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Ultrasound sludge lysis: heavy metals stability enhancement

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ABSTRACT

Heavy metals in sludge are of great concerns worldwide due to their high toxicity. The toxicity of heavy metals strongly depends on their stability in the sludge. This study investigated the stability of typical sludge heavy metals (As, Cd, Cr, Cu, Ni, Hg, and Pb) during ultrasonic sludge treatment process. Results showed that sonication enhanced the stability of sludge heavy metals, which was beneficial for sludge disposal and reclamation. Content of stable fractions increased and content of unsteady fractions decreased after 15-min sonication at 2.0 WmL^{-1}. The stability of each heavy metal in sludge was significantly different during sonication. For arsenic, unsteady fractions decreased from 94 to 9% and stable fractions increased from 0 to 68% after 15-min sonication; for mercury and lead, stability showed little change due to the high residual fraction. Sonication changed the stability order of heavy metals in sludge. In the untreated sludge, the stability order was As < Ni < Cd < Cu < Cr < Pb < Hg; after 15-min sonication, the order was Cd < Ni < Cu < Cr < As < Pb < Hg.

Keywords: Sludge; Sonication; Heavy metals; Speciation; Stability

1. Introduction

Large quantities of waste sludge are produced in biological wastewater treatment processes. The sewage sludge consists of organic matters, heavy metals, and other harmful matters, resulting in high cost of sludge disposal and bringing serious secondary pollution to environment [1]. Therefore, sewage sludge from wastewater treatment plants poses a growing environmental problem [2], and heavy metals in sludge are of great concerns due to their high toxicity.

Researches proved that the environmental risks caused by sludge heavy metals greatly depend on their chemical fractions [3], since the chemical fractions decide the mobility, bioavailability and stability of heavy metals in the environment [4]. Unsteady fractions of heavy metals in sludge may penetrate through soil when used for land application, causing groundwater pollution [5]. Besides heavy metals in sludge with unsteady fractions are easy to be assimilated by plants and then accumulate in food chain, which can cause serious health problems to human and animals [6]. Therefore, the stability of heavy metals is important for sludge treatment, disposal and reuse. Heavy metals with high stability cause low risk in environment and one of the objectives for sludge treatment is to enhance the stability of sludge heavy metals.

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Various sludge treatment methods have been studied in literatures, and the stability of heavy metals was found to be changed during treatment processes, such as thermal treatment [2], sludge composting [7–9], and so on. The toxicity of sludge heavy metals changed correspondingly. Ultrasound radiation has been improved to be an effective sludge treatment method [10–12], which effectively improved the sludge biodegradability [13], enhanced the sludge dewaterability [14], and reduced the excess sludge [15]. Large amount of researches were devoted to the changes of sludge characteristics during sonication, such as the release of organic matters [11]and heavy metals [16], diminishing of floc size [12], and so on. However, little information about the heavy metal stability during sludge sonication is available.

Therefore, this paper investigated the stability of heavy metals during ultrasonic sludge treatment, and the chemical fractions of heavy metals were studied. Seven typical heavy metals in sewage sludge were selected, namely arsenic, nickel, cadmium, copper, chrome, lead, and mercury.

2. Materials and methods

2.1. Sludge and reagents

Sludge used was taken from a local wastewater plant in Harbin. Table 1 showed the basic property of the untreated sludge. Ultra-pure water was used for all experiments and analyses. All reagents used were of analytical reagent grade or higher.

2.2. Sonication

Sludge sonication was performed in a JY90-II ultrasonic horn-system (Ningbo Haishukesheng Ultrasonic Equipment Co., China) that emitted 25 kHz ultrasound waves through a tip with a surface area of 2.12 cm^2. The range of ultrasonic power was from 0 to 250 W. Each time 100 mL^{-1} of sludge was put in a 150 mL^{-1} beaker for sonication, and the probe was dipped 1 cm below the sludge surface in the center of the beaker. The ultrasonic intensity was 2.0 $WmL^{-1}$and the sonication time was 15 min, which were chosen according to previous study.

2.3. Analysis method

After certain sonication time sludge was sampled to study the changes of heavy metal chemical fractions. The samples were centrifuged at 4,000 rpm for 30 min using a TCL-16G desk centrifuge (Anting Scientific, China) in order to separate the solid phase (sludge) and the liquid phase (supernatant).The liquid phase was used for the measurement of SCOD; the solid phase was used for the analysis of heavy metal fractions.

Supernatant was filtered through a 0.45-μm membrane before analysis. SCOD, total sludge solid (TSS), and volatile solid (VSS) in sludge were measured according to APHA standard methods [17]. The pH of samples was monitored with a PHS-3C pH meter (Shanghai Precision Scientific Instrument Co., China). All measured values of each index were average values calculated from duplicate samples.

