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Effect of pH and Acid on Heavy Metal Solubilization of Domestic Sewage Sludge

Luke N. Ukiwe* • Emeka E. Oguzie

Department of Chemistry, Federal University of Technology, P.M.B 1526, Owerri, Nigeria

Corresponding author: * luggil2002@yahoo.com

ABSTRACT

Heavy metal removal from domestic sewage was solubilized using HCl, HNO_3, and H_2SO_4 at pH 1.0, 2.0, 3.0, and 4.0. Results of analysis of digested samples analyzed with Atomic Absorption Spectrophotometer showed that selenium (1030.9159, 1043.3573, 1097.0605, 1097.9538 mg/l) was the highest metal solubilized at pH 1.0, 2.0, 3.0 and 4.0, respectively while nickel (0.0000, 0.3560, 0.0000, 0.2002 mg/l) was the least solubilized metal at the same pH levels using H_2SO_4, which was also observed to be the most suitable acid for solubilization of metals. In the absence of complexing ligands as in the male sewage sample, solubilization of metal was highest at low pH levels.

Keywords: aerobic, anaerobic, acidification, Atomic Absorption Spectrophotometry, bioleaching, chemical leaching and oxidation, digestion, effluents extraction, municipal, wastewater

INTRODUCTION

Sewage is correctly the subset of wastewater that is contaminated with faces or urine (Tchobanoglous *et al.* 2003). Sewage sludge (SS) is the residual semi-solid that is contaminated with feaces or urine left from domestic, municipal, or industrial wastewater treatment or water treatment processes (Massoud *et al.* 2005). Sludge is the inevitable by-product that by definition and intention, consist of every waste material a given wastewater treatment plant is capable of removing, or is incidentally removed, from the sewage in the process of treating the wastewater (Orlando 2004). Water treatment sludge is the accumulated solids or precipitate that has been removed from a sedimentation vessel, in a water treatment plant. The accumulated solids in water treatment sludge result from chemical coagulation, flocculation, and sedimentation of raw water.

Sewage treatment or domestic wastewater treatment is the process of removing contaminants from wastewater, both runoffs (effluents) domestic (Marchioretto *et al.* 2002). There are two types of water treatment sludges:

(a) Coagulation sludge; these are sludges with a gelatinous appearance containing high concentrations of aluminium or iron salts with a mixture of organic and inorganic materials and hydroxide precipitates.
(b) Softening sludge; these sludges contain mainly calcium carbonate and magnesium hydroxide precipitates with little organic and inorganic substances.

Both types of sludges dewater, but dewatering of coagulation sludges is very difficult.

Increase urbanization and industrialization has culminated in a dramatic growth in the volume of municipal sludge. The sludge contains substances that enter in human metabolism. Hence, the amount of sewage humans generate is a measure of the level of their civilization and human migration from local to urban communities.

Characteristics of domestic sewage

The sewage discharged from dwellings mirror the existing variety forms of the inhabitants. These include single and multi family homes, condominiums, apartment houses, cottages and resort centers etc. The characteristics of the sewage produced in these areas can be influenced by several factors (Robert *et. al* 2004; Ishiodu 2006), which include:

(1) Primary influences; these are plumbing fixtures and appliances present in the households as well as their frequency of use.
(2) Secondary influences; these are characteristics associated with the residing households in terms of the number of resident family members, age levels, mobility and the socioeconomic status of the family.
(3) Tertiary influences; these are influences due to seasonal or yearly occupancy, geographic location, and extent of civilization of the inhabitants.

