Effect of Aeration and Acidification on Heavy Metal Solubilization of Sewage Sludge

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ABSTRACT

The effect of aeration and acidification on heavy metal solubilization was studied. Results obtained using the following experimental protocols: (i) aeration only, (ii) aeration before acidification, (iii) aeration after acidification, (iv) simultaneous aeration and acidification, and (v) acidification only for 24 hrs, showed Cu and to a lower extent Mn as the highest metals extracted; Cu (0.8691 mg/l) when aeration was applied before acidification and Mn (0.6521 mg/l) when aeration was applied after acidification. When aeration was applied without acidification, Cu extraction efficiency dropped (0.6019 mg/l). Ni and Pb gave results indicating that the protocol, when aeration was applied after acidification Ni (0.2828 mg/l) and Pb (0.3995 mg/l), was a better extraction process than when simultaneous aeration and acidification was used Ni (0.1096 mg/l) and Pb (0.2536 mg/l). The extraction yield of Cd obtained from all the situations studied also indicated that Cd was the least metal extracted and specifically, the least metal extracted using the aeration before acidification protocol, Cd (0.0236 mg/l).

INTRODUCTION

Heavy metal (HM) concentration in sewage sludge varies from site to site depending on the contribution of domestic and industrial input into the sewerage system. HM are so tightly incorporated or absorbed in minerals and organic solids that only under extreme conditions would chemical leaching be achieved for satisfactory solubilization of these metals. These conditions include; chemical acidification, pH, chemical oxidation, and aeration. HM must be released into the liquid phase of sludge particles if it has to be removed. This liquid (leachate) containing the solubilized HM is thus separated from the sludge particles, precipitated and physical separation techniques such as centrifugation is applied to remove the HM. Extraction yield of metals is very sensitive to type of acid used. To achieve the best conditions for HM solubilization, both aeration and acidification are applied in mobilization of metals in the sludge. Mobility and bioavailability of metals depend on their chemical form (Loska and Wiechuła 2000). Thus, it is important to determine metal speciation while evaluating the amounts of metals leached under changing environmental conditions.

Aeration of sewage sludge

Aeration has been reported to cause an increase in the amount of copper released from organically bound forms (labile organic material) and a decrease in the organic-sulphide fraction (stable organic, humic and fulvic acid) (Gerringa 1991). Conversely, Loska and Wiechuła (2000) showed that aeration of above-sediment water caused considerable decrease in sulphide forms of copper at pH 2–5, while at the same time, there was a slight increase in the adsorbed form of copper in bottom-sediment water and organically bound form of bottom-sediment water at the above pH levels. Enhanced stabilization of anaerobically digested sludge can lead to decrease in the organic content of the sludge by implementing a post-aeration treatment after anaerobic digestion. Investigation showed that during digesting sludge, post-aeration anoxic phases for denitrification are needed to provide stable process conditions. Using this approach, the pH value is kept in a more favorable range for micro-organisms and additional inhibition of the biological process due to nitrite accumulation can be avoided. By optimizing the aeration/pause ratio, considerable amount of total nitrogen in digested sludge can be removed and this significantly improves nitrogen removal efficiency at the wastewater treatment plant (Parravicini *et al*. 2008). Besides the removal of HM from sludge, aeration and composting have also been tested successfully in the removal of bis-2-diethylhexyl phthalate (DEHP) from municipal sewage sludge with two dewatered sludge; raw sludge and anaerobically digested sludge. Results from the study indicated that composting removed about 58% DEHP from raw sludge and 34% DEHP from anaerobically digested sludge after 28 days stabilization in rotary drum, while aeration at 20°C removed DEHP from raw sludge and 62% DEHP from anaerobically digested sludge during the same period of days. The study concluded that both composting and aeration have the potential to reduce DEHP typically in sewage sludge to levels acceptable for agricultural use (Sanna *et al*. 2003). Thermophilic aerobic digestion (TAD) is a possible alternative for rapid sludge degradation in producing biosolids. Aeration rate and detention time are two important parameters influencing TAD processes due to rapid growing of thermophilic bacteria population, limited solubility of oxygen at high temperatures and the need to avoid cooling of the TAD process. Investigation on the effects of aeration rate and detention time on thermophilic aerobic digestion of mixed sludge and its dewaterability demonstrated that increasing the aeration rate decreases the required detention time and affect TAD by reducing vector attraction. But when oxidation-reduction potential (ORP) values were changed from negative to positive values and pH values were also increased from around neutral to slightly basic, there was an increase in the detention times, hence TAD dewaterability of mixed sewage sludge pro-

