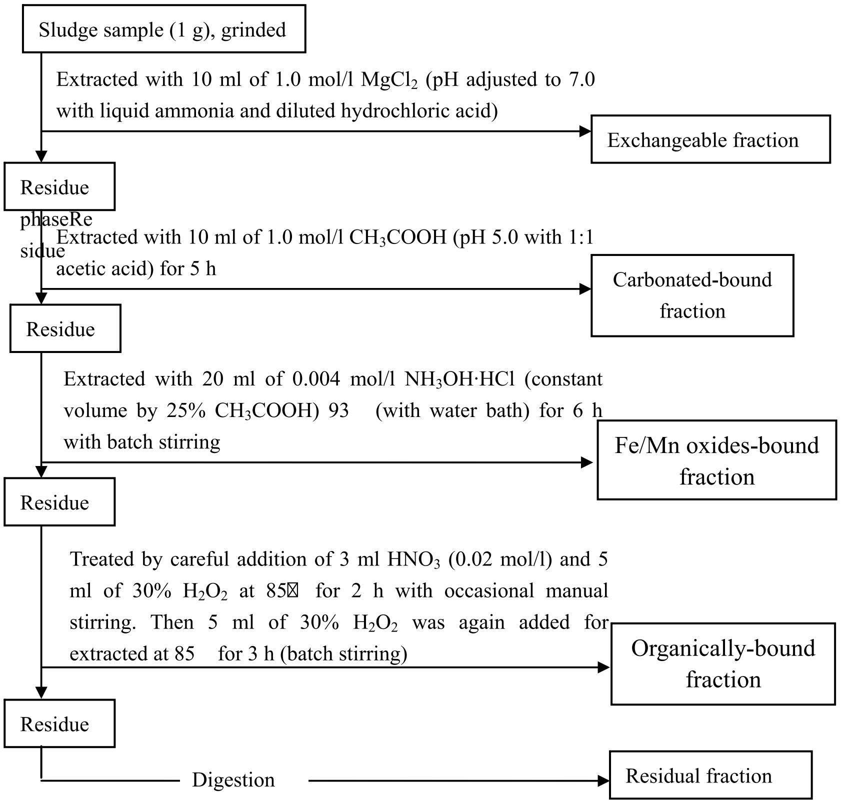
Supporting information

Schematic diagram of sequential extraction procedure



Extracted with 10 ml of 1.0 mol/l $MgCl_2$ (pH adjusted to 7.0 with liquid ammonia and diluted hydrochloric acid)

Extracted with 10 ml of 1.0 mol/l CH_3COOH (pH 5.0 with 1:1 acetic acid) for 5 h

Extracted with 20 ml of 0.004 mol/l $NH_3OH{\cdot}HCl$ (constant volume by 25% CH_3COOH) 93 (with water bath) for 6 h with batch stirring

Treated by careful addition of 3 ml HNO_3 (0.02 mol/l) and 5 ml of 30% H_2O_2 at 85⊠ for 2 h with occasional manual stirring. Then 5 ml of 30% H_2O_2 was again added for extracted at 85 for 3 h (batch stirring)