The effective management of any sludge flow requires a reasonably accurate knowledge of its characteristics. Three processes have been studied for the sequential chemical extraction (SCE) and characterization of anaerobically digested sludge (Tessier *et al*. 1979; Slims and Kline 1991). Although SCE is still an imperfect method referring to specificity and selectivity, it provides valuable information regarding the variety of extraction of certain metal forms with several conditions of temperature, pH, and type of chemical reactions. Effect of SS addition on heavy metal concentrations in agricultural soils studied by Nagar *et al.* (2004) indicated that the soil samples characterized, for texture, pH, salinity, cation exchange, organic matter and total and extractable concentrations of Ca, Mg, Fe, Al, and P, and evaluated for the effect of these parameters on long-term application of sewage sludge on the geochemical fate of heavy metals in agricultural soils, indicated that enhanced soil metal contents may result in reduced plant growth. The physicochemical and mineralogical characterization of SS and clay were studied in order to identify the major technological constraints and to define the sludge pretreatment requirements. Result proved that bricks with a sludge content of up to 40wt % were capable of meeting the relevant technical standards while bricks with more than 30wt % sludge addition were not recommended for use since they are brittle and easily broken even when handled gently (Abdul *et al.* 2004).

Received: 23 November, 2008. Accepted: 18 December, 2008.

Original Research Paper

Composition of sewage sludge

Sewage sludge (SS) is largely constituted of those substances responsible for the offensive nature of untreated sewage. These include non-toxic organic carbon compounds, heavy metals such as Zn, Pb, Cu, Cr, Ni, Cd, Hg, As, dioxins, pesticides, linear alkyl-sulphonates, pathogens and other microbiological pollutants. Others include inorganic compounds such as silicates, aluminates, calcium and magnesium containing compounds, water, varying from a few percent to more than 95%. The effects of the use of tannery sludge as soil amendment material to investigate the composition of SS was studied. Results show that millet crop exhibited higher concentration of Co, Pb, Zn, Cr and Cu than sorghum, indicating that with repeated applications of tannery waste as soil amendments material, millet crops could accumulate heavy metals to toxic levels (Tudunwada *et al.* 2007). Warri River, South Western, Nigeria, has served as a depository site for effluents, wastewaters and other pollutants from industrial and municipal wastes in Warri and its environs. Results obtained from analysis showed that wastewater contained Cd, Cr, Co, Ni, Zn, Pb, Mn, Fe, C, $CaCO_3$, organic matter and organic nitrogen (Okuo and Iyasele 2004). Pollution studies on the Qua-Iboe River estuary Ibeno, Nigeria, which is a discharge point for effluents from Exxon-Mobil waste treatment plant revealed the presence of Ni, Cr, Cd, Fe, Pb, Cu, Zn and Mn. This study showed that the last three metals (Cu, Zn, Mn) were present within WHO acceptable limits though the other metals were present in levels deleterious to human health (Oze *et al.* 2007). Activated carbons developed from organic SS have been used to remove Hg (11) from aqueous solution. Chemical activation (using H_2SO_4, H_2SO_4, H_3PO_4) was used to improve the quality of the activated carbons. Results revealed that $ZnCl_2$ activated carbon had the highest capability for Hg (11) adsorption (Zhanga *et al.* 2005).

Sewage sludge processing

There are numerous processes that can be used to clean up waste water depending on the type and extent of contamination. The most important aerobic treatment system is the activated sludge process. Activated system for wastewater treatment produce large amounts of sludge. Normally, this sludge is stabilized by anaerobic digestion and further dewatered and disposed in landfills. Anaerobic processes are also widely applied in the treatment of industrial and biological sludge. Anaerobic digestion is a bacterial process that is carried out in the absence of oxygen. One major feature of anaerobic digestion is the production of biogas, which can be used in generators for electricity production. Anaerobic co-digestion of food waste and SS for hydrogen production performed under various volatile solids concentrations and mixing ratios of two substrates revealed higher hydrogen production potential of food waste than SS. though hydrogen production potential increased (Kim *et al.* 2004). A study conducted on a bioleaching process to remove Cr from tannery sludge with Acidithiobacilli bacteria and comparing the buffering capacity of tannery sludge and municipal SS effects on initial sulphuric acid addition of recycled rate of acidified bioleached sludge on subsequent bioleaching reaction revealed that there was an increase in the rates of pH reduction and Cr solubilization with increase initial sulphuric acid addition (Zhou *et al.* 2005). The transformation of heavy metal forms during SS bioleaching with elemental sulphur as substrate was investigated. Cu, Pb and Zn were turned to exchangeable forms during bioleaching and was solubilized mostly by a direct mechanism. After bioleaching the SS could be applied to land more safely because the heavy metals mainly existed in stable forms (Chena *et al.* 2005).

