Evaluation of Sludge Properties in Sewage Sludge from Guarchia Wastewater Treatment Plant in Benghazi-Libya

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ABSTRACT

Raw sewage sludge samples collected from Guarchia wastewater treatment plant at Benghazi city have undergone complete evaluation of organic composition parameters including pH, Total Volatile Solid (TVS), Total Nitrogen (TN), Total Phosphorus (TP), Total Organic Matter (TOM) and Total Organic Carbon (TOC). Also, evaluation of some trace metals such as Zn, Cd, Cu and Pb have been performed. Monthly and spatial variations in sludge properties have been described.

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Introduction

Until the late 19th century, there have been much concern with the effective and safe disposal of the mankind liquid and solid wastes. The installation of sewerage systems for piping liquid wastes away from major population centers was the single greatest contributor to the dramatic reductions in infectious diseases which occurred during that time. The liquid wastes were usually discharged untreated to a river or the ocean but, with the increasing world population, improved sanitary systems and the adventure of more stringent standards on wastewater treatment, this option has become increasingly untenable [1,2]. The processes applied to the treatment of sewage result in the separation of sewage into two streams, a clarified water containing 20-30 mg/l of suspended solids and a sludge stream of 1-3% solids dry weight, which contains 80-90% of nutrients and pollutants present in the raw sewage.

The nature of the sewage sludge varies, depending on both the wastewater composition (mainly organic and inorganic materials, plant nutrients, trace elements, organic chemicals and some pathogens) and on the treatment processes used [3]. Our current research deals with the evaluation of sludge properties in sewage sludge from Guarchia Wastewater Treatment including parameters such as pH, Total Volatile Solid (TVS), Total Nitrogen (TN), Total Phosphorus (TP), Total Organic Matter (TOM), Total Organic Carbon (TOC), some trace metals concentrations such as Zn, Cd, Cu and Pb, using atomic absorption spectrophotometry (AAS). Benghazi city contains about 36 wastewater-pumping stations from which the raw sewage sludge flow to Guarchia treatment plant. Accordingly, a monthly sample was collected from every station during the period from Dec. 2005 to Jun. (2006).

Experimental

Each dried sample was ground with glass pestle and mortar then

passed through a 2mm mesh stainless steel sieve. The dried ground samples were then stored in plastic bags into a refrigerator for analysis. The required temperature for TN, OM and TP determination was 50 °C. The pH, TS and TVS for each sludge sample were measured directly after sample collection with no need for drying [4,5]. For determining the trace-metal concentrations, each dried sample was ground with glass pestle and mortar then passed through a 2mm mesh stainless steel sieve. The required temperature for trace-metal determination was 105 °C.

pH Measurements

The pH for each sludge sample was measured using a pH meter, inserting the probe into the suspension of the sludge [5].

Total Solid Content (TS)

The water content is a measurement of sediment moisture expressed as a percentage of the whole sediment weight. The sediment moisture content equals the difference between wet weight of the sediment and dry weight following oven drying at 50-105 °C to a constant weight.

$$\text{TS (as \% of wet sludge)} = \frac{wt'}{wt} (100)$$

where wt' is weight of sample after drying; wt is weight of sample before drying.

Total Volatile Solids (TVS)

This represents the fraction of total solids lost up on ignition at a temperature of 550±10 °C for 1 h [6].

$$\text{Volatile matter (as \% of dried solids)} = \frac{wt'}{wt} (100)$$

where wt' is weight lost during ignition; wt is weight remaining after drying.

Organic Matter and Organic Carbon in Dried Sewage Sludge (OM % & OC %)

This involves reduction of $K_2Cr_2O_7$ by OC-compounds followed by determination of unreacted dichromate by redox titration by ferrous ammonium sulfate. The actual measurement is of oxidizable OC but the data are converted to percentage OM using a constant factor, assuming that OM contains 58 % of OC. However, since this proportion is not constant, the results are multiplied by 1.334 as OC [4].

$$N = \frac{10}{V_{blank}}$$

Percentage OM in sludge

$$\% \text{ Oxidizable OC (w/w)} = \frac{[V_{blank} - V_{sample}] 0.3 \times N}{wt}$$

% Total OC (w/w) = 1.334 x % Oxidizable OC

% OM (w/w) = 1.724 x % Total OC

Where N = Normality of ferrous ammonium sulfate (~ 0.5 M)

10 = Volume of (1 N) $K_2Cr_2O_7$ solution

V_{blank} = Volume of ferrous ammonium sulfate solution required to titrate the blank (in ml)

V_{sample} = Volume of ferrous ammonium sulfate solution required to titrate the sample (in ml)

wt = weight of dried sludge (g)

0.3 = $3 \times 10^{-3} \times 100$; where 3 is the equivalent weight of C.