Research Note

duced biosolids with higher specific resistance to filtration (lower dewaterability), given aerated thermophically digested sludge with good settling behavior and good air drying on sand bed (Attar *et al.* 2005). These authors also conceded that the current knowledge and understanding of dewatering TAD aerated biosolids are still limited and incomplete. Changes of aerated sludge composition have been reported to reflect specified infrared spectroscopic patterns. In a study to demonstrate the effect of sludge treatment and additional aerobic post-stabilization revealed by infrared spectroscopic and multivariate data analysis, Smidta and Parravicini (2009) indicated that when anaerobically digested sludge was subjected to aeration in lab-scale reactors in order to determine if post-aeration after anaerobic digestion provides enhanced organic matter degradation and stabilization, spectra data evaluated by means of multivariate statistics and visualized by principal component analysis gave discriminate analysis that distinguishes additionally aerated sludge from all the other degradation stages of sludge because of changes in the spectral pattern by increasing stabilization.

Acid solubilization of sewage sludge

When acids are added to sludge, the HM present in the sludge dissolves and exist in solution. This is a proton exchange process from the acid through the solubilization of HM in sludge. After extraction, HM are removed to prevent environmental impact associated with the discharge of extracting fluid to the environment. Removal of the HM is accomplished by physical separation steps (Babel and Dacera 2006). Optimum conditions of HM removal from sludge can be achieved through variations of concentration of acids, temperature, and contact time (Ukiwe and Oguzie 2008). Stylianou *et al.* (2007) reported in their study on the "effect of acid treatment on the removal of heavy metals from sewage sludge," that the optimum combination of extraction was achieved when a ratio of 1:5 of sludge quantity (g) per volume of acid (ml) was applied at a contact time of 30 min at 80°C. These experimental conditions resulted in the highest HM removal efficiency of Ni, Cu, Cr, Pb, and Zn. The effect of nitric acid concentration and sonication time on the removal efficiencies of HM from sludge has also been investigated. Result obtained indicated that when nitric acid concentrations were varied from 0 to 0.65 M and sonication time also varied from 0 to 20 min, the removal efficiencies of Cu, Zn, and Pb increased with increasing nitric acid concentration and sonication time. The study also noted that nitric acid concentration of 0.325 M and sonication time of 20 min resulted in maximal HM removal efficiencies. Additionally, the study also revealed that Cu was not significantly removed regardless of the nitric acid concentration and sonication time (Deng *et al.* 2009). Acid thermal hydrolysis, alkaline thermal hydrolysis, and Fenton's peroxidation are waste-activated sludge processes used as key technologies to treat wastewaters, thus ensuring a minimum residual impact on the environment when wastewaters are applied on the environment for soil improvement in agricultural use. Acid thermal hydrolysis reduces the HM content in filter cake except for Cu, Hg, and Pb, while alkaline thermal hydrolysis releases Cu, Pb, and Cr. It was shown that Fenton's peroxidation transfers Cd, Cu, and Ni from the filter cake into the filtrate. Following these processes, land application of the residual cake was thus reconsidered (Dewil *et al.* 2006). HM solubilization efficiencies have been increased with the use of chelates such as EDTA (ethylenediamine tetra acetic acid), EDDS (ethylenediamine disuccinic trisodium salt), and NTA (nitrilotriacetic acid). It has been observed that EDTA extracted about 50% Cr, Pb, and Zn from sludge at pH 4.5 (Van and Vandecasteele 2001). EDDS has also been used appreciably than other chelating agents due to its greater rate of degradation and its strong chelating characteristic. Nevertheless, its biodegradation rate varies largely depending upon the examined conditions (Evangelou *et al.* 2007).

