

Heavy metals released from sewage sludge of Basrah city, Iraq using chemical method

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Abstract – Samples of anaerobically digested sludge were obtained from the anaerobic unit of a waste water plant in Abo Al-Kaseeb (Basrah, Iraq) during 2012. The removal of heavy metals (Pb, Cu and Zn) were studied using sulphuric acid as a chelating agent by using A.A. Spectrophotometry. Metal removal was found to be depending on pH, solid concentration, specific types of metals and period of acidification. The rate of removal efficiency and solubilisation increased with time, low pH and low solid concentration. Limitation in solubilisation were existed, regardless of the period of acidification dependent on pH, and solid concentrations of the metal. The pattern of metals solubilisation with respect to time was similar. It increased to reach a maximum solubilisation in a relatively short period of time, and then remained the same for the duration of the 24 hrs. acidification period. This is a leading work which may open a future studies in the treatment of sewage sludge in Basrah city.

Key Words: Heavy metals, Removal, Sludge and Solubilisation.

Introduction

The treatment of waste water leads to the generation of large quantities of sludge which must be disposed (Naoumet *et al.*, 2001). The using of sludge on agricultural land to recycling valuable components: organic matter, N, P and other plant nutrients (Fuentes *et al.*, 2004). Due to the physical-chemical processes involved in wastewater treatment, heavy metals tend to accumulate in the generated sludge and the levels of heavy metals become high in the sludge. In order to make use of agricultural land as a disposal way of sewage sludge, it is necessary to reduce the levels of heavy metals in sludge (Cheung, 1988). After the invasion of Iraq, the majority of waste water treatments plants were stopped working or directed into the channels branched of rivers as in Shatt Al-Arab river at Basrah city leading to a real ecological and health problems to the citizen of Basrah city (Al-Jaberi, 2010).

There is a problem concerning fresh water supply in Basrah city because of the changes in the characteristics of Shatt Al-Arab river water quality as a results of increasing water pollution, or the level of salinity (Al-Yaseri, 2010; Al-Khuzie, 2015). The efforts were made to use sulphuric acid as a leaching agent to remove Cd, Pb and Zn from sewage sludge of one treatment plant in Basrah city, south of Iraq and test the ability to reuse the treated water on agriculture land There is no available information on heavy metal concentrations in anaerobic sewage sludge in treatment plants of Iraq. This is a leading attempt to focus on their concentration and study the ability to use sulphuric acid as leaching agent to remove them. Sludge contain variable concentrations of many trace elements including cadmium, copper, zinc and lead which may be potentially phytotoxic or a pose a threat to the animal or human food chain (Logan and Chancy, 1983). The heavy metal content of sewage sludge was about 0.5 % to 2 % on a dry weight basis (Wong and Henry, 1984).

However, in some cases, extremely high concentrations of 4 % w/w of chromium, copper, lead and zinc have been reported (Lester *et al.*, 1983). The reduction of heavy metals in sewage sludge can be achieved either by source control of discharge to sewer systems or by removing metals from sludge. Several chemical methods for solubilisation of heavy metals from sewage sludge have been suggested (Bloomfield and Pruden, 1975; Olver *et al.*, 1975; Scott and Horling, 1979; Cornwell *et al.*, 1980; Jenkins *et al.*, 1981; Flynn *et al.*, 1984; Marchioretto *et al.*, 2002; Muka and Ibrahim, 2006; Gaber *et al.*, 2011). The use of sulphuric acid is preferred compared to hydrochloric acid and nitric acid because of its low cost and improved filterability of leach mixture (Scott and Horling, 1979; Hayes *et al.*, 1980; Muka and Ibrahim 2006; Gaber *et al.*, 2011) have also indicated that when compared under identical conditions of sludge, pH and time, the efficiencies of hydrochloric, nitric and Sulphuric acids for Solubilisation of sludge heavy metals were very similar.