Worldwide policy on sewage sludge management

In many developing countries the bulk of domestic and industrial wastewater is discharged without any treatment or after primary treatment only. In Venezuela, about 97% of the country's sewage is discharged raw into the environment while in Brazil, the number of wastewater treatment plants are increasing, hence, the sludge production is growing (Santos and Tsutiya 1997). Marchioretto *et al.* (2002) showed that in Vietnam, large volumes of sludge generated in municipal wastewater treatment plants from big cities such as Ho Chi Minh and main economic areas of the South are, so far, disposed to open field. This results in serious problems due to the shortage of disposal capacity and leaching of heavy metals to underground waters, surface waters and even soils. In the USA, regulatory influences on both federal and state levels have encouraged the beneficial use of SS while research and technology in the field have helped alleviate public concern regarding the human health and environmental impacts of sludge (US EPA 1999). A relatively developed Middle Eastern country such as lran, Tehran's untreated sewage is being injected into the city's groundwater (Massoud and Ahmed 2005). Most of sub-Saharan Africa is without wastewater treatment. Wastewater treatment utilities in Nigeria are chronically underfunded due to government's lack of interest in providing basic amenities for the masses. Hence, operation and maintenance of many wastewater treatment plants are poor. Federal government agencies such as the National Environmental Protection Agency (NEPA) have laws guiding the generation, treatment and disposal of sludge. Due to the lack of political will to enforce these laws, Nigerians view waste management as open dump sites, ocean and river dumping of sludge, landfill incineration but very little thoughts is given to resource recovery, recycling, composting and reuse (Ishiodu 2006).

Education and communication play an important function in increasing public acceptance towards sludge reuse. Standardized techniques for sludge sampling and analysis need to be established to ease the enforcement of local and international regulations. Adequate monitoring and enforcement policies are important for future management programs (Jimenez *et al.* 2003).

Heavy metal removal from sewage sludge

Heavy metals can be removed from SS by chemical leaching with inorganic and organic acids or by bioleaching. Heavy metals concentrations in SS vary from one site to another, depending on the contribution of domestic and Industrial input into the sewerage system. Heavy metals are usually so tightly bound or incorporated in organic solids and minerals that physical separation of the constituents becomes extremely difficult.

Some benefits of heavy metals removal from SS include:

(i) Sludge can be disposed to landfills with lower risk of heavy metals leaching to surface and groundwater or uptake by plants.
(ii) Sludge can be used to improve the soil.
(iii) Sludge can be applied with lower risk as energy source in co-incineration.
(iv) Sludge that has been dewatered can be applied with lower risk as raw material for cement and bricks manufacture.

There are three approaches available to reduce the concentration of heavy metals in SS (Marchiorette *et al.* 2002). Firstly; there should be control of industrial sources and other point sources where wastewaters discharge into sewer system. Secondly, control of diffuse sources using lead-free gasoline and thirdly, by the extractive removal of heavy metals from SS. The latter process makes use of extreme acidic conditions for sufficient solubilization and release of metals to the liquid medium. To solubilized heavy metals from sewage sludge into the sludge liquid, an acidification process must be applied. The liquid containing the solubilized metals could be separated by physical separation process which includes centrifugation. Chemical precipitation further converts the soluble metallic forms which are thus removed from the liquid by sedimentation, flotation or membrane filtration.

