# Characterization of leachates of the special handling wastes with different storage ages

<sup>1</sup> Diana Ibarra Rodríguez, <sup>2</sup> Mercedes T. Oropeza Guzmán, <sup>1</sup>J. Bernardino Velázquez Fernández, <sup>3\*</sup> I. Paz Hernández Rosales

<sup>1</sup>Posgrado en Ciencias Biológico Agropecuarias - Km 9, carretera Tepic – Vallarta, Xalisco, Nayarit, México
<sup>2</sup>Centro de Investigación y Desarrollo Tecnológico en Electroquímica, Tijuana, México.
<sup>3</sup> Universidad Autónoma de Nayarit, Ciudad de la Cultura Amado Nervo s/n, Tepic, Nayarit C.P. 63190,

México

**ABSTRACT:** In present work, the aim was to evaluate the physical-chemical composition of a leachate from two special handling wastes of different ages; two years and two days of storage in the city of Tepic, Nayarit, Mexico. Some physical parameters (turbidity, density, particle size and suspended solids), chemical (pH, Z potential, electrolytic conductance, chemical oxygen demand, total organic carbon, metals (Cd, Cu, Fe, Hg, Pb y Ni), ammonia nitrogen, Kjeldahl nitrogen, inorganic nitrogen and total nitrogen) parameters were determined. The results agreed other previous studies described within the bibliography and values were observed within the ranks given by the authors.

*Key words:* Leachate, Z potential, urban solid waste, special handling waste. \*Corresponding author Tel +52 311 211 88 21 E-mail address: paz.rosales@gmail.com

#### I. INTRODUCTION

In Mexico, according to the General Law for Prevention and Full Disposal of Wastes, they are classified in: Urban Solid Wastes (USW), Special Handling Wastes (SHW) and Hazardous Wastes [1]. The SHW, are those wastes generated in production processes that posses features to be considered neither hazardous or USW, or those produced by large generators (i.e., >10 tons per year). Because of the recent regulation of SHW there is no data about the volumes produced of for certain kinds of these wastes [2]. The volumes have been estimated for four out of eight kinds of service. Most of them belonged to demolition, household, commercial and industrial waste gathering a 77 % of the total. 18% belongs to sludge from municipal sewage treatment, 3% produced by transportation and 2% come from clinical units. Thereby, calculus yielded approximately 16,800 tons of USW/day. In Nayarit state, Mexico, there is no information about dailygenerated quantity of USW. In the city of Tepic, the estimated amount of USW is 414.5 tons/day, 37.56% of it, is organic matter [3]; [4]; [5]. Nevertheless, no physical characterization has been carried out. This characterization would allow making decision regarding projection and design of management/disposal systems. Thus, special attention must be paid to both stages: parameters 'design and simple. Moreover, results will allow, on one hand, to identify the wastes' kinds deposited in a landfill. On the other hand, it will be possible to estimate the composition and volume of deposited wastes and to identify probable sources of pollution. In this regard, a chemical characterization of organic matter would help to evaluate the retrievable amount of bioenergy as well as other possible uses such as compost. The chemical properties are the conditioning factor to determine the retrieval and final treatment.

One of the problems caused by waste mishandling is the leachate production, for it is a consequence of waste high humidity level. These leachates can infiltrate and percolate through the soil reaching water bodies and groundwater [6]. Along with the infiltration, dissolved materials are dragged causing a large organic and inorganic load to water. Therefore, these materials represent the main sources of soil contaminants for water bodies and groundwater close to waste depots. Main landfill leachate parameters are Chemical Oxygen Demand (COD), pH, suspended solids (SS), ammonia nitrogen (NH<sub>3</sub>-N), Kjeldahl nitrogen and heavy metals [7]. The aim of this research was to determine the USW leachate's physical and chemical parameters from Tepic, Nayarit, Mexico.

