

# Total concentration and bioavailability of lead in urban sewage sludge: Test case in the WWTP of the city of Dolores Hidalgo, México

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**Abstract-** In recent years, the production of sludge from wastewater has greatly increased worldwide due to demand for better water quality and the imposition of stricter environmental laws. One of the main problems of pollution of the sewage sludge is the concentration and availability of heavy metals which may contain, because these sludges represent a risk to the environment and to human health. Hence the importance of finding alternatives to generate stable and non-hazardous waste for proper disposal or reuse in order to contribute to sustainable development. One of the alternatives for the disposal of sludge is its use for agricultural soil improvement, because they are an important source of nutrients due to its content of organic matter, macronutrients like N, P and K and some micronutrients such as Cu and Zn. However, it should be considered the risk posed by the use of sludge because may contain high concentrations of potentially toxic elements such as heavy metals, thus concentration and speciation studies of metals are needed to obtain more detailed information on their bioavailability. The sludge used in this study are samples from a urban-municipal WWTP in state of Guanajuato. This sludge was found to not meet the maximum permissible lead (Pb) content in dry basis according to the provisions of the NOM-004-SEMARNAT 2002, because they exceed the maximum lead limit by approximately 25%. The lead availability was determined by the speciation

without any pretreatment in land and landfills. Considering the above, there are two problems: first, the dumping of sludge in inappropriate places can generate severe pollution problems, and secondly, the beneficial properties such as nutrient content and organic matter that could be exploited in agriculture or soil improvement, are being wasted, hence the importance of determining the bioavailability of heavy metals.

Knowledge of the distribution of heavy metals in sludge is important to understand its bioavailability. The distribution of these metals in the exchangeable, reducible, oxidizable and residual fractions can be evaluated using a sequential extraction analysis [4], which is based on sequential solubilization of metals, using chemical reagents that increment its extraction capacity in each successive stage of fractionation [5].

A large number of sequential extraction methods have been reported in the open literature, many of which are variations of the procedure of Tessier [6]. To harmonize the different sequential extraction schemes, the (BCR) proposed an extraction protocol in three stages [7]. The origin of heavy metals, particularly lead, in sewage sludge used in this study is mainly

method of the Community Bureau of Reference (BCR) where it was observed that the exchangeable and reducible fraction occupy approximately 24% of the lead in the sludge sample. While the residual fraction and oxidizable fraction occupy 45% and 30%, respectively.

**Index Terms-** Bioavailability, lead, urban sewage sludge, speciation.

## I. INTRODUCTION

The sewage sludge is a solid, semisolid or liquid waste, obtained from the treatment of wastewater and are composed of microorganisms which remove organic matter from wastewater which use as food [1]. The handling and disposal of this residue becomes increasingly complex problem due to the large amount of sludge produced from treatment of wastewater. Only in Mexico, in the early 90s, it was estimated that the sludge production was 12 million tons per year [2]. One of the main problems of pollution of the sewage sludge is the concentration and availability of heavy metals which may contain, because these sludge represent a risk to the environment and to human health [3], despite these

associated with pottery and ceramics, which are important economic activities in the city of Dolores Hidalgo, México. In the above activities, it is used the litharge or lead monoxide, which is the main component of silicates used to give a glossy or glazed finish to the pieces [8].

The objective of this research is focused on determining the total concentration of lead, as well as its distribution in the different fractions of the sewage sludge from the wastewater treatment plant (WWTP) in the city of Dolores Hidalgo, in order to determine their bioavailability and proper use without affecting the environment.

## II. METHODS AND MATERIALS

### A. Sampling of sewage sludge

The sludge samples were collected from the WWTP of the city of Dolores Hidalgo, Mexico, at three different points: the first was taken immediately after leaving the filters press, the second in the drying beds, with a period of 8 days of drying,

and the third in the dry stack sludge, with about 9 months drying. According to the Mexican standard NOM-004-SEMARNAT-2002 [9], 4 kg were collected from each sample to secure reliability and representativeness in the later study. The samples were placed in polyethylene bags and stored in a recipient with ice for transport to the laboratory of university. To homogenize the composite samples, the quartering method established in the aforementioned Mexican standard was used. Samples were identified with numbers 1, 2 and 3, according to the chronological order in which they were taken.

#### B. Determination of moisture content in sewage sludge

Approximately 60 g of each of the composite samples were placed in an oven at 105 °C to have a constant weight. The percentage of moisture content in the sewage sludge was calculated by the difference between the weights of the sample in dry and wet, according to the following expression [10],

$$\%M_s = \frac{W_w - W_d}{W_w} \times 100\% \quad (1)$$

where  $W_w$  is the weight of the wet sample and  $W_d$  corresponds to the weight of dry sample, both weights measured in grams.