Materials and Methods

All anaerobically digested sludge samples were obtained from the anaerobic treatment unit of a wastewater plant in Abo Al-Kaseb (Basrah, Iraq). The metal concentrations of the sludge samples varied depending on the sampling dates. Copper and lead were the metals of greatest importance as their concentrations were above that recommended for sludge application to the land (Flynn *et al.*, 1984). The composition of important metals in the studied sludge was shown in Table (1).

Table 1. Metal composition of the sludge.

Metals	Composition (mg/kg of dry solid)
Pb	520
Cu	2500
Zn	740

The experiments were initiated as soon as possible after obtaining the samples from the wastewater treatment plant to avoid excessive chemical transformations within the sludge samples because of prolonged storage. Deionized water was added when necessary for dilution of samples to the desired solids concentrations. Thicker sludge samples than those obtained from the plant were prepared by centrifuging the sludge. The solids concentration in the sludge as obtained from the wastewater treatment plant was 16 to 19 g/l. throughout experiments. Analysis was carried immediately before and after acidification and at regular time intervals. Samples were centrifuged to separate the solids and liquid at 10000 rpm for 20 min and metals in the supernatant were determined by A.A. Spectrophotometry according to Public Health Association (1978).

Results

Removal of lead from sludge at different pH was shown in Figure (1a). Solids concentration effects on lead removal were shown in Figures (1 b & c). Maximum lead removal was 88% at pH 1.5 and solids concentration 0.5%. The maximum efficiency of Pb removal decreased with increased solids concentration and pH (Table 2). The period of time necessary to approach the maximum lead solubilisation varied, ranging from 4 to 13 hrs. depending on the pH and solids concentrations.