Total Nitrogen (TN %) in Dried Sludge

Applying Kjeldahl semimicro methods, using 50 ml Kjeldahl digestion flask, for TN analysis of sediments, the sample must be more finely ground and thoroughly mixed than for the macro-Kjeldahl analysis to minimize sample error. The method involves digestion of sample to convert organic-N to inorganic-N as $(NH_4^+ - N)$ then determination of TN in the digest as $(NH_4^+ - N)$. The digestion involves heating the sample with H_2SO_4 -containing substances that promote oxidation of OM and conversion of organic-N to inorganic-N ($NH_4^+ - N$), being salts such as K_2SO_4 or Na_2SO_4 , which increase the temperature of digestion, and catalysts such as Hg, Cu, or Se, which increase the rate of oxidation. The $(NH_4^+ - N)$ is determined by collecting the NH_3 liberated by distillation with alkali and analyzing the distillate by titrimetric procedure [7].

$$wt' = \frac{V \times 0.14}{1} \quad (100)$$

$$\% N = \frac{wt'}{wt} \quad (100)$$

where wt' is weight of TN ($NH_4^+ - N$) in sample; wt is weight of sample; V is volume of H_2SO_4 required for titration and %N is percentage of TN in sample.

Total Phosphorus in Dried Sludge

The molybdophosphate complex is formed in H_2SO_4 matrix and reduced with ascorbic acid and absorbance is measured at 840-880 nm. The color is stable from 10 min to 24 h after formation [4]. The sample (0.3-0.5 g) in an uncovered crucible was ignited in a muffle at 550 °C for 2 h. After cooling in desiccator, the sample was transferred to a 100-ml calibrated flask, where 50 ml of HCl (1N) was added. The mixture was filtered after shaking overnight for 14-18 h at 25 °C. A solution of ascorbic acid in ammonium molybdate (8 ml) was added to the filtrate. Absorbance of the

solution was measured at λ_{max} using 1 cm cuvette. A standard curve was prepared by analyzing aliquots of a KH_2PO_4 solution.

$$\text{Conc. of (P)} = (\text{Abs} \times F_1 \times D)/wt$$

where Abs = absorbance of sample solution; F_1 = factor of standard curve (x/y); D = Dilution factor; wt = weight of sample after ignition.

Trace-Metal Analysis

Digestion of Dried Sludge Material

To a finely ground dried sludge (0.1 g) in a freshly cleaned Teflon bomb, 1 ml of aqua regia ($HNO_3:HCl$, 1:3 v/v) was added. The Teflon vessel was placed in a rack where hydrofluoric acid (1 ml) was carefully and slowly added. The bomb was tightly closed and placed on a hot-plate for 1 h then removed from the heat source and allowed to cool to room temperature. The contents of the bomb were transferred into a 25 ml volumetric flask by rinsing it several times with de-ionized water, adding the rinsing to the volumetric flask. The flask was shaken to complete the dissolution and the solution was made up to 25 ml with Milli-Q water. The solution was analyzed for trace metal by flame AAS.

Measurement of Trace Metal in the Digested Dried Sludge by Flame AAS [7]

The trace-metal determination was made by digestion with hydrofluoric and nitric acid mixture, where hydrofluoric acid and aqua regia are used to release the total metal content from dried sludge into solution in a sealed Teflon decomposition vessel referred to as a Teflon Bomb [6].

The metal standard solution was prepared for the calibration curve as follows: An appropriate quantity of stock standard solution (1000 ppm) was diluted with Milli-Q water to the mark (50 ml) and shaken well. The calibration curve was determined according to the expected concentrations of the sample and linearity of the AAS response for the element considered. Standards for the calibration curve were prepared with at least three concentrations plus zero (the zero with no analyst).

Calculation

$$C (\mu\text{g/g}) = \frac{(y - x) V \cdot F}{wt}$$

C = Concentration of metal in the original sample (in $\mu\text{g/g}$ of dry weight).

y = Concentration of metal in sample solution ($\mu\text{g/ml}$).

V = Volume of dilution of digested solution (ml).

x = Mean concentration of metal in reagent blanks (ml).

wt = Dry weight of sample (g).

F = Dilution factor if needed ($F=1$, in the case of no further dilution than initial dilution during digestion procedure).

Monthly Variations in the Sludge Properties

Dry Matter (T.S %) and Volatile Solids (V.S %)

Dry matter and volatile solids are the most important parameters in sludge characterization involved in all the application/disposal methods. Dry matter plays a role in the transport, application and spreading operations. Methods and systems of application to land also depend to a great extent on rheological properties. The reduction of volatile solids through stabilization is very important, mainly to avoid odour problems [8].