#### C. Drying and screening samples

Once the composite samples were homogenized by quartering method, these were dried in an oven at a constant temperature of 105 °C for 72 h. The dried samples were pulverized in a mortar and were screened through a No.12 mesh to obtain samples with particles below 1.7 mm, which were stored in polyethylene bags at room temperature.

#### D. Determination of total heavy metals in sewage sludge

The heavy metal content in sewage sludge was determined by acid digestion. To carry out the acid digestion of the sludge, 0.5 g of sample were placed in a test tube with screw and 5 ml of concentrated nitric acid (JT Baker analytical grade) were added, then, the sample was placed in a thermoreactor C-9800 HANNA Instruments for test tubes at high temperature for 2 hours. Subsequently, 5 ml of hydrogen peroxide 30% (JT Baker analytical grade) were added and the tubes are left in the thermoreactor for 1 additional hour. After the digest time is completed, the tubes are allowed to cool to room temperature. The sample at room temperature is filtered through a Whatman 40 filter to remove insoluble particles and interference. Finally, the content of heavy metals was quantified by atomic absorption spectrometry using a flame atomic absorption spectrometer (FAAS) Perkin Elmer, model AAnalyst 100. The operation conditions of the spectrometer used in the determination of total heavy metals in sewage sludge are shown in Table A of Appendix.

#### E. Determination of the bioavailability of lead (Pb) by sequential extraction

To determine the bioavailability of lead, sequential extraction method of BCR, which distinguishes three fractions in

descending order according to their availability, was used. The method is summarized in Table 1.

Table 1. Fractions of the sequential extraction method of the BCR.

No.	Solid phase (fraction)	Reactive	Mol/L	Time/°T
1	Exchangeable	HCH <sub>2</sub> COOH	0.11	16h/°RT
2	Reducible	NH <sub>2</sub> OH.HCl/ HNO <sub>3</sub>	0.1	16h/°RT
3	Oxidizable	H <sub>2</sub> O <sub>2</sub>	30%(W/V)	1h/°RT
		H <sub>2</sub> O <sub>2</sub>	30%(W/V)	1h/85°C
		CH <sub>3</sub> COONa	1	16h/°RT

RT. Room Temperature.

##### 1) Exchangeable fraction

A sample of 1 gram of sludge (dry and sieved) was placed in a polypropylene centrifuge tube with 15.2 ml of acetic acid 0.11 M. The sample was shaken in a horizontal shaker, model TTR-200, for 16 hours at room temperature.

The extract was separated from the solid residue by centrifugation for 5 min. The supernatant liquid was filtered through Whatman No. 40 paper and stored at 4 °C in a polyethylene container for a subsequent analysis by FAAS. The solid residue remaining in the centrifuge tube was washed with distilled water by shaking for 5 min and centrifuged for 5 min to remove the washing water.

##### 2) Reducible fraction

To the clean residue from the previous stage, the second extractant solution was added, consisting of 15.2 ml of hydroxylamine hydrochloride (JT Baker, analytical grade) to 0.5 M (pH 2 with concentrated nitric acid) and it was shaken for 16 hours. The separation of the extraction solution and the washing of the residue were carried as described in the exchangeable fraction. In this fraction, the liquid obtained by decantation was again filtered through Whatman No. 40 paper and stored at 4 °C in a polyethylene container for a subsequent analysis by FAAS.

##### 3) Oxidizable fraction

To the residue from the previous stage, 10 ml of 30% hydrogen peroxide (JT Baker) was added into the polypropylene centrifuge tube with lid. The residue was digested for 1 hour at room temperature and then an additional digestion was performed by heating the residue at 85 °C in a water bath for 1 hour. The stopper of the centrifuge tube was removed and the content of the tube was reduced by evaporation to a volume of approximately 1 ml. Then the third extractant solution, 19 ml of ammonium acetate (JT Baker) to 1.0 M (pH 2 with concentrated nitric acid), was added and it was shaken for 16 hours.

The separation of the extraction solution and the washing of the residue, were developed in the same manner as the exchangeable fraction. Similarly to the previous fraction, the liquid obtained by decantation was again filtered through Whatman No. 40 paper and stored at 4 °C in a polyethylene container for a subsequent analysis by FAAS.

The solid residue of the third stage of the extraction process was dried at room temperature and was used to determine the residual fraction by acid digestion.

### III. RESULTS AND DISCUSSION

The results of the moisture content and the total heavy metal content in the samples of the sludge, as well as lead bioavailability are presented in this section.