The heavy metals precipitation step involves pretreatments (aeration and centrifugation) and the addition of chemical substances to adjust the pH of the solution. It has been shown that pretreatment conditions are efficient to solubilized mainly lead and zinc. Copper and chromium are difficult to solubilize through pretreatment conditions. This could be due to the chemical distribution of the metals in the sludge since copper and chromium are entrapped in organic solids effectively reducing their ability to be solubilized (Hayes and Theis 1978). To promote the solubilization of heavy metals it is necessary to decrease the pH of the sludge to about 1–2. At this pH level, formation of soluble metal complexes and oxidizing insoluble reduced metal forms to soluble forms are favored. Several acids have been tested to solubilized sludge but the most common are inorganic acids such as hydrochloric acid (Fytianos *et al.* 1998), nitric acid (Naoum *et al.* 2001), sulphuric acid (Cheung 1988), and phosphoric acid (Yoshizaki and Tomida 2000), also organic acids such as citric and oxalic acids (Veeken and Hamelers 1999) have also been used. Chelates such as EDTA (Ethylenediaminetetracetic acid), (Perez-Cid *et al.* 2002) and NTA (nitrilotriacetic acid) (Samanidou and Fytianos 1990) are also used. High heavy metals solubilization efficiencies have been obtained when the appropriate conditions of the inorganic and organic acids are applied. These conditions include; pH, redox potential, and reaction time. Selective removal of heavy metal ions by ion-exchange is a process were undesirable ions are replaced by others which do not contribute to contamination of the environment (Browski *et al.* 2004). Electrokinetic treatment (EK) can be applied to remove heavy metals from sludge. EK efficiency is increased when the sludge is acidified (pH 2.7) thus the mobility of heavy metals in sludge is significantly increased (Wang *et al.* 2005). Water hyacinth (*Eichhornia crassipes*) is extremely tolerant towards toxic metals and has a high capacity of uptaking heavy metals from SS in a phytoremediation process (Abou-Shanab 2007)

The objective of the present study was to assess the effect of acid and pH on the removal ratio of heavy metals from domestic SS.

MATERIALS AND METHODS

The sewage samples used in this research was obtained from the septic tank of a male and female hostel of the Federal University of Technology, Owerri, Nigeria. The tank has a capacity of approximately 900 m^3/day in each hostel. Two 25 L containers were used to collect the sewage sample from the male and female hostel tanks. These containers were sealed and allowed to stand for 30 min so that solid particles could settle. From these stock solutions, a quantity of sample from each hostel containing 1 L of sewage was fetched with two clean 2 L containers previously washed and rinsed with deionized water. For optimum conditions for metals solubilization (Marchioretto *et al.* 2002), 1 L sewage sample each from the male and female hostels was measured into two separate 2 L conical flasks and subjected to aeration followed by continuous centrifugation (Micro Centrifuge Model 5415C) for 24 h at 150 rpm at 28°C. Starting with the male hostel sample, about 30 ml of the sludge sample was measured into a 50 ml beaker and further filtered through Whatman No. 42 filter papers. The resultant solution was poured into a 100 ml beaker where 10 ml of a 50% (v/v) H_2SO_4 was added and stirred. To 40 ml of this mixture in a 250 ml beaker a little amount of aqueous solution of a 1 M NaOH solution was added to adjust the pH to 4.0 using a pH meter (Model PHS 25). The solution was then thoroughly stirred and heated on a Bunsen burner for 30 mins at 80°C. The resultant solution was cooled to room temperature, filtered and 5 ml of this solution was measured into a clean 10 ml sample holder bottle which had been previously rinsed with deionised water. This solution was used for Atomic Absorption Spectrophotometry (AAS Model ALFA 4). The above procedure was repeated twice for H_2SO_4 at pH 4 for the male hostel sample and the absorbance (AAS) was performed 3 times for each of the three experiments. The three AAS absorbance readings were then averaged and the mean obtained. The three AAS mean absorbances of the three experiments were further averaged to get the final mean absorbance. Thus three treatments were sampled and the concentration (mg/l) of the metal ions in the sludge was determined by preparing concentration standards of Pb, Ni, Co, Se, and Hg ions respectively using appropriate amounts of their salts with deionised water. The absorbance of these concentrations were obtained at 217.0, 232.0, 240.7, 196.0, and 253.7 nm wavelengths for Pb, Ni, Co, Se, and Hg respectively, using 2.5–20, 2–8, 2.5–9, 45–185, and 73–290 absorption optimum working range for the above metals. The flame type used was Air Acetylene Oxidizing (AAO) for Co, Pb, and Hg respectively, while Air Acetylene Reducing (AAR) was used for Ni. Nitrous oxide/acetylene reducing was used for Se analysis. Plots of absorbance of standards of the metal ions against their concentrations were obtained. The concentration of the sample was derived by interpolating the final mean absorbance to the appropriate concentration on the graph. This procedure was repeated at pH 3.0, 2.0, and 1.0 using HCl and HNO_3 for the male sample and also repeated at pH 4.0, 3.0, 2.0, and 1.0 using H_2SO_4, HCl, and HNO_3 respectively for the female samples.