The chemical fraction of heavy metals in the solid phase was analyzed by a five-step sequential extraction procedure, and the operating steps were shown in Fig. 1. The five-step extraction method [18] has been proved to be a successful method for determining the speciation of heavy metals and widely applied to evaluate both the actual and potential mobility of metals in the environment. According to the extraction procedure, heavy metals chemical fractions were classified as exchangeable fraction, carbonated-bound fraction, iron-manganese (Fe/Mn) oxides-bound fraction, organically-bound fraction, and residual fraction. The equipment used was a 5300DV ICP-MS (PE, USA), and the detection limit of ICP-MS was 0.003, 0.001, 0.005, 0.005, 0.003, 0.005, and 0.003 mg L^{-1} for arsenic, cadmium, chrome, copper, mercury, nickel, and lead, respectively.

Table 1
Physical-chemical characteristics of the untreated sludge

(a) Basic characteristics						
pH	Water content (%)	TSS (mg L^{-1})	VSS (mg L^{-1})	SCOD (mg L^{-1})	Temperature (°C)	
6.89	99.38	4050.00	2969.20	210.00	22.00	
(b) Heavy metals content in the untreated sludge (mg kg^{-1})						
Cu	Ni	Cr	Pb	Hg	As	Cd	Total metal
140.20	59.99	40.52	29.92	3.55	2.43	0.55	277.15

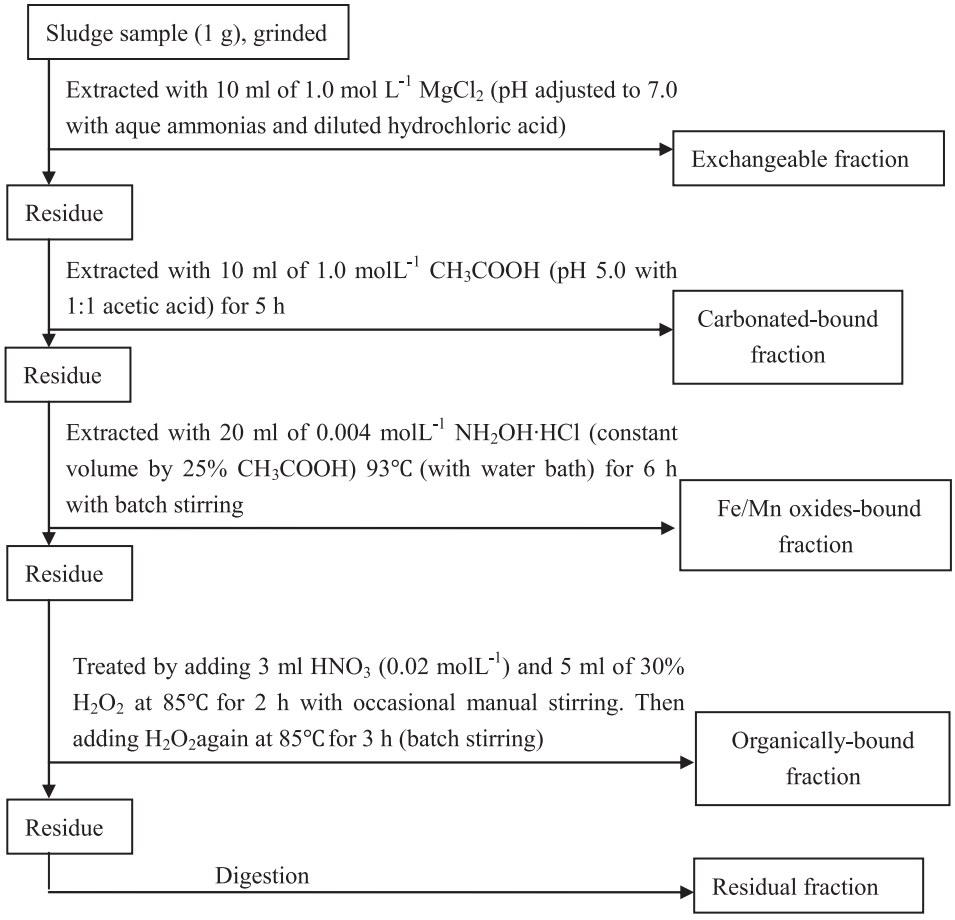

Fig. 1. Schematic diagram of sequential extraction procedure.

3. Results and discussion

After 15-min treatment, the sludge disintegration ratio reached 31.2 and 32.5% of volatile solid was reduced. The total heavy metal contents (sum of all seven metals) were 384 mg kg^{-1} after sonication. The chemical distributions of seven heavy metals of the untreated sludge and the sonicated sludge are summarized in Tables 2 and 3, respectively.