#### A. Moisture content in sewage sludge

The sludge samples under study are composed of a high water content, which must be removed by dehydration to more adequately manipulate the sludge and significantly reduce its volume. In Figure 1 the percentage of moisture content in each of the samples taken is shown. In this figure it can be observed as the moisture content decreases in the sludge samples greatly, from the output of the filters until its final disposal.

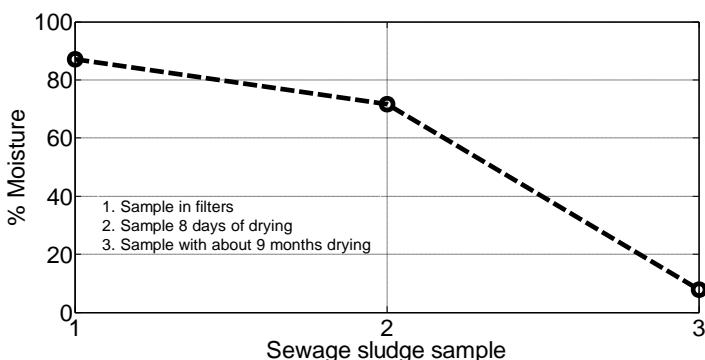


Figure 1. Percentage of moisture content in the sludge samples collected from the WWTP.

#### B. Total heavy metals in sewage sludge by FAAS

The results of the total heavy metals in sewage sludge for each of the three samples analyzed are presented in Figure 2 and Tables 2, 3 and 4.

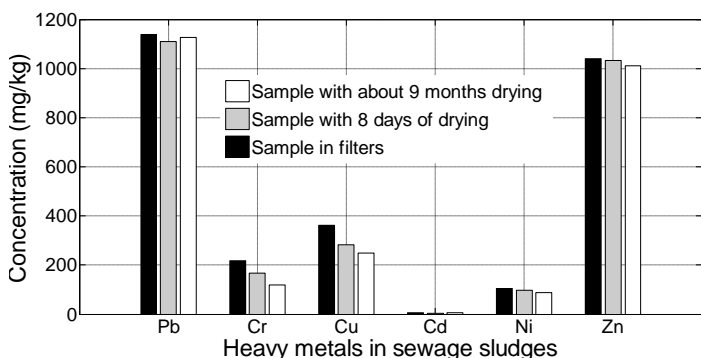


Figure 2. Average total concentration of heavy metals in the sludge samples.

Figure 2 shows that the metals with the highest concentrations in the three samples of sewage sludge are lead and zinc, however,

this last element does not represent potential risk to health or the environment, unlike lead.

The data in the tables show that the concentrations of Cr, Cu, Cd, Ni and Zn are much lower than the minimum limits established in NOM-004-SEMARNAT-2002, which are considered excellent values, while the concentration of Pb is outside the maximum limit permitted by approximately 32-35%.

Table 2. Average total concentration of heavy metals in the sludge samples and its comparison with the NOM-004-SEMARNAT-2002: Sludge sample collected from the filters.

Metal	Sludge sample in filters	Excellent (mg/kg, dry basis)	Good (mg/kg, dry basis)
	Concentration (mg/kg, dry basis) Media ± S, n=3	NOM-004-SEMARNAT-2002	
Pb	<b>1139.37 ± 14.97</b>	300	840
Cr	218.27 ± 2.20	1200	3000
Cu	362.05 ± 8.76	1500	4300
Cd	4.81 ± 0.32	39	85
Ni	105.21 ± 3.81	420	420
Zn	1039.03 ± 13.72	2800	7500

S: Population standard deviation.

NOM-004-SEMARNAT-2002. Sludge and Biosolids: Specifications and maximum permissible contaminant limits for their use and final disposal.

Table 3. Average total concentration of heavy metals in the sludge sample and its comparison with the NOM-004-SEMARNAT-2002: Sludge sample with 8 days of drying.

Metal	Sludge sample 8 days of drying	Excellent (mg/kg, dry basis)	Good (mg/kg, dry basis)
	Concentration (mg/kg, dry basis) Media ± S, n=3	NOM-004-SEMARNAT-2002	
Pb	<b>1109.36 ± 35.48</b>	300	840
Cr	166.46 ± 5.88	1200	3000
Cu	282.68 ± 8.14	1500	4300
Cd	4.62 ± 0.26	39	85
Ni	94.57 ± 3.27	420	420
Zn	1033.15 ± 21.47	2800	7500

S: Population standard deviation.