Data analysis

Data analysis were performed using statistical method. Data were reported as arithmetic mean and standard deviation. Analysis of variance (ANOVA) was employed to measure difference between mean levels of metals at various pH. The standard error of the difference between mean levels of metals at various pH and the generalized *t*- test were employed to estimate the significance of these values.

Table 1 Concentration [mean (mg/l)] of heavy metals of female sewage sample at pH 1.0.

Acids / Heavy metals	H_2SO_4		HCl		HNO_3	
	Mean (mg/l)	SD × 10^{-2}	Mean (mg/l)	SD × 10^{-2}	Mean (mg/l)	SD × 10^{-2}
Pb	0.0737	0.2	0.3373	1.0	0.2722	0.0
Ni	0.0000	0.0	0.0000	0.0	3.8919	1.2
Co	1.2507	0.3	0.5513	1.9	0.4260	0.0
Se	1067.6735	0.0	639.0538	0.0	1062.1586	0.0
Hg	32.8521	1.0	11.6109	0.2	16.4652	0.3

Table 2 Concentration [mean (mg/l)] of heavy metals of female sewage sample at pH 2.0.

Acids / Heavy metals	H_2SO_4		HCl		HNO_3	
	Mean (mg/l)	SD × 10^{-2}	Mean (mg/l)	SD × 10^{-2}	Mean (mg/l)	SD × 10^{-2}
Pb	0.5132	1.9	0.9163	0.0	0.3754	1.9
Ni	0.3745	1.9	3.8398	0.2	0.0000	0.0
Co	1.4418	0.3	0.2128	2.9	1.9545	0.2
Se	1049.6061	0.0	108.6835	0.0	995.5585	0.2
Hg	32.8521	9.9	36.9984	0.0	28.5211	0.0

RESULTS AND DISCUSSION

The results obtained from this study are given in **Tables 1**–**8**.

SS is an end product. It could be used as a material and source for nutrients in soil. A safe use of SS as a soil conditioner requires SS with low heavy metal content. Heavy metals sometimes found in SS may present environmental problems. The sludge application rate is governed by the cumulative metal loading of the soil. The levels of potentially toxic elements in the sludge are defined and compared to levels elsewhere in the context of the suitability of the sludge for agricultural use (Robert *et al.* 2004). Heavy metals in SS can be reduced by either source control of discharge to sewer systems or by removing the metals from the sludge. Heavy metals cannot be removed by a physical separation process without being previously solubilized. Chemical leaching with acids or complexing agents is an effective option to enhance metals solubilization (Tyagi *et al*. 1993).

Tables 1–**8** show the mean concentration (mg/l) of Pb, Ni, Co, Se, and Hg for H_2SO_4, HCl, and HNO_3 at pH 1.0, 2.0, 3.0, and 4.0 respectively for domestic SS samples. Se appears to be the most solubilized metal using H_2SO_4 (1134.1473 mg/l) at pH 4.0 in the female sample, while Ni is the least solubilized metal using H_2SO_4 (0.0000 mg/l) at pH 1.0 and pH 4.0 also in the female sample.