## **II. PROBLEM'S APPROACH**

The USW storage in controlled landfills would significantly help protect environment. Nevertheless, the USW confinement generated a leachate, which is a highly polluted liquid, hard to treat by conventional means [8]. Tchobanoglous *et al.*, [9] have noted that the leachate's management is the key to the prevention of the pollution of the aquifers by the landfill. To take over the landfill leachate, four alternatives could be used: 1) recycling, 2) evaporation, 3) treatment followed by evacuation, and 4) dischargement into sewage [10]. The selection of the leachate's treatment process is a complex task due to the pollutant load within this liquid [11] and depends highly upon the physical chemical characteristics of the leachate. The current challenge in Mexico is to develop treatments for all leachates. Coagulation and flotation assays have been carried out in Tuxtla Gutierrez, Chiapas [12]; coagulation-flocculation, flotation, adsorption and Fenton oxidation in Mérida, Yucatán for [13]. In Nayarit, there are no landfill or city amenities for leachate treatment. Also, there are no private facilities for that service, for instance "REDESO" (located in the city of Tepic). Bioremediation has proven to be successful to treat soils polluted by hydrocarbons and pesticides [14]. It has several advantages: it is friendly with the environment, aesthetical, energy saving and low cost/benefit ratio. However, since a bioremediation strategy should be tailored, characteristics of the substrate should be known. The main characteristics are those regarding physical chemical features and the microorganisms it would contain.

#### **III. JUSTIFICATION**

In Tepic, "the Iztete" landfill has 32 years old. During the first years (1980-84), the construction a sink to store leachate had started. Unfortunately, it was not finished In the first enabling stage of this dump (1980-1984), a sump was built for the leachate's uptake, this public work did not conclude, thereupon it has not been used [15]. Years later, although a geomembrane was disposed to keep infiltrations off the subsoil, it never fulfilled its function due to lack of maintenance [16]. Because of this, the leachates leak out of the sink into the nearby river, thereby infiltrating through the subsoil. Since the infiltrate has no previous treatment, it becomes a hazardous pollutant depending on its own components. Nowadays, Tepic population is 380,249 who generate 414.47 USW tons per day. Recoverable wastes comprise 28.82% of the USW and 37.03% of USW is organic matter, i.e. 155.68 tons [5]. In spite being only the 37.03%, it is a great volume that is daily deposited in landfills holding a high humidity content to which frequent rainfall would be added. Physical-chemical characterization of the leachate is required to choose the proper biodegradation treatment or bioremediation technology.

## IV. MATERIAL AND METHODS METHODOLOGY

The study was cross-sectional, descriptive/analytical and comparative. The experimental strategy consists of three stages Fig. 1) physical-chemical characterization of USW, 2) collection and storage leachate from USW, *Special Handling Waste's Leachate* ( $L_{SHW}$ ): a from the two years old storage; *Old Special Handling Waste's Leachate* ( $L_{SHW/O}$ ) and a sample from two days old storage; *New Special Handling Waste's Leachate* ( $L_{SHW/O}$ ); and 3) chemical characterization of leachate.



FIGURE 1. Experimental strategy for physico-chemical characterization of USW and L<sub>SMW</sub>

#### Sample collection and storage

The leachates were collected in previously disinfected 1-liter high-density polythene containers. Two samples were taken, one from a "new" leachate ( $L_{SHW/N}$ ) (two days old), another from an "old" leachate ( $L_{SHW/O}$  (Two years old). The  $L_{SHW/N}$  was taken from a garbage truck's container; the  $L_{SHW/O}$  was taken from stored containers of the same company.

#### > Physical characterization:

- *pH*. The sensION<sup>TM+</sup> Portable pHmeter was used to determine the pH.
- *Turbidity and suspended solids*. Turbidity was measured by using absorptiometrics with HACH DR/890 Colorimeter. As for the suspended solids via the photometric method [17]- [18].
- Size particle and Zeta potential. These parameters were determined by using a Malvern Zetasizer Nano-ZS. The tests were carried out for L<sub>RME/N</sub> and L<sub>RME/V</sub>, placing12 µL of each sample in the quartz cells. As for the Zeta potential (Zp), 150 µL of each leachate were placed in a folded capillary cell made of two golden electrodes.
- Density. Determination was carried