Chemical Engineering Journal 152 (2009) 177–182

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Extraction of heavy metal from sewage sludge using ultrasound-assisted nitric acid

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ARTICLE INFO

Article history:
Received 19 January 2009
Received in revised form 1 April 2009
Accepted 8 April 2009

Keywords:
Sewage sludge
Nitric acid
Ultrasound
Synergistic effect
Heavy metal extraction

ABSTRACT

The effects of nitric acid concentration and sonication time on the removal efficiencies of heavy metals from sludge were investigated. Nitric acid concentrations were varied from 0 to 0.65 M and sonication time from 0 to 20 min. The extracted metals Cu, Zn, and Pb were determined. The results indicated that the removal efficiencies of Cu, Zn, and Pb increased with increases in nitric acid concentration and sonication time. The optimal nitric acid concentration for heavy metals extraction was 0.325 M, while a maximal sonication time of 20 min resulted in maximal heavy metals removal efficiencies. The removal efficiencies of Cu, Zn and Pb reached 9.5%, 82.2%, and 87.3%, respectively, at the optimal concentration of nitric acid assisted by ultrasound for 20 min. Additionally, the residual contents of Zn and Pb in sludge met Chinese legal standards, while Cu was not significantly removed regardless of the nitric acid concentrations and sonication time. The order of heavy metal removal efficiencies was Pb > Zn > Cu. During heavy metal extraction, contribution proportions of ultrasonication and nitric acid to the extraction were 18–22% and 78–82%, respectively. Ultrasound alone was not effective enough to remove heavy metals from sludge and the role played by nitric acid predominated over that of ultrasound. However, ultrasound was synergistic with nitric acid when these were used together to extract heavy metals from sludge. Possible mechanisms of heavy metal extraction are also discussed.

1. Introduction

Biological wastewater treatment processes produce large amounts of surplus sludge. Proper waste treatment and final disposal methods are important for reducing excess sludge. Traditional sludge disposal methods include landfilling, incineration, and agricultural use [1]. In recent years, many countries have developed a series of regulations [2] that forbid the landfilling of solid wastes with high organic matter content due to land consumption and landfilling leachate pollution. Incineration seems to be a good option for sludge disposal; however, it can cause air pollution due to emissions and thus requires expensive off-gas treatment. Moreover, incineration contributes to the greenhouse effect and leads to the production of highly contaminated and hazardous slags and fly ashes, which must be treated [3]. Therefore, the only option left for sludge disposal is land use. The disposal method appears to be an economical and promising option because sludge can supply crops with large amounts of organic matter and inorganic nutrients and improve soil structure. Compared with landfilling and incineration, land use for sludge as organic fertilizer is a more sustainable alternative. Nevertheless, a large number of heavy metals in sludge exceed Chinese legal standards (GB4284-1984) and can become a constraint for sludge application in agriculture in China [4]. Unlike organic pollutants, heavy metals are persistent environmental contaminants that cannot be destroyed [5]. Thus, removing heavy metals from sludge before composting is a necessity for achieving more sustainable sludge treatment.

Currently, there are a few clean-up techniques for removing heavy metals from sludge, including chemical extraction [6], thermal treatment [7], bioleaching treatment [8], cementation and ion exchange [9]. Chemical extraction of heavy metals has received extensive attention due to its simple operation, short extraction time and high removal efficiency. Extraction efficiency of heavy metals depends on pH, temperature, contact time, and extracting agent type. Previous studies showed that low pH, high temperature, and long contact time can improve heavy metal extraction [3]. Various inorganic acids (HNO_3, HCl and H_2SO_4) [10], organic acids (oxalic and citric acid) [3], and strong complexing agents (NTA and EDTA) [11] have been proposed as effective extracting agents. Nevertheless, high extraction efficiency requires a large number of dosages, which results in high processing costs and difficulty in pH adjustment of the sludge compost. Thus, it is necessary to reduce the dosages of extracting agents.

Previous studies have showed that ultrasound, as an assisted extraction method, can efficiently release heavy metals from sludge and shorten extraction time [12–14]. Thus, ultrasound may be

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doi:10.1016/j.cej.2009.04.031

Table 1
Heavy metal content of sewage sludge compared to Chinese legal standards for heavy metals in sludges for agricultural use (GB4284-1984).

Heavy metal	Value (mg/kg)	Legal standards (mg/kg)
Cu	286 ± 3	≤250
Zn	1258 ± 13	≤500
Pb	751 ± 6	≤300
Cd	2 ± 0.1	≤5
Cr	99 ± 1.4	≤600

regarded as an efficient tool to enhance extraction efficiency of heavy metals together with the use of extracting agents. This study utilized ultrasonic energy to assist nitric acid extraction for heavy metals from sewage sludge in order to improve the ability to extract heavy metals with nitric acid and reduce the dosage of nitric acid required. The advantages of heavy metal extraction by nitric acid over extraction by other inorganic acids include the fact that elemental nitrogen in nitric acid can act as a nutrient source for fertilizers. Additionally, the mechanisms by which ultrasound facilitates heavy metal extraction are also discussed.