Table 1 and Figure1 show the differences in the total solid content and volatile solid at Guarchia plant during the study period. The total solid ranged from 22.50 to 31.75 % and its average value was 27.49 ± 3.29 %, while the range of volatile solid was from 51.12 to 71.00 % and its average value was 58.96 ± 6.12 %. The maximum and minimum content of both were obtained in March and January respectively.

Hydrogen ion concentration (pH)

As shown in Table 1, the pH values of sewage sludges at Guarchia plant were increasing from slightly acidic to neutral, these values ranged from 6.56 reported in December to 7.25 found in January. Figure 1 reveals the variation of pH values at Guarchia plant.

Table 1: Variations in the Sludge Properties at Guarchia Plant during Dec. 2005 – Jun. 2006

Parameter	Dec.	Jan.	Feb.	Mar.	Apr.	May	Jun.	Average	Std. Deviation
T.S %	22.50	29.50	24.75	31.75	26.25	27.20	30.50	27.49	3.29
V.S %	51.12	57.12	58.25	71.00	55.50	59.27	60.50	58.96	6.12
pH	6.56	6.69	6.73	6.85	7.13	7.05	7.19	---	0.241
OM %	37.87	40.25	56	58.74	76.5	55.61	55.34	54.3	12.81
OC %	21.96	23.35	32.49	43.07	44.37	32.25	32.1	32.7	8.63
TN %	4.86	4.43	4.25	4.00	3.81	3.64	2.46	3.92	0.76
C/N	4.519	5.27	7.64	10.77	13.05	8.31	13.05	8.94	3.46
TP%	2.20	1.91	2.45	2.29	1.75	1.93	2.64	2.16	0.32
Zn (µg/g)	727.50	1045.0	555.0	1092.5	862.5	1322.5	815.00	917.14	255.58
Cd (µg/g)	8.75	11.25	8.50	5.25	5.25	5.00	8.50	7.5	2.38
Cu (µg/g)	108.25	327.75	71.75	102.5	178.75	212.25	153.75	165	86.46
Pb (µg/g)	142.50	307.50	57.50	215.0	567.50	305.0	295.00	270	161.34

Figure 1: Monthly Variations in the (TS, VS , pH and OM content) of Sludges Collected from Guarchia Treatment Plant

Figure 2: Monthly Variations in the (OC, TN, C/N and TP content) of Sludges Collected from Guarchia Treatment Plant

Total nitrogen (TN %) and total phosphorus (TP %)

The contents of TN and TP at Guarchia plant are presented in Table 2 and Fig.2. During the study period the distribution of TN was decreasing from 4.86 % (in Dec.) to 2.46 % (in Jun.), with an average $(3.92 \pm 0.76 \%)$, while the range of TP content was ranging from 1.75 to 2.29 % and its average content was $2.16 \pm 0.32 \%$.

Total carbon to total nitrogen ratio (C/N)

A wide range in the record of C/N ratio at Guarchia Plant is presented in Table 1 and in Figure 2. The Different records of C/N ratio showed an increasing from 4.51 to 13.05; its minimum record was obtained in December, while the maximum value was obtained in June and the average value was (8.49 ± 3.46) . This wide range is due to the different content of OC% reported at the plant during the study period

Trace metals (Zn, Cu, Pb and Cd)

The obtained results of trace metals at Guarchia Plant are given in Table 1. The most striking feature is the predominance of zinc and lead followed by copper and cadmium. These metals ranged from 555 to 1322 $\mu\text{g/g}$ for Zn; 57 to 307 $\mu\text{g/g}$ for Pb; 71 to 327 $\mu\text{g/g}$ for Cu and 5.00 to 11.25 $\mu\text{g/g}$ for Cd. According to the average concentrations of trace metals content at Guarchia plant, content of metals can be arranged as the following: $\text{Zn} < \text{Pb} < \text{Cu} < \text{Cd}$ Fig.3 shows the monthly variations of Zn, Pb, Cu and Cd contents at Guarchia plant.

Based on the calculated standard deviation values for different properties of sludges collected from Guarchia plant (Table 1), these sludges had relatively similar physicochemical properties; with some differences in their contents of T.S, V.S, OC and OM, but no similarity in their contents of Cu, Pb and Zn was obtained during the study period; the only exception was for Cd which always revealed similar content in these sluges.

These variations may be related to that, Guarchia plant serves as Waste Water Treatment Plant for wastewater generated by Benghazi city that it collects the sewage from different pumping stations located at the city; these stations vary in their types, sizes and nature of their surrounding areas. Moreover, the plant only accepts the quarter quantity of the total pumped effluent

(per day) from the city; thus it is difficult to identify the sources of this quantity, or to ensure that this quantity was always from the same sources during the study period. In addition, Guarchia plant receives sewage, not only from existed wastewater collection network, but also from pumping trucks that collect the sewage from industrial, residential and other sources. The unsystematically inputs from these trucks to the plant makes it more difficult to identify the type, source and quantity of the added sewage.