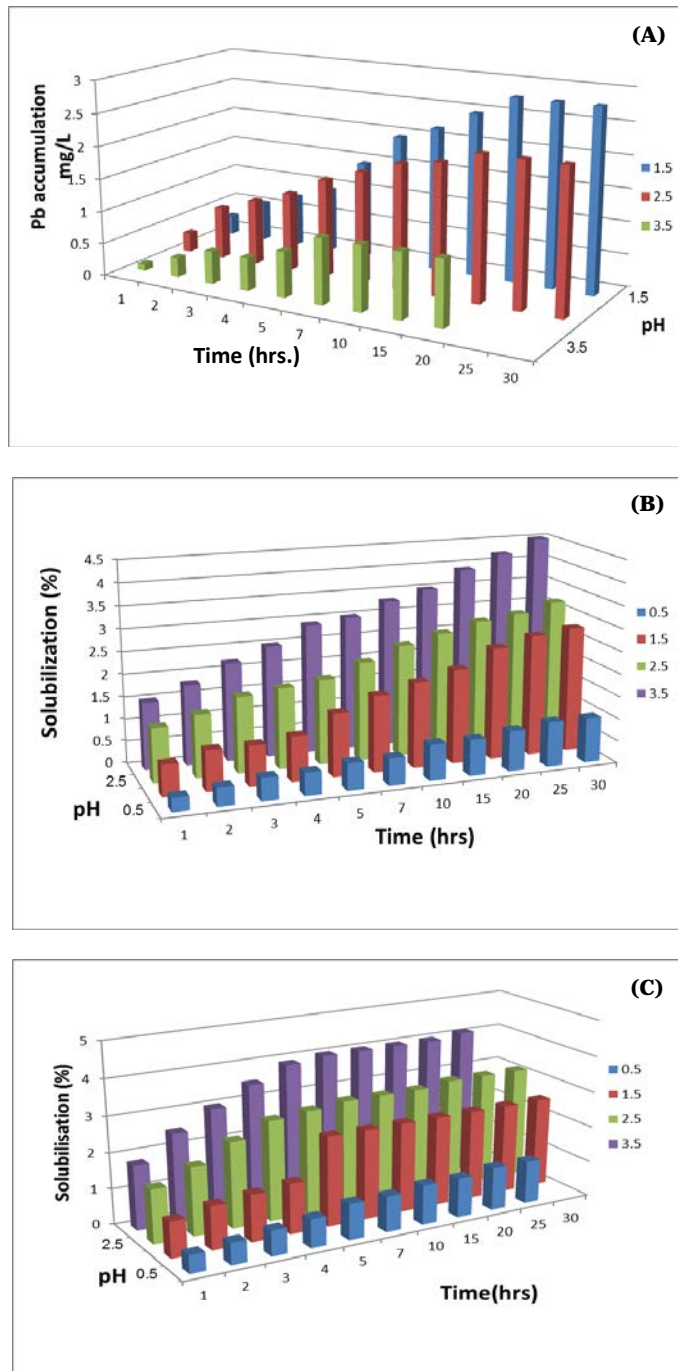


Figure 1. (a) Solubilisation of Pb at different pH (sludge concentration = 19 g/l); (b) and (c) solubilisation of Pb from an aerobically digested sludge, pH = 1.5 and 2.5 respectively.

Table 2. Maximum metal solubilisation from sludge solids.

pH	Solid Concentration (g/l)	Metals		
		Zn Maximum removal efficiency (%)	Pb Maximum removal efficiency (%)	Cu Maximum removal efficiency (%)
0.5	5	91.33	84.17	88.95
	15	88.00	77.60	78.36
	25	80.35	63.44	72.50
	35	78.16	50.10	60.00
	45	89.75	23.18	55.09
1.5	5	88.43	62.19	45.37
	15	73.00	55.13	62.45
	25	64.22	49.11	44.56
	35	63.22	47.90	55.90
	45	58.67	-	46.37
2.5	21	-	43.52	39.33
	25	58.40	17.63	16.83
3.5	21	58.00	-	2.00
4.0	25	22.22	-	-

Zinc solubilisation from sludge solids is indicated in Figures (2 a-c) for a range of pH from 1.5 to 4.5. This figure demonstrates combined effects of pH and sludge solids concentration on metal removal from sludge solids. It indicates that the removal efficiencies were lowered with increased pH and the solid concentration (Table 2).

The metal solubilisation efficiency was calculated at a time when metal concentration in solution reached its maximum value. At lower pH, relatively higher solubilisation of zinc took place immediately after acid addition to the sludge (Table 3).