Samples were collected at the discharge point of the tank. Samples were collected at once (both male and female samples) this is with a view to avoid problems encountered with time and period during sampling.

Overall, for both male and female samples, Se was the most solubilized using H_2SO_4 at pH 1.0–4.0 using H_2SO_4 while Ni was the least solubilized metal at all pH levels using HCl. H_2SO_4 was the most effective acid for solubili-

Table 3 Concentration [mean (mg/l)] of heavy metals of female sewage sample at pH 3.0.

Acids	H_2SO_4		HCl		HNO_3	
Heavy metals	**Mean (mg/l)**	**SD × 10^{-2}**	**Mean (mg/l)**	**SD × 10^{-2}**	**Mean (mg/l)**	**SD × 10^{-2}**
Pb	0.3753	1.0	0.6439	0.0	0.1483	1.9
Ni	0.1873	7.3	2.0725	0.2	1.3783	0.4
Co	1.4367	0.3	0.5127	1.9	2.5793	0.2
Se	1006.2547	0.1	961.5624	0.0	887.3933	0.0
Hg	12.8521	0.7	42.1112	0.0	26.5136	0.0

Table 4 Concentration [mean (mg/l)] of heavy metals of female sewage sample at pH 4.0.

Acids	H_2SO_4		HCl		HNO_3	
Heavy metals	**Mean (mg/l)**	**SD × 10^{-2}**	**Mean (mg/l)**	**SD × 10^{-2}**	**Mean (mg/l)**	**SD × 10^{-2}**
Pb	0.3066	0.0	0.0867	0.0	0.5445	0.0
Ni	0.0000	0.0	0.3780	0.0	3.3637	1.0
Co	0.2501	2.0	1.3400	0.2	3.7124	0.2
Se	1134.1473	0.0	1101.0617	0.0	1070.8317	0.0
Hg	12.8521	0.7	24.8009	0.0	26.0215	0.0

Table 5 Concentration [mean (mg/l)] of heavy metals of male sewage sample at pH 1.0.

Acids	H_2SO_4		HCl		HNO_3	
Heavy metals	**Mean (mg/l)**	**SD × 10^{-2}**	**Mean (mg/l)**	**SD × 10^{-2}**	**Mean (mg/l)**	**SD × 10^{-2}**
Pb	0.1763	4.6	0.0000	0.0	0.3500	4.0
Ni	0.0000	0.0	0.0000	0.0	1.2453	0.0
Co	0.8890	0.0	0.4230	3.9	0.4838	1.7
Se	1030.9159	0.2	1033.1000	0.2	1034.7956	0.1
Hg	24.4705	0.0	46.8931	0.1	43.1744	0.0

Table 6 Concentration [mean (mg/l)] of heavy metals of male sewage sample at pH 2.0.

Acids	H_2SO_4		HCl		HNO_3	
Heavy metals	**Mean (mg/l)**	**SD × 10^{-2}**	**Mean (mg/l)**	**SD × 10^{-2}**	**Mean (mg/l)**	**SD × 10^{-2}**
Pb	0.3500	4.0	0.0285	0.0	0.1549	1.9
Ni	0.3560	0.0	0.0000	0.0	1.0333	1.0
Co	2.8064	9.8	0.1649	1.9	2.0160	0.2
Se	1043.3573	0.1	1033.5179	0.1	1037.2451	0.3
Hg	13.9863	0.2	14.0487	0.3	19.8076	0.2

Table 7 Concentration [mean (mg/l)] of heavy metals of male sewage sample at pH 3.0.