2. Experimental

2.1. Materials

Samples of sewage sludge were collected from Datansha Municipal Wastewater Treatment Plant in Guangzhou, China, which utilizes an anaerobic–anoxic–oxic process at a flow rate of 550,000 tons daily. The collected sludge was immediately transferred to the lab and stored in a plastic box at 4 °C prior to use. Heavy metal contents of the sludge samples are presented in Table 1.

2.2. Experimental set-up

The ultrasonic apparatus used in this study has been described in detail in our previous work [15]. It was equipped with an MS73 titanium cylindrical probe with a diameter of 20 mm and a length of 135 mm. It operated at a frequency of 20 kHz and supplied an adjustable power of 300–2000 W. During treatment, the probe was immersed into the sludge at a depth of 10 mm, the power output was 500 W and the sonication time was varied between 0 and 20 min.

3. Methods

3.1. Experimental procedure

Sludge samples of 500 ml were prepared in 1000 ml beakers and a series of concentration of nitric acid varying between 0 and 0.65 M was added and mixed well prior to sonication. Ultrasound was used to assist nitric acid in extracting heavy metals from sludge by varying sonication time from 0 to 20 min. The treated sludge samples were immediately centrifuged in polypropylene centrifuge tubes at 5000 rpm for 30 min at 25 °C (Universal 32 R centrifuge, Hettich, Germany). The supernatant was removed, acidified to pH 1 and stored at 4 °C for analysis of soluble heavy metals. The total heavy metal contents of sewage sludge were also determined by digestion with concentrated nitric and perchloric acid, as described by Walker et al. [16]. The removal efficiency of heavy metal was defined as the heavy metal content of the supernatant divided by the total metal content of the sewage sludge. The pH and oxidation reduction potential (ORP) of sludge samples were measured before and after sonication.

The heating effect during ultrasonication is inevitable and must be taken into account in the design of treatment processes [17]. As reported in the literature [3], a rise in sludge temperature can cause significant heavy metal release. In our work, the change in sludge temperature during ultrasonication was observed and identified to be insignificant [15]. Therefore, no efforts were made to control sludge temperature. Each treatment was performed in triplicate, and average values and standard deviations were obtained.

3.2. Analytical methods

Heavy metals were determined according to standard methods [18] by flame atomic absorption spectrometry (Z-2000, Hitachi).

4. Results and discussion

4.1. Effect of sonication time

Among the five kinds of heavy metals evaluated, Cu, Zn, and Pb exceeded Chinese legal values (Table 1). Thus, only these three heavy metals were investigated. Fig. 1 presents the soluble heavy metal contents of the sludge extracted by 0.065 M nitric acid assisted by ultrasound. The heavy metal contents in the supernatant increased with increasing sonication time whether or not the sludge was extracted by 0.065 M nitric acid. For untreated sludge, the increases were low at less than 5 min and became more rapid with increases in sonication time. The soluble Cu, Zn, and Pb contents increased from 0.4018, 0, 5.125 mg/kg initially to 6.633, 25.63, 12.48 mg/kg, respectively, at 20 min. For the sludge extracted by 0.065 M nitric acid, the soluble Cu, Zn, and Pb contents increased from 0.4018, 445.2, 412.9 mg/kg initially to 10.86, 511.6, 511.6 mg/kg, respectively, at 20 min. Thus, extended ultrasound exposure facilitated the release of heavy metals from sludge. Nevertheless, the extraction efficiency was low for only 20 min of sonication time, while the addition of nitric acid significantly improved the extraction efficiency of heavy metals, except for Cu (Table 2). It is clear that ultrasound alone is not an effective method for extracting heavy metals from sludge. Of course, the extension of sonication time may facilitate to extract more heavy metals from sludge, but it brought about negative effects such as higher energy consumption and stronger break-up of sludge floc structures that caused more difficulty in dewaterability [19].

The extraction efficiency was improved when ultrasound was used to assist nitric acid in extracting heavy metals. When 20 min ultrasound was applied to the sludge extracted by 0.065 M nitric

Table 2
Effect of sonication time on extraction efficiency of heavy metals from the sludge extracted by nitric acid and the changes in sludge pH and ORP.

Sonication time (min)	The initial sludge					The sludge extracted by 0.065 M nitric acid assisted by ultrasound				
	pH	ORP (mV)	Cu (%)	Zn (%)	Pb (%)	pH	ORP (mV)	Cu (%)	Zn (%)	Pb (%)
0	6.65	27.5	0.1	0	0.8	1.57	330.5	0.1	35.4	55.0
1	6.65	27.0	0.1	0	0.7	1.56	328.0	0.2	35.4	59.2
2	6.64	27.5	0.5	0	0.7	1.53	329.0	0.1	36.1	62.7
5	6.65	28.0	0.5	0.2	0.9	1.51	329.0	0.3	38.3	63.1
10	6.63	28.5	1.2	1.2	1.1	1.49	330.5	1.2	40.5	64.8
20	6.62	30.5	2.3	2.0	1.7	1.51	331.5	3.8	40.7	68.2