Hauser *et al.* (2007) reported that EDDS has been effective than EDTA in extracting metals, specifically, calcium. Interaction experiments have demonstrated that EDTA and NTA are more efficient than malate and citrate in solubilizing metals with minimum differences in extraction efficiencies between EDTA and NTA (Peñalosa *et al.* 2007).

The aim of the present research is to determine the effect of aeration and acidification on HM solubilization of domestic sewage sludge using hydrochloric acid for digestion. Hydrochloric acid has been found effective in metals solubilization of sludge (Naoum *et al.* 2001).

MATERIALS AND METHODS

The sewage sample used in this research was obtained from the septic tank of the male ward of the Federal Medical Centre, Owerri, Nigeria. The tank has a capacity of about 800 m³/day. A 50 L plastic container previously washed and rinsed with deionised water was used to collect the sewage sample from the tank and transported to the chemistry laboratory of the Federal University of Technology, Owerri, Nigeria. The plastic container was allowed to stand for 24 hrs to allow solid particles and debris to settle. From this stock solution samples were continuously drawn. Firstly, a quantity of sample containing 2 L of sewage was measured into a 2 L beaker previously washed and rinsed with deionsed water. About 800 ml of sewage sample was measured from the 2 L sample into a 1000 ml beaker and centrifuge (Micro Centrifuge Model 5415C) for 2 hrs at 200 rpm at 28°C. The resultant solution was filtered through Whatman No. 42 filter papers into a 1000 ml beaker and labeled "sludge filtrate". This was used accordingly in the following experimental procedures using five protocols:

Aeration only

About 30 ml of the filtrate was measured into a 100 ml conical flask. The flask was connected to a potable electronic pump using rubber hose previously washed and rinsed with deionised water. The mixture was thus aerated for 24 hrs. The resultant liquid was further digested at 80°C for 1 hr with intermittent addition of deionised water to prevent drying up of the mixture. The mixture was thus cooled and filtered through Whatman No. 42 filter papers. About 10 ml of this filtrate was measured into a 10 ml plastic sample holder bottle previously washed and rinsed with deionsed water. This 10 ml filtrate was used for analysis with Atomic Absorption Spectrophotometer (Model SOLAAR V10) for the elements Cd, Ni, Cu, Mn, and Pb. Three repetitions were made and the mean concentration (mg/l) of HM was obtained by method described by Ukiwe and Oguzie (2008).

Aeration before acidification

About 30 ml of the sludge filtrate was measured in a 100 ml conical flask and the filtrate aerated for 24 hrs as in above for "Aeration only", and the addition of 10 ml of a 30% (v/v) HCl solution to the aerated sludge filtrate followed after aeration and the mixture stirred thoroughly and digested for 1 hr at 80°C with intermittent addition of deionised water to prevent drying up of the mixture. The mixture was thus cooled and filtered through Whatman No. 42 filter papers. About 10 ml of this filtrate was measured into a 10 ml plastic sample holder bottle previously washed and rinsed with deionsed water. This 10 ml filtrate was used for analysis with Atomic Absorption Spectrophotometer (Model SOLAAR V10) for the elements Cd, Mn, Pb, Ni, and Cu. Three repetitions were made and the mean concentration (mg/l) of HM was obtained by method described as in above for "Aeration only".