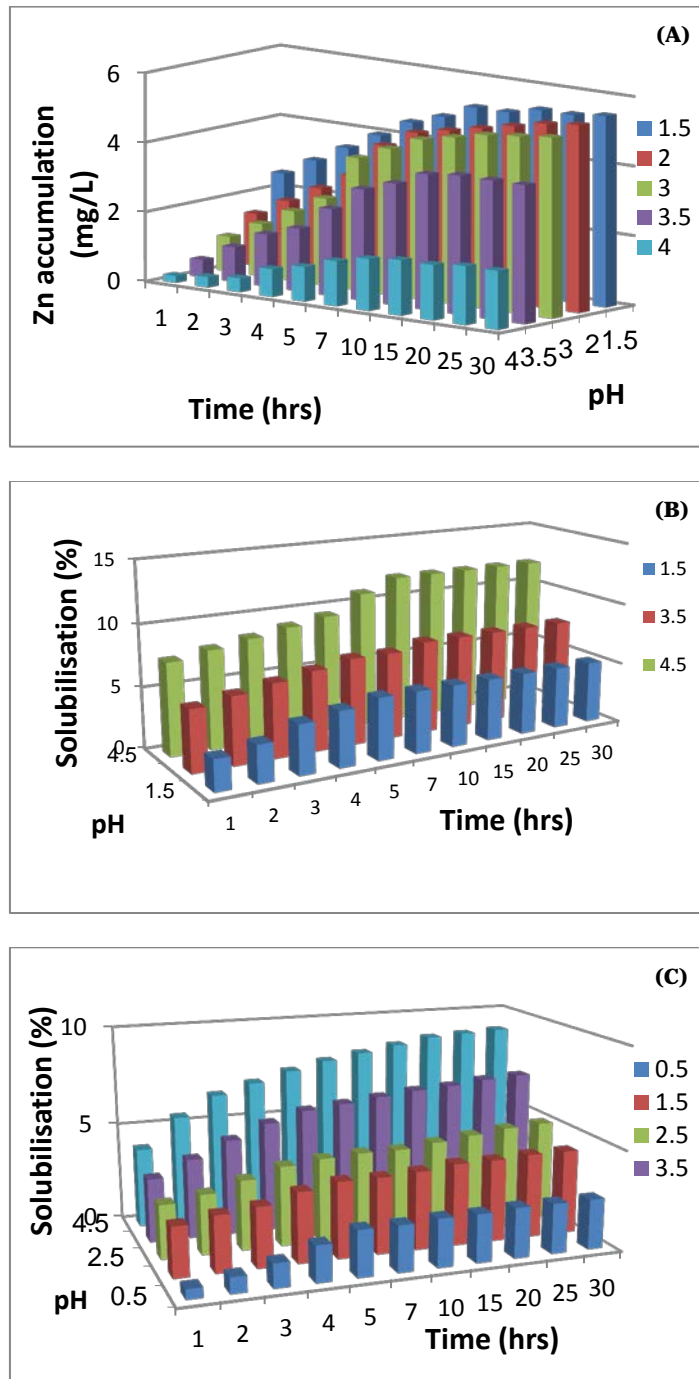


Figure 2. (a) Solubilisation of Zn at different pH (sludge concentration 19 g/l); (b) and (c) solubilisation of Zn from anaerobically digested sludge, pH=1.5 and pH=2.5, respectively.

Table 3. Initial metal solubilisation.

pH	Sludge Solid concentration (g/l)	Metals		
		Zn Solubilisation (%)	Pb Solubilisation (%)	Cu Solubilisation (%)
1.5	5	-	19.5	0.0
	15	52.00	6.9	0.0
	21	37.2	5.2	0.0
	35	37.9	3.9	0.0
	45	29.5	-	0.0
2.5	5	-	0.0	0.0
	15	26.0	0.0	0.0
	21	-	0.0	0.0
	35	20.1	2.1	0.0
	45	22.0	-	0.0
2.5	15	11.1	0.0	0.0
	21	7.4	0.0	0.0
3.5	21	3.7	-	0.0
4.0	21	3.7	-	0.0

Generally the lower the pH, the less time was required for achieving maximum zinc solubilisation. The pattern of copper solubilisation with respect to time was shown in Figures (3 a-c). Copper was not solubilized till after 1.5 hour after acidification at pH 1.5.