3.1. Change of stability of total heavy metals

Fig. 2 reports the chemical distributions of all seven heavy metals in sum. The stability of heavy metals mainly depends on their speciation in the sludge [19]. 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 of pH. Therefore, F1 and F2 present a low stability of the associated metals [7]. Fe/Mn oxide-bound fraction (F3) occupies second places regarding the low stability of the metals because metals associated with this fraction are thermodynamically unstable under anoxic conditions [20]. Organically-bound fraction (F4) is susceptible to oxidizing conditions [18]. The heavy metals bound to the residual fraction (F5) contain mainly primary and secondary minerals, which may hold metals within their crystal structure and so F5 is identified as a stable fraction [20]. Therefore, the F1

Table 2
Heavy metals fraction distributions in the untreated sludge

Chemical fraction	Heavy metal content (mg kg^{-1})						
	As	Ni	Cd	Cu	Cr	Pb	Hg
F1	1.34	14.15	0.00	0.77	0.12	0.00	0.00
F2	0.86	5.15	0.02	3.98	0.00	0.00	0.00
F3	0.00	22.70	0.30	2.22	0.37	0.40	0.00
F4	0.13	13.41	0.23	120.87	23.94	0.34	0.00
F5	0.00	4.56	0.00	12.35	16.09	29.18	3.55

Notes: F1: Exchangeable fraction of heavy metal, F2: Carbonated-bound fraction, F3: Iron-Manganese (Fe/Mn) oxides-bound fraction, F4: Organically-bound fraction, F5: Residual fraction.

Table 3
Heavy metals fraction distributions in the sonicated sludge, 2.0 WmL^{-1}, 15 min

Chemical fraction	Heavy metal content (mg kg^{-1})						
	As	Ni	Cd	Cu	Cr	Pb	Hg
F1	0.40	10.68	0.00	0.77	0.12	0.00	0.00
F2	0.00	5.27	0.02	3.98	0.00	0.00	0.00
F3	1.02	19.78	0.30	2.22	0.37	0.40	0.00
F4	3.01	22.46	0.23	120.87	23.94	0.34	0.00
F5	0.00	9.66	0.00	12.35	16.09	29.18	3.55

Notes: F1: Exchangeable fraction of heavy metal, F2: Carbonated-bound fraction, F3: Iron-Manganese (Fe/Mn) oxides-bound fraction, F4: Organically-bound fraction, F5: Residual fraction.

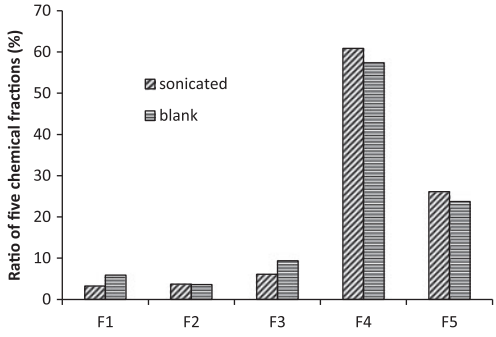

Fig. 2. Changes of total heavy metal chemistry fraction distribution after sonication, 2.0 WmL^{-1}, 15 min.

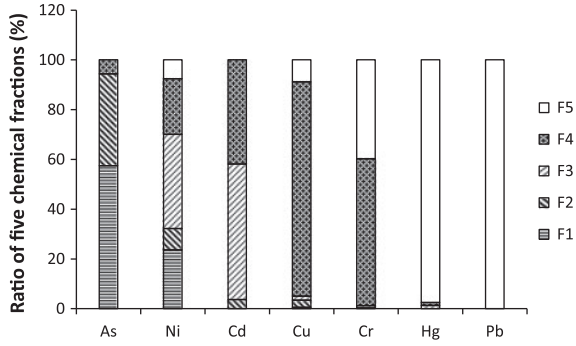

Fig. 3. Each heavy metal chemistry fraction distribution before sonication.

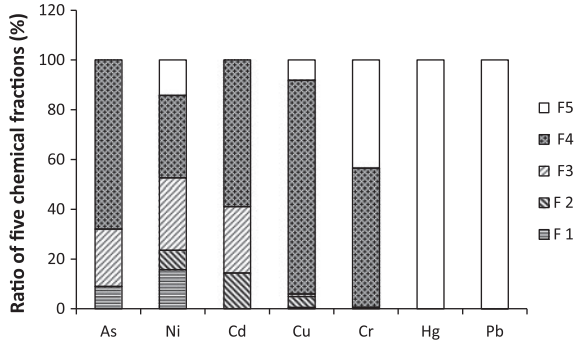

Fig. 4. Each heavy metal chemistry fraction distribution after sonication, 2.0 WmL^{-1}, 15 min.

and F2 represent the unsteady fraction and F4 and F5 represent the steady fraction.