Acids	H_2SO_4		HCl		HNO_3	
Heavy metals	**Mean (mg/l)**	**SD × 10^{-2}**	**Mean (mg/l)**	**SD × 10^{-2}**	**Mean (mg/l)**	**SD × 10^{-2}**
Pb	0.2408	0.7	0.1550	0.0	0.1483	0.0
Ni	0.0000	0.0	0.0000	0.0	0.5277	0.0
Co	1.2938	0.0	1.1313	1.0	0.0017	0.0
Se	1097.0605	0.2	694.0158	0.2	1089.0787	0.0
Hg	17.4781	0.2	27.9711	0.2	24.8003	9.3

Table 8 Concentration [mean (mg/l)] of heavy metals of male sewage sample at pH 4.0.

Acids	H_2SO_4		HCl		HNO_3	
Heavy metals	**Mean (mg/l)**	**SD × 10^{-2}**	**Mean (mg/l)**	**SD × 10^{-2}**	**Mean (mg/l)**	**SD × 10^{-2}**
Pb	0.7601	5.5	0.1483	2.9	0.2722	2.8
Ni	0.2002	1.7	1.0473	0.2	0.4349	1.6
Co	11.6338	0.0	9.3215	0.0	0.4353	3.8
Se	1077.9538	0.3	418.9527	1.0	175.1041	0.0
Hg	10.9023	0.2	19.6501	0.4	12.8774	0.2

zation of metals followed by HNO_3, while HCl was the least effective acid for metal solubilization. A trend was observed in the amount of heavy metals extracted from the male SS. **Tables 1**–**4** show that extraction of metals is highest at pH 1.0 and decrease as pH increases. But an opposite trend is noticed with the female sludge samples (**Table 5**–**8**) were metals extraction increased as pH increases. A suggested explanation for this could be the presence of chelating ligand such as EDTA in the female sludge sample since most cosmetics substances used by the female students in the hostel were manufactured using this substance. Heavy metals are bound by ligands and exist as insoluble salts. Hence, solubilization of these bound metals is possible only at high pH levels.

The standard error of the mean for Pb for H_2SO_4, HCl, and HNO_3 (Pb was used to express the assertion that the distribution was normal in other heavy metals analyzed and the samples were taken at random) between pH 1.0–2.0, pH 2.0–3.0, and pH 3.0–4.0 for females was 0.0915, 0.1252, and 0.0831, respectively while that for males at same pH levels was 0.1305, 0.0401 and 0.0483 respectively. The generalized *t*-test was used to test the significance difference between the means of sets observation at the above pH ranges using the three types of acids. The generalized *t*-test between pH 1.0 – 2.0, 2.0 – 3.0, and 3.0 – 4.0 is 0.4, 0.07, and 1.09 respectively. Testing these values at df 6, these values show no significance at 5% confidence levels.

The solubilization yield of heavy metals is very sensitive to type of acid and pH of sludge. In one study, HCl was superior to HNO_3 and H_3PO_4 in extraction efficiency of Cu, Cr, Zn, and Pb when solubilization was conducted after chemical oxidation with peroxide (Marchioretto *et al*. 2002). Bioleaching process is also an economically attractive alternative for extracting metals from sludge. However, some metals such as Pb are adverse to this process. Pb cannot be solubilized with the bioleaching process but can be solubilized by acetic acid as Pb–acetate compound. Solubilization of metals is a difficult process which cannot be solely determined with pH–solubility data but with other factors such as redox potential of the system (Dusing *et al*. 1992). The examination of spatial and temporal patterns in heavy metals concentration in street dust in Bahrain showed that solubilizing the dust samples with HCl and HNO_3 (1:1), the levels of heavy metals extracted was in the pattern Pb > Zn > Ni > Cu > Cd. The high levels of Pb, Zn, and Cu obtained indicate high effiency of metal extraction is achieved with a combination of acids (Ismail *et al*. 1996). Another study aimed at understanding the concentration trends of heavy metals on soils due to vehicular emissions revealed that at soil pH of 5.09 to 8.57, concentration of heavy metals fell below normal ranges (Mohammed *et al.* 2005).

The solubilization of metals is a complex phenomenon that depends on many indicators in addition to sludge pH. However, sludge pH is considered the most critical of all these factors.

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