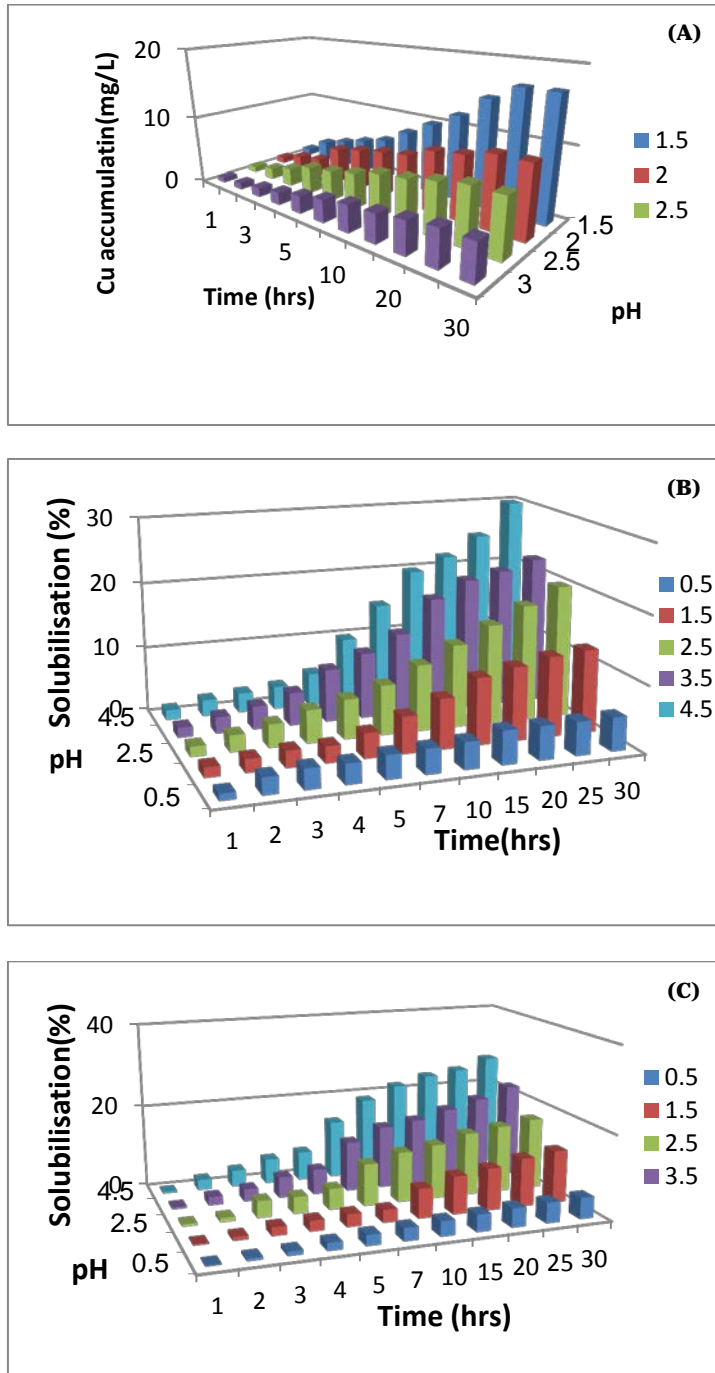


Figure 3. Solubilisation of Cu at different pH (sludge concentration-19g/l); (b) and (c) solubilisation of Cu from anaerobically digested sludge, pH=1.5 and pH=2.5 respectively.

Discussion

As the pH was increased the lag time for copper solubilisation was increased. Similar results have been reported by Wozniak and Huang (1982) on secondary activated sludge. They found that Cr, Ni and Zn were removed in large amounts immediately after acid addition. But, initial removal of Cd, Cu and Pb usually represented less than 10 % of the maximum value under given conditions of pH and solids concentration. Muka and Ibrahim (2006) also observed that zinc and nickel were most readily solubilized with an efficiency of 87 % and 44 % respectively, only 6-8 % of the chromium and lead were extractable and no appreciable amount of copper (0.5 %) was solubilized with the hot acid. Longer times are required to solubilize copper than zinc and lead. The effects of solids concentration on metal solubilisation were also more pronounced for copper than for zinc or lead. Solids concentration effects decreased considerably by lowering the pH. This observation reflects the nature or form of the Cu in the sludge. Low solubility of sludge copper may be due to an organic complex. Olive and Carey (1976) have suggested that Cu exists as an organic complex in sludge. The strong affinity of Cu for the organics of sludge was demonstrated by (Cheng *et al.*, 1973).