Aeration after acidification

To 30 ml of the sludge filtrate measured into a 100 ml conical flask was added 10 ml of a 30% (v/v) HCl solution and the flask sealed and kept for 24 hrs. After this period, the mixture was aerated as in above for "Aeration only", for 24 hrs and then digested for 1 hr at 80°C with intermittent addition of deionised water to prevent drying up of the mixture. The mixture was thus

Table 1 Concentration of heavy metals in sewage sludge.

Experimental protocols	Aeration only[i]		Aeration before acidification[ii]		Aeration after acidification[iii]		Simultaneous aeration and acidification[iv]		Acidification only[v]	
Heavy metals	Mean (mg/l) ± SD × 10^{-1}	SEM x 10^{-2}	Mean (mg/l) ± SD × 10^{-1}	SEM x 10^{-2}	Mean (mg/l) ± SD × 10^{-1}	SEM x 10^{-2}	Mean (mg/l) ± SD × 10^{-1}	SEM x 10^{-2}	Mean (mg/l) ± SD × 10^{-1}	SEM x 10^{-2}
Cd	0.0354 ± 2.8	0.1	0.0236 ± 1.2	6.9	0.0322 ± 1.3	7.5	0.0369 ± 2.1	0.1	0.0284 ± 0.1	0.5
Ni	0.3511 ± 0.4	2.3	0.1513 ± 3.1	0.1	0.2828 ± 1.6	9.2	0.1096 ± 1.0	5.7	0.1947 ± 3.6	0.2
Cu	0.6019 ± 0.8	4.6	0.8691 ± 0.5	2.8	0.6120 ± 1.0	5.7	0.6476 ± 0.6	3.4	0.6576 ± 0.2	1.1
Mn	0.3722 ± 0.3	1.7	0.4260 ± 0.2	1.1	0.6521 ± 0.5	2.8	0.4820 ± 0.3	1.7	0.6207 ± 0.5	2.8
Pb	0.3188 ± 3.3	0.1	0.3190 ± 2.2	0.1	0.3995 ± 2.8	0.1	0.2536 ± 8.4	0.4	0.1976 ± 3.2	0.1

SEM: Standard Error of the mean; t-test between protocols; (i) and (ii) = 0.13; (ii) and (iii) = 0.19; (iii) and (iv) = 0.55; (iv) and (v) = 0.19

cooled and filtered through Whatman No. 42 filter papers. About 10 ml of this filtrate was measured into a 10 ml plastic sample holder bottle previously washed and rinsed with deionsed water. This 10 ml filtrate was used for analysis with Atomic Absorption Spectrophotometer (Model SOLAAR V10) for the elements Cd, Mn, Pb, Ni, and Cu. Three repetitions were made and the mean concentration (mg/l) of HM was obtained by method described as in above for "Aeration only".

Simultaneous aeration and acidification

To 30 ml of the sludge filtrate measured into a 100 ml conical flask was added. 10 ml of a 30% (v/v) HCl solution and the mixture aerated for 24 hrs as in above for "Aeration only".   The mixture was further digested for 1 hr at 80°C with intermittent addition of deionised water to prevent drying up of the mixture. The resultant mixture was then cooled and filtered through Whatman No. 42 filter papers. About 10 ml of this filtrate was measured into a 10 ml plastic sample holder bottle previously washed and rinsed with deionised water. This 10 ml filtrate was used for analysis with Atomic Absorption Spectrophotometer (Model SOLAAR V10) for the elements Cd, Mn, Pb, Ni, and Cu. Three repetitions were made and the mean concentration (mg/l) of HM was obtained by method described as in above for "Aeration only".

Acidification only

To 30 ml of the sludge filtrate measured into a 100 ml conical flask was added. 10 ml of a 30% (v/v) HCl solution and the mixture was thoroughly mixed and the flask sealed and kept standing for 24 hrs. After this period the mixture was digested for 1 hr at 80°C with intermittent addition of deionised water to prevent drying up of the mixture. The resultant mixture was thus cooled and filtered through Whatman No. 42 filter papers. About 10 ml of this filtrate was measured into a 10 ml plastic sample holder bottle previously washed and rinsed with deionised water. This 10 ml filtrate was used for analysis with Atomic Absorption Spectrophotometer (Model SOLAAR V10) for the elements Cd, Mn, Pb, Ni, and Cu. Three repetitions were made and the mean concentration (mg/l) of HM was obtained by method described as in above for "Aeration only".