NOM-004-SEMARNAT-2002. Sludge and Biosolids: Specifications and maximum permissible contaminant limits for their use and final disposal.

Table 4. Average total concentration of heavy metals in the sludge sample and its comparison with the NOM-004-

SEMARNAT-2002: Sludge sample with about 9 months drying

Metal	Sludge sample with about 9 months drying	Excellent (mg/kg, dry basis)	Good (mg/kg, dry basis)
	Concentration (mg/kg, dry basis) Media ± S, n=3	NOM-004-SEMARNAT-2002	
Pb	<b>1126.38 ± 2.08</b>	300	840
Cr	119.79 ± 0.81	1200	3000
Cu	248.74 ± 2.02	1500	4300
Cd	4.88 ± 0.19	39	85
Ni	88.32 ± 10.29	420	420
Zn	1012.29 ± 11.74	2800	7500

S: Population standard deviation.

NOM-004-SEMARNAT-2002. Sludge and Biosolids: Specifications and maximum permissible contaminant limits for their use and final disposal.

Failure to comply with the specifications of the NOM-004-SEMARNAT-2002 regarding "Maximum permissible limits for heavy metals in biosolids," is set out in paragraph 4.3 of the same standard as these sewage sludge cannot be used and based on the NOM-052-SEMARNAT-2005 (section 6) where procedures are established to determine whether a waste is hazardous, it is defined in Section 6.3.1 that sludge and biosolids are regulated by the NOM-004-SEMARNAT -2002. Therefore and in accordance with the provisions of the two Mexican Official Standards mentioned above, these sewage sludges are classified as hazardous waste.

Based on the results obtained in the above tables, it was decided to work only with a sludge sample to determine the bioavailability of lead, since the total of the heavy metals is very similar for each of the three samples. In this case, the sample of sludge selected was the sample 8 days of drying.

C. Bioavailability of lead (Pb)

The average concentrations of lead in the sample of sewage sludge and its distribution in the three fractions determined by the method of the BCR and the residual fraction are presented in Figure 3. This figure shows that the exchangeable and reducible fraction, which are the most available in the sample, occupy about 24% of total lead in the sludge sample, while the oxidizable fraction occupies 31% of total and the residual fraction, which is the more stable and less available, occupies 45% of total lead.

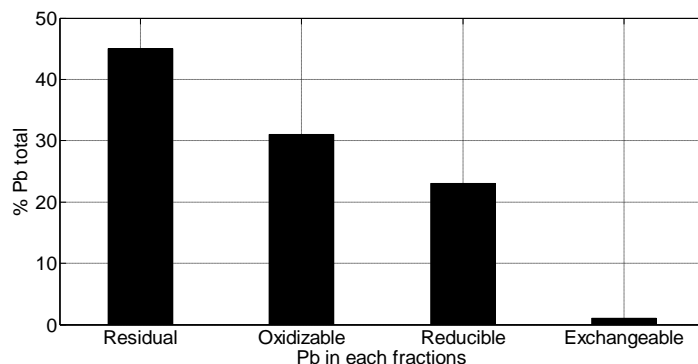


Figure 3. Percentage distribution of Pb in the three fractions extracted by sequential extraction method and the residual fraction.

IV. CONCLUSIONS

The total concentrations of Cd, Cr, Cu, Ni and Zn determined in the sewage sludge samples do not exceed the limits set by Mexican standards, specified in NOM-004-SEMARNAT-2002, while the Pb exceeds these limits by 33% approximately. It must be pointed out that excessive lead content in sewage sludge is due to the activities of pottery and ceramics that are developed as an important part of economic activity in the city of Dolores Hidalgo, México.

Lead concentrations in the fractions obtained by sequential extraction procedure shows that the highest values correspond to more stable chemical forms, such as the oxidizable fraction and the residual fraction, indicating a very low bioavailability of the metal.

Based on the results of lead in samples of sewage sludge and in accordance with the provisions of NOM-052-SEMARNAT-2005, it can be stated that the sewage sludge collected from the WWTP of the city of Dolores Hidalgo, are classified as hazardous waste, which limits its use and exploitation. Therefore, it is recommended to propose a technique for lead extraction of the sludge, in order to exploit their properties as biofertilizers in various crops.

APPENDIX

Table A. Operation conditions of the spectrometer used in the determination of total heavy metals in sewage sludge.

Metal	Wavelength (nm)	SLIT (nm)	Integration time (sec)
Pb	283.3	0.7	0.1
Cu	324.8	0.7	0.1
Cd	228.8	0.7	0.3
Ni	232	0.2	0.3
Zn	213.9	0.7	0.5
Cr	357.9	0.7	0.1

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