Clearly, heavy metals in both the untreated sludge and sonicated sludge were stable. For the untreated sludge, the unsteady fractions (sum of F1 and F2) accounted for 9.5%, while the stable fractions (sum of F4 and F5) accounted for 81.0%. For the sonicated one, the unsteady fractions (sum of F1 and F2) accounted for 6.9%, while the stable fraction (sum of F4 and F5) accounted for 87.0%. Comparing to the values for the untreated sludge, obviously the stability of the sludge increased after sonication. In general, sonication broke up the unsteady fractions and enhanced the stable fractions of heavy metals in sludge and thus decreased the sludge biotoxicity.

3.2. Changes of stability of each heavy metal in sludge after sonication

Fig. 3 shows the chemical fraction distribution of each heavy metal for the untreated sludge. Fig. 4 reports the chemical fraction distribution of each heavy metal for the ultrasonic treated sludge. Clearly, sonication changed the stability of these seven heavy metals in sludge.

Sonication strongly enhanced the stability of arsenic. The content of F1 and F2 decreased along with sonication time from 94.4 to 9.0% and that of F4 increased substantially from 5.6 to 67.9%, which illustrated that the unstable arsenic in the sewage sludge was stabilized by sonication. F3 changed dramatically during sonication; it increased from 0 to 23%. Such a dramatic change might because that Fe/Mn oxide matters in the sludge were released by sonication and combined with arsenic.

For nickel and cadmium, F3 was the highest fraction of in the untreated sludge, accounting for 37.9 and 54.5%, respectively. This fraction is thermodynamically unstable under anoxic conditions. Chemical fractions distribution change of both metals was not substantial after 30-min sonication. An interesting phenomenon was that the percentage of F3 and F4 in nickel and cadmium changed oppositely during sonication. For nickel, the sum of F3 and F4 contents during sonication was almost constant during

sonication, indicating that a part of F3 and F4 fractions transformed mutually.

For copper and chrome, F4 was the dominating fraction in both untreated and sonicated sludges. As a whole, the stability of copper and chrome changed little with increased sonication duration. Copper could easily form complexes with organic matters due to the high stability of organic copper compounds [21], and therefore, F4 was the dominating fraction and changed little with increased sonication duration. Chrome existed in the forms of F4 and F5 in sludge. The contents of other three fractions were low, and their changes were negligible during sonication.

For lead and mercury, the content of F5 was 99.0 and 100.0%, respectively, showing that they were very stable in the sewage sludge. Little change was obtained during sonication (Fig. 4). Clearly, sonication did not decrease the high stability of lead and mercury.

3.3. Changes of stability order of seven metal in sludge after sonication

Clearly, the chemical fractions distribution of each heavy metal was different in the sludge. The higher the steady fraction (sum of F4 and F5) is, the steadier the metal is; the higher the unsteady fraction (sum of F1 and F2) is, the more active the metal is. Thus, we can arrange the stability order of these heavy metals according to their chemical fraction distributions.

For the untreated sludge, obviously, arsenic has the highest unsteady fractions ratio. For nickel, the most unsteady fractions (sum of F1 and F2) accounted for 19.3%, and F3 accounted for 22.7%. For chrome and copper, F4 was the major form existing in sewage sludge. For mercury and lead, F5 was the main existing form. Therefore, the stability order of these seven typical heavy metals in the untreated sludge was As < Ni < Cd < Cu < Cr < Pb < Hg.

After sonication, the stability order of sludge heavy metals was that Cd < Ni < Cu < Cr < As < Pb < Hg. The most activated metal in the untreated sludge was arsenic, while after sonication, it became the third most stable one. On the other hand, the cadmium turned to be the most active metal after sonication.

4. Conclusions

Heavy metals in sludge are one of the main factors for sewage sludge risk to the environment. The risks to the environment and biosystem of heavy metals are determined by their stability. This paper studied the stability of seven typical sludge heavy metals during ultrasonic sludge treatment. Several conclusions could be obtained.

(1) Sonication enhanced the stability of sludge heavy metals, which was beneficial for sludge disposal and reclamation.
(2) The stability order of the seven heavy metals in untreated sludge was As < Ni < Cd < Cu < Cr < Pb < Hg; after sonication, the stability order was Cd < Ni < Cu < Cr < As < Pb < Hg.
(3) The stability of each heavy metal in sludge behaved differently. For arsenic, the unstable fractions decreased from 94 to 9%; for lead and mercury, little change was observed during sonication for their large amount of stable fractions.

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