SOLUBILIZATION OF HEAVY METALS IN SLUDGE DURING SONICATION: IMPACT OF SONICATION TIME AND POWER DENSITY

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Abstract

Heavy metals in sludge have been one of the limiting factors for sludge reclamation, and therefore the changes of heavy metals during sludge treatment process should be concerned. This study investigated the detailed profile of changes of seven typical heavy metals (As, Cd, Cr, Cu, Ni, Pb, and Hg) in the activated sludge during ultrasonic treatment process. The influences of sonication time and ultrasonic power density were studied. Results showed that heavy metals in sludge were released into the aqueous phase under ultrasound irradiation, but the solubilization degree was low. After sonication of 1.2 W/mL for 30 min, the solubilization degree of organic matter (SCOD) in sludge increased to 36.0%, while the solubilization degree of total heavy metals (SHM) only increased to 7.0%. Sonication time and power density greatly affected the heavy metals solubilization degree. SHM increased almost linearly with sonication time within the first 15 min and then stabilized. A minimum power density of 0.8 W/mL was required for heavy metal solubilization. Pearson correlation coefficient analysis showed that the effect of sonication time on heavy metal release was higher than that of power density. Each heavy metal behaved differently during the ultrasonic treatment. Arsenic and nickel release were easier and the solubilization degree reached 58.4% and 34.9% after 30 min of sonication, respectively. The content of copper was high in the activated sludge; but the solubilization degree was low. Cadmium was stable and could not be released by sonication.

Key words: heavy metals, power density, sludge, solubilization, sonication time

Received: August, 2011; Revised final: July, 2012; Accepted: July, 2012

1. Introduction

The rapid growth of industrialization and urbanization in the 21st century has resulted in the production of large quantity of urban sewage (Manea et al., 2013; Zaha et al., 2011). Many wastewater treatment plants are constructed for wastewater purification, which cause a large amount of excess sludge (Murray and Nelson, 2008).

In China, the amount of sewage sludge is increasing by an average of 5% every year. Excess sewage sludge is the major issue of wastewater treatment plant, as it accounts for 60% of the total plant working cost (Mohammed et al., 2009; Wang et al., 2008). Therefore, various technologies for sludge treatments and disposals have been developed, among which ultrasonic radiation is a promising one (Bougrier et al., 2005; Chu et al., 2001; Nickel and Neis, 2007; Wei et al., 2003).

When ultrasound is applied to sludge, acoustic cavitation occurs, and high shear forces are produced and act on sludge, which greatly change sludge characteristics. The floc size of sonicated sludge can be cut by 50% (Bougrier et al., 2006; Gonze et al., 2003; Nah et al., 2000; Onyeche et al., 2001). Large organic matter in sludge can be released by sonication and therefore aerobic digestion rate is improved (Bougrier et al., 2006; Gronroos et al.,

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sludge biodegradability is improved (Tiehm et al., 2001) and the gas production is increased by 8-17 times (Trouqu and Forster, 2002). After ultrasonic pretreatment, the sludge dewatering time and sludge volume are cut down by 50% (Yin et al., 2004). The sewage sludge is reduced by 60%-100% when the sonicated sludge is recycled into aeration tank as substances for microorganisms (Cao et al., 2006; Yoon et al., 2004; Zhang et al., 2007).

Sludge from wastewater treatment plants contains various toxic heavy metals (Stasinakis and Thomaidis, 2010). Heavy metals in the sewage sludge are of great concerns due to their health impacts (Nomeda et al., 2008). They may penetrate through soil when sludge is used for land application and cause groundwater pollution (Asik and Katkat, 2010; Pavel et al., 2012). Besides, heavy metals can be assimilated by plants and then accumulate in food-chain, and therefore cause serious health problems to humans and animals.

Ultrasound have great effects on sludge components, and detailed information about the changes of COD, nucleic acids, polysaccharides, nitrogen and phosphorus, and bacteria during sludge sonication has been obtained (Bougrier et al., 2005; Chu et al., 2001; Nickel and Neis, 2007; Wei et al., 2003). It is reasonable to believe that the behaviors of heavy metals in the sludge are affected by sonication. Researchers have reported that ultrasounds can accelerate the chemical release of heavy metals during the realization of sequential extraction schemes applied to sludge samples (Dimitar et al., 2004). In our previous work, we have found that the content of sludge heavy metals changed in the sonication-cryptic growth system (Zhang et al., 2007). The changes of heavy metals during sonication are important since they affect the sludge aerobic composts, and landfill.