The strong complexation power of Cu^{+2} relative to other metals has been demonstrated using amino di-acetic acid, a chemical structure similar to the complexation sites of waste proteinaceous matter in sludge. The copper release profile, studied by (Hayes *et al.*, 1980) for AATD, raw sludge and anaerobically digested sludge, also showed a definite lag before measurable solubilisation was observed. This is in agreement with the pattern of copper solubilisation in the present investigations. However, the lag observed by Hayes *et al.* (1980) was minimum for AATD sludge and was found to increase for anaerobic sludge at pH 2.0 acidified with nitric acid. This behavior is not easily explained on the basis of discrete precipitate solubilisation but rather suggests the possibility that other mechanisms of heavy metal immobilization, such as complication to organic solids, precipitation, protective organic entrapment of precipitates and intracellular uptake, may exert some control over metal solubilisation in acidified sewage sludge's (Mukka and Ibrahim, 2006). Veeken (1999) was studied the extraction for heavy metals Cu and Zn and for competing metals Ca and Fe from sludge using organic acids and found that the rate of extraction increased with increasing temperature and citric acid concentration. Cu can be extracted for 60-70 % and Zn for 90-100 % by citric acid at pH 3-4.

The economic evaluation of the extraction and subsequent composting process showed that the total costs of the treatment process below the costs of incineration. Naoum *et al.* (2001) used hydrochloric, sulphuric nitric and phosphoric acids to extract heavy metals Cr, Cu, Ni, Pb and Zn. They found that the optimum condition was achieved when the sludge samples were in contact with H_2SO_4 20 % v/v for 60 minutes. In order to estimate the metal leachability, the heavy metal content as well as the metal distribution in the residue was investigated and it was found that most of the heavy metal content was extracted while the remaining was removed from the initial mobile phases to the more stable ones. The removal of heavy metals by acidifying sludge was investigated by Stylianou *et al.* (2007). They found that the optimum condition was achieved when the sludge samples were in contact with H_2SO_4 20 % for 30 min at 80 °C as these experiment conditions resulted in the highest heavy metal removal efficiency, and more specifically 74 % for Ni, 86 % for Cu, 99 % for total Cr, 11 % for Pb and 72 % for Zn.

When they test the metal distribution in the residue, they observed that acid treatment leads to changes in the sludge metal partitioning. The study of Gaber *et al.* (2011) revealed that at pH 2.45 citric acid seemed to be highly effective in extracting Cu, Zn mostly after 1 day of extraction time, Cr, Ni at 5 day leaching time, while Pb removal at the same pH was also high but at a longer leaching time of 10 days. At pH 3, citric acid seemed to be also highly effective in extracting Cr, Cu, Pb and Zn at 1 day leaching time, although a relatively higher removal was also attained for Ni at only 4 hrs leaching time (Marchioretto *et al.*, 2002).

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استخراج العناصر الثقيلة من النفايات شبه الصلبة لمحافظة البصرة / العراق بأستعمال طريقة كيميائية

فريال حميم إبراهيم

مركز علوم البحار، جامعة البصرة، البصرة، العراق

المستخلص - تم أخذ عينات من النفايات شبه الصلبة في مرحلة اللاهوائية من أحد معامل معالجة النفايات في أبي الخصيب - محافظة البصرة/العراق خلال عام 2012. تم دراسة إزالة المعادن الثقيلة (Zn و Cu و Pb) بأستخدام حامض الكبريتيك وبمساعدة جهاز مطيافية الأمتصاص الذري. وجد بأن إزالة العناصر من النفايات الصلبة كان معتمداً على الأس الهيدروجيني وتركيز المواد الصلبة ونوع العنصر وفترة التحميض. كما وجد أن سرعة الأذابة وكفاءة الأزالة لجميع العناصر المدروسة تزداد مع زيادة الوقت وقلة الأس الهيدروجيني وإنخفاض تركيز المواد الصلبة. حصل تحديد في مقدار الأذابة في بعض الحالات بغض النظر عن وقت التحميض، وهذه التحديدات تعتمد على الأس الهيدروجيني وتراكيز العناصر في المواد الصلبة وكانت طريقة إذابة العناصر مع الوقت متشابهة لجميع العناصر المدروسة حيث كانت تزداد لتصل إلى أعلى حد لها في وقت قصير ثم تبقى كما هي على طول فترة الـ 24 ساعة فترة التحميض.