In general, sludges collected from Guarchia plant during the study period had a high percentage of phosphorus, and, organic matter and nitrogen; which decrease as the degree of mineralization increases. All of the physicochemical parameters closely reflect those in the bibliography for sludges of similar characteristics, some of which have been used for soil amendment [9,10].

Table 2 shows the trace metals concentrations in the sludge samples of the present study and data from literature. All the sludges from literature show an increase in the concentration of trace metals in the order of $\text{Zn} > \text{Cu} > \text{Pb} > \text{Cd}$, whereas sludges of the present study show an increase in the order of $\text{Zn} > \text{Pb} > \text{Cu} > \text{Cd}$. The arrangement of metals concentrations in sewage sludge is related to the source and composition of wastewater. The found contents of Zn, Cu and Cd in the present study were within the ranges found by other authors in this field [10-12]. The only exception was for Pb that was higher than the range. This exception is most properly related to the composition of wastewater produced by the city; also, the low degree of mineralization and stabilization for sludge produced by Guarchia plant may effect the distribution of metals in these sludges, "it is clear that sludge stabilization influences the distribution of the metals and the fraction to which they bond." The accumulation of sewage sludge from urban Waste Water Treatment Plants is a growing environmental problem, which makes the increased rate of its production in developing countries a great matter of concern whenever the aspect of the final disposal is taken into account. Sludge disposal is a large-scale crucial environmental problem [10-13]. which requires a large array of technical, regulatory, institutional and economic measures to improve the situation. The land application technique is one of the methods being considered and is thought to be very effective and efficient. Sludge may be applied to agricultural land, forest,

disturbed land or dedicated disposal sites. There is an increasing interest in the agricultural application of sludges due to the possibility of recycling valuable components such as organic matter, nitrogen, phosphorus and other plant nutrients. However, any form of disposal need to be controlled in order to protect human health and the environment, considering that sewage sludge potentially carries chemical pollutant such as persistent organic pollutants and trace metals. This fact has received more and more concern in recent years, and detailed information on trace metals present in sewage sludge is necessary before their land application [14-16].

Table 2: Concentrations of Trace Metals ($\mu\text{g/g}$) Found in the Sewage Sludges of the Present Work, Compared to Different Works

Author	location	Zn	Cd	Cu	Pb
Fuentes et.al.(2004b)	Murcia, Spain	458	1.14	146	87
Koreish et.al. (2005)	Alexandria, Egypt	821	10.6	482	182
Pereira & Kuch (2005)	Balingen, Germany	1310	4.0	649.7	88.8
Pereira & Kuch (2005)	Rio de Janeiro, Brazil	1386.7	2.7	226.3	110.7
Present study	Benghazi, Libya	917.14	7.5	165	270

In Libya, up to now, there is no specific legislation regarding the maximum equivalent concentration levels of trace metals in sewage sludge considered for agricultural use or final deposition in soils. A comparison with the recommended maximum trace metal levels for agricultural use in USA and in EU is made in Table 3. The averages values of trace metals concentrations recorded in Guarchia plant during the study period (Table 1) were within the maximum permitted levels established by European legislation. Thus it is possible to say, sludges produced by Guarchia treatment plant may, a priori, be used for soil amended since they all have a high organic matter content, and are rich of nutrient (N and P) and do not have a trace metal content (Zn, Cd, Cu and Pb) in excess of the limits laid down by the European legislation. Since each component of the sludge has its own environmental impact, different properties of sludge must be taken into account when choosing the disposal route. It is very important here to point out that, the content of some other metals such as Ni, Cr, Hg and Fe should be taking into account when deciding any rout of sludge disposal [10, 13-17].

Based on the recommended maximum trace metal levels for agricultural use in USA (Table 3), sludges produced by Gurachia treatment plant should not be permitted for any agricultural uses due to their high levels of Pb (Table 1); which had excesses the limits laid down by the USA legislation.

Table 3: Current International Legislation Concerning Levels of Trace Metals ($\mu\text{g/g}$) in Sewage Sludge and Final Disposition

	Zn	Cd	Cu	Pb	reference
EU (agriculture)	2500	20	1000	750	Fuentes et. al.(2004b)
USA (agriculture)	1400	20	750	150	Pereira & Kuch (2005)

The environmental impact of such agricultural recycling practices still has to be controlled in order to avoid organic and inorganic contamination of natural resources [17]. However, sludge disposal is a worldwide problem and sludge must be treated in such a manner to minimize the odour potential, reduce the number of pathogenic organisms and other potentially harmful constituents to an acceptable level before spreading it onto agricultural lands or non-agricultural lands [1, 18].

Figure 3: Monthly Variations in the Metal Contents ($\mu\text{g/g}$) of Sludges Collected from Guarchia Treatment Plant

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