Therefore, this paper assessed the detailed changes of heavy metal during ultrasonic sludge lysis process and focused on the impact of sonication duration and ultrasonic power density on heavy metals during sonication, which are the most important parameters for sonication efficiency. Seven typical sludge heavy metals were selected, namely arsenic, copper, nickel, cadmium, chrome, mercury and lead.

2. Materials and methods
2.1. Indexes definition

Sludge solubilization degree, \( S_{COD} \) (mg/L) is an index to represent how much organics are released during sonication. According to Gonzé et al. (2003), this index can be calculated using Eq. (1).

\[
S_{COD} = \frac{(COD_s - COD_{s0})}{COD_{p0}} \times 100
\]  

where \( COD_s \) is the soluble COD concentration in the supernatant after the sludge sonication; \( COD_{s0} \) is the initial soluble COD concentration in the supernatant of the untreated sludge; \( COD_{p0} \) is the initial particulate COD concentration in sludge.

Solubilization degree of the solid mass, \( S_{TSS} \) an index used to represent how much sludge solid mass is reduced during sonication, which can be calculated by Eq. (2) (Gonzé et al., 2003; Zhang et al., 2007):

\[
S_{TSS} = \frac{(TSS_0 - TSS)}{TSS_0} \times 100
\]

where \( TSS_0 \) is the total sludge solid of the untreated sludge and \( TSS \) is the total sludge solid after sludge sonication.

Solubilization degree of heavy metal, \( S_{HM} \) is an index used to represent how much heavy metal is released during sonication. According to the definition of \( S_{COD} \) \( S_{HM} \) can be calculated by Eq. (3):

\[
S_{HM} = \frac{(C_f - C_{f0})}{M_f} \times V \times \frac{100}{M_i}
\]

where \( M_f \) is the quality of heavy metal in sludge, which is constant, since heavy metals are not transformed into other elements during sonication; \( C_{f0} \) is the concentration of heavy metals in supernatant before sonication; \( C_f \) is the concentration of heavy metals in the supernatant after sonication and \( V \) is the volume of supernatant.

2.2. Sludge and reagents

The sludge was collected from a wastewater treatment plant in Harbin, China. Tables 1 and 2 show the characteristics of the sludge.

Ultra-pure water was used for all experiments and analysis. It was generated in the lab by using a Millipore ultra-pure water generator (Milli-Q 10, Millipore Pvt. Ltd., USA). All reagents were of analytical reagent grade or higher.

2.3. Experiments

The sonication equipment was a horn-system (JY90-II, Ningbo Haishu Kesheng Ultrasonic Equipment Co., China) that emitted 25 kHz ultrasound waves through a probe with a surface area of 2.12 cm². The range of ultrasonic power was from 0 to 250 W. Each time 100 mL sludge was put into a 150 ml beaker for sonication, and the probe was dipped 1 cm below the sludge surface in the center of the beaker. The content of the sludge was concentrated to 9000-10000 mg/L before ultrasound sonication treatment.

The sludge pH was not controlled during sonication and kept near neutral. The beaker was put in a water bath cooled using tap water, the temperature increased by 10-20oC, depending on the operational conditions.
Table 1. Physical-chemical characteristics of untreated sludge (basic properties of activated sludge)

<table>
<thead>
<tr>
<th>pH</th>
<th>Water content (%)</th>
<th>TSS (mg/L)</th>
<th>VSS (mg/L)</th>
<th>SCOD (mg/L)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.9</td>
<td>99.4</td>
<td>4050.0</td>
<td>2969.2</td>
<td>210.0</td>
<td>22.0</td>
</tr>
</tbody>
</table>

Table 2. Physical-chemical characteristics of untreated sludge (heavy metals content in the untreated sludge (mg/kg))

<table>
<thead>
<tr>
<th>Copper</th>
<th>Nickel</th>
<th>Chrome</th>
<th>Lead</th>
<th>Mercury</th>
<th>Arsenic</th>
<th>Cadmium</th>
<th>Total metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>140.20</td>
<td>59.99</td>
<td>40.52</td>
<td>29.92</td>
<td>3.55</td>
<td>2.43</td>
<td>0.55</td>
<td>277.15</td>
</tr>
</tbody>
</table>

The temperature was not strictly adjusted during the sludge sonication since the rise of the sludge temperature during sonication process had a positive impact on sludge disintegration (Dewil et al., 2006).