Statistical method

Data was reported as arithmetic mean, standard deviation and standard error of the mean. The standard error of the difference between mean HM concentrations (mg/l) of the various experimental procedures was used to measure difference in HM concentration between experimental protocols. The generalized t-test was also used to estimate if there was significance in HM concentration between experimental protocols.

RESULTS AND DISCUSSION

Table 1 shows the concentration (mg/l) of the effect of aeration and acidification in different situations on HM extraction of domestic sewage sludge. Chemical acidification with aeration has been shown to result in the highest extraction percentages of most HM (Marchioretto *et al.* 2002). In the study, the extraction yield was shown to be very sensitive to type of acid used and HCl was reported superior to other acids such as HNO_3 and H_3PO_4. **Table 1** reveals that

Cu and to a lower extent Mn are the highest metals extracted; Cu (0.8691 mg/l) when aeration was applied before acidification and Mn (0.6521 mg/l) when aeration was applied after acidification. Aeration produces an increase in the concentration of Cu easily release from organic bound compounds (Loska and Wiechuła 2000). When aeration was applied without acidification, Cu extraction efficiency dropped (0.6019 mg/l). This highlights the fact that Cu exist as organic complex in sludge and only in prolonged exposure to air under extreme acid conditions would Cu be extracted effectively from sludge. The situation were only acidification was used for metal extraction, substantial amounts of Cu (0.6576 mg/l) was also extracted. This was due to the extreme acidic condition applied during extraction. It should be noted that copper extraction from liquid sludge require aeration to be competitive to the extraction using dried sludge sample. The reason is that the metal is more easily solubilized from dried sludge samples than the liquid sludge sample. Ruud *et al.* (1988), suggested that during the drying process the organic matter is easily oxidized leading to mineralization. Hence, the particle size of the minerals are reduced and homogenized during crushing which favors Cu extraction since the metal predominates in the organic fraction of the sludge.

Results obtained for Ni and Pb indicated that the protocol when aeration was applied after acidification Ni (0.2828 mg/l) and Pb (0.3995 mg/l) was a better extraction process than when simultaneous aeration and acidification was used Ni (0.1096 mg/l) and Pb (0.2536 mg/l). The extraction yield of Cd obtained from all the situations studied also indicated that Cd was the least metal extracted and specifically, the least metal extracted using the aeration before acidification protocol, Cd (0.0236 mg/l).

The standard error of the mean concentration (mg/l) of HM using aeration only and aeration before acidification is 0.089 and 0.144. The standard error of the difference between mean concentration of HM using aeration only and aeration before acidification is 0.169. The generalized t-test was used to test the significance difference between the means of sets observation between HM concentration using aeration only and aeration before acidification. The generalized t-test between these sets observation is shown in the table. Testing this value at 8 degree of freedom, $P < 0.01$, indicating no considerable difference in extraction profile of HM between protocols.

Recent studies have revealed that organic acids and oxalic acids appear to be more promising as chemical extracting agents for the removal of HM from contaminated sludge because they are biodegradable and can attain a higher metal extraction efficiency at mildly acidic pH compared to other extracting agents (Dacera and Babel 2006). Nevertheless, the sufficient removal of HM from sludge still remains a challenge. It has been reported that phosphoric acid in combination with hydrogen peroxide show good removal rates of HM comparable to HCl (Yoshizak and Tomida 2000). In the process, the study noted, the phosphoric acid used is almost recovered for reuse. Options of research using combination of organic and inorganic acids together with aeration is advocated by the present study as further research for optimum solubilization efficiency of HM from sewage sludge.

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