The sonicated sludge was centrifuged at 4000 rpm for 10 min by a TCL-16G desk centrifuge (Anting Scientific Apparatus plant, China) in order to separate the solid phase and the liquid phase (supernatant). The diameter of the centrifuge was 600 mm. The supernatant was used for the measurement of SCOD and aqueous heavy metal concentrations; the solid phase was used for the analysis of heavy metal content changes.

2.4. Analytic procedures

SCOD, suspended solid content (TSS) and volatile solid content (VSS) were measured according to APHA standard methods (APHA, 1998). The pH of samples was monitored with a PHS-3C pH meter (Shanghai Precision Scientific Instrument Co., China).

The heavy metal concentration was measured by a PerkinElmer Optima 5300 DV ICP (Perkin Elmer Inc., USA). The operational parameters of the ICP-OES were: 1) Observation mode was horizontal; 2) Temperature of the ray room was 34.8 centigrade; 3) Radio-frequency power was 1.1 kW; 4) Argon gas pressure was 248 kPa; 5) Cooled gas flow was 2 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 25s. The heavy metal concentration in the supernatant was measured directly while that in the solid phase was firstly digested by a HNO₃-HF-HClO₄ digestion process before measurement. The detailed digestion process can be seen in the supporting information. The detection limit of ICP-OES was 0.003, 0.001, 0.005, 0.005, 0.003, 0.005, and 0.003 mg/L for As, Cd, Cr, Cu, Hg, Ni, and Pb respectively.

The standard curve method was employed for element measurement. The standard solution of each element with the concentration of 1 mg⁻¹mL was bought from Perkin Elmer Inc., which was stepwise diluted for standard curve. Standard recovery test with 6 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%. All data reported were the average of three or more experimental runs.

Pearson correlation coefficient was employed for investigating the impact of sonication parameters on heavy metal solubilization (Dunea and Lordache, 2011).

3. Results and discussion

According to the previous work (Zhang et al., 2008), power density of 1.2 W/mL and sonication time of 15 min were applied for investigating the impacts of sonication time and power density on the sludge heavy metals, respectively.

3.1. Impact of sonication time

3.1.1. Sludge solubilization

Sludge solubilization degree was evaluated by the release of sludge matters and the decrease of total solid mass. The impact of sonication time on sludge solubilization degree was reported in Fig. 1. Solubilization degrees of organic matter (S_{COD}) and total sludge solid (S_{TSS}) significantly depended on the sonication time and increased steadily during 30 min of sonication. Heavy metals were released by sonication; the solubilization degree of total heavy metal (S_{HM}) was nonlinear with sonication time. It increased steadily in the first 15 min of sonication and then remained stable. Longer sonication seemed to be ineffective to heavy metal release.

![Fig. 1. Impact of sonication time on sludge solubilization, 1.2 W/mL](image)

Sonication was more effective on the release of organic matter in sludge than heavy metals. After 30 min of sonication, S_{COD} reached 36.0% while S_{HM}
3.1.2. Impact of sonication time on heavy metal solubilization

In order to assess the potential effect of sonication time on the heavy metals release, soluble concentrations of seven typical sludge heavy metals (As, Ni, Cd, Cu, Cr, Pb, and Hg) in the supernatant were measured during sonication, and the solubilization degree of each heavy metal was calculated according to the release concentration and total content in the sludge (Fig. 2).

![Fig. 2. Impact of sonication time on heavy metal solubilization, 1.2 W/mL](image)

Clearly, heavy metal release was greatly affected by sonication time, and the relationship between them was not linear. The solubilization degree of heavy metals increased sharply at the initial 15 min of sonication, and then it changed smoothly. Previous studies also have showed that too long sonication time did not benefit the solubilization of organics (Bougrier et al., 2005; Gonze et al., 2003). It seemed that a release platform of matter existed during sludge sonication.

Different heavy metals showed different patterns. It seemed that sonication selectively released heavy metals from the sludge. Nickel and arsenic could release quickly and the solubilization degree reached to 58.4 % and 49.5%, respectively. Possible reason might be that both nickel and arsenic are more unstable in the sludge than other metals. Sonication for 15 min was needed for the release of chrome and mercury.

However, with further sonication, the solubilization degree of both metals slowed down. $S_{IM}$ of mercury was higher than that of chrome after 30 min of sonication (26.0% vs. 21.0%) in spite of its lower content in the untreated sludge. Most possible reason was that longer sonication time heated up the sludge temperature. With the rapid stirred by sonication and raised sludge temperature, some mercury volatilization might occur. The content of copper accounted for about 50% of the total heavy metals in the sludge, however, the solubilization degree was low. Cadmium and lead seemed very stable in the sludge that sonication of 1.2 W/mL for 30 min was ineffective for them and the solubilization degree of both metals was naught.

The different solubilization of each metal by sonication could explain the low solubilization degree of the total heavy metals. Arsenic was easily released by sonication but its content in the sludge accounted for less than 1% of the total heavy metal content. The content of copper and lead vs. the content of the total metals were more than 60%, but their releases were rather low or even could not be released by sonication. Therefore, according to Eq. (3), the solubilization degree of the total heavy metals was low.

3.1.3. Contents of sludge heavy metals in the solid phase

The content changes of heavy metals in the solid phase during sonication were investigated (Fig. 3). The heavy metal content was defined as net weight of heavy metal in the sludge/TSS. A concentration phenomenon of heavy metals after 30 min of sonication was observed. The total heavy metal content in the solid phase increased from 277.2 to 366.3 mg/kg-DS (increases by 32.2%) after 30 min of sonication.

The sludge floc was broken by sonication, which caused great reduction of TSS (Saktaywin et al., 2005); however, the total heavy metal release was low (Fig. 1). Therefore, heavy metal content in the sludge solid was higher than the untreated samples in spite of the release of heavy metals.

The content change of each metal in the solid phase behaved differently.
For copper, the content was much higher than other metals and increased substantially during sonication, since it was lightly released and the content in the untreated sludge was high. For lead, chrome and nickel, the contents in the solid phase changed slightly initially, and after 15 min, the contents increased.

3.2. Impact of ultrasonic power density

3.2.1. Sludge solubilization

Impact of power density on sludge solubilization is summarized in Fig. 4. The solubilization of organic matter increased continually in a linear-like pattern with power density increasing from 0 to 1.6 W/mL; beyond 1.6 W/mL, SCOD was nearly stable. The solid mass decreased steadily and STSS kept increasing with power density increasing from 0 to 2.0 W/mL. The solubilization degree of heavy metals was low (lower than 10.0%) in the wide power density range from 0 to 2.0 W/mL.

Ultrasonic power density greatly impacted the solubilization of heavy metals. The change of SHM was more complex and quite different from that of SCOD and STSS. Power density at the range of 0.8-1.6 W/mL seemed to be much effective for heavy metals solubilization. Low ultrasonic power density (below 0.8 W/mL) had little effect on the solubilization of them, and the effective power density work range was 0.8-1.6 W/mL. The SHM of both chrome and mercury reached a peak value at power density of 1.6 W/mL.

Copper had the highest content in the untreated sludge but its solubilization degree was low. The SHM of copper increased slowly with the power density below 1.6 W/mL and then stabilized. For lead, the solubilization started from 1.6 W/mL; further enhancing sonication decreased its release. For cadmium, sonication of 2.0 W/mL for 15 min was ineffective for its release. The results illustrated that the release of heavy metals by sonication did not depend on the content of heavy metals in the untreated sludge, but depended on the stability of heavy metals.

3.2.2. Impact of ultrasonic power density on each heavy metal

The concentrations of seven typical sludge heavy metals in the supernatant were measured during sonication with the increased power density. The solubilization degree of each heavy metal is assayed and reported in Fig. 5. Clearly, ultrasonic power density greatly affected the solubilization of heavy metals in a way which was different from that of sonication time. Heavy metals release during sonication was fall-after-rise with the increased power density from 0 to 2.0 W/mL. The results showed that the release of each heavy metal had a certain working range of power density.

The impact of power density on solubilization of each heavy metal was different. Nickel was released by sonication with a quite low power density (below 0.8 W/mL), and the solubilization degree was the highest at a power density of 1.6 W/mL. Arsenic had the highest solubilization degree among all seven metals, and could be effectively released in the power density work range of 0.8-1.2 W/mL. Power density of 1.2 W/mL was much effective for the release of arsenic, with a liquid concentration of 20.33 µg/L and SHM of 38.2%. For chrome and mercury, low power density inputting (lower than 0.8 W/mL) had little effect on the solubilization of them, and the effective power density work range was 0.8-1.6 W/mL. The SHM of both chrome and mercury reached a peak value at power density of 1.6 W/mL.

Nickel and arsenic were more unsteady and easy to be released by sonication than other heavy metals; while copper and cadmium were stable in the sewage sludge and their solubilization was poor, which might be the major reason for the low
solubilization of the total heavy metals during sonication.

3.2.3. Contents of sludge heavy metals in the solid phase
The impact of ultrasonic power density on heavy metal content in the solid phase was studied (Fig. 6). Similar to section 3.1.3, the heavy metals were concentrated in the solid phase in spite of their release by sonication.

The total metal content increased from 277.2 to 431.0 mg/kg DS by sonication with power density of 2.0 W/mL for 15 min. Firstly, at low power density, the content of each heavy metal changed slightly, and then sharply increased when ultrasonic power density reached 1.6 W/mL. The possible reason was that TSS decreased significantly at high power density (Fig. 4), while the release of heavy metals reached a peak at the same time (Fig. 5). Besides, more organic matter was released under higher power density (Fig. 4). The soluble heavy metals in the liquid phase might be re-absorbed by small sludge particles or dissolved organic matters and therefore could still stay in the solid phase, contributing to the content increase of heavy metals in the solid phase as well.

3.3. Comparison of sonication time and power density for their impacts on heavy metal solubilization
Pearson product-moment correlation coefficient was employed for analyzing the impacts of sonication time and power density on heavy metal release (Table 3).

In statistics, the Pearson product-moment correlation coefficient is a common measure of the correlation between two variables. The correlation coefficient value stands for the correlation degree between two variables. The significance value means the linear correlation. The range of Pearson product-moment correlation coefficient is from +1 to -1. +1 means that there is a perfect positive linear relationship between variables. -1 means that there is a perfect negative linear relationship between variables.

A correlation of 0 means there is no linear relationship between the two variables. Clearly, the total heavy metal solubilization was not linearly with both sonication time and ultrasonic power density. The correlation coefficient of the total heavy metal release versus sonication time was 0.874, while that of the total heavy metal release versus power density was 0.727. The results illustrated that the effect of sonication time on heavy metal solubilization was higher than that of power density.

The impact of sonication time and power density on each metal release behaved differently. For cadmium, the correlation coefficient of both sonication time and power density was naught, showing that sonication could not release cadmium in the setting sonication conditions in this our study. For arsenic, sonication time was more effective for its release; therefore, the adjustment of sonication time could be an effect way for controlling arsenic removal from sludge.

<table>
<thead>
<tr>
<th>Sonication time</th>
<th>Pearson correlation coefficient</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultrasonic power density</td>
<td>Pearson correlation coefficient</td>
<td>0.874*</td>
</tr>
<tr>
<td></td>
<td>Significance</td>
<td>0.052*</td>
</tr>
<tr>
<td></td>
<td>0.727*</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.084*</td>
<td></td>
</tr>
</tbody>
</table>

*2-tailed test of significance is used

Fig. 5. Impact of ultrasonic power density on heavy metal solubilization, 15min

Fig. 6. Impact of ultrasonic power density on heavy metal content in the solid phase, 15 min

Table 3. Pearson correlation coefficient between sonication parameters and heavy metal solubilization
4. Conclusions

Sonication caused sludge heavy metal release, but the effect was low compared to the solubilization of organic matter. Sonication time and power density were two important parameters influencing the changes of sludge heavy metals. Solubilization of heavy metals has a power density work range of 0.8-1.6 W/mL.

Pearson correlation coefficient showed that the effect of sonication time on solubilization of the total heavy metal was higher than that of power density. Heavy metals were concentrated in the solid phase after sonication. Each metal behaved differently and further study should focus on the chemical structure of heavy metals during sonication.

Acknowledgements

This work was supported by the Chinese Ministry of Science & Technology (2008ZX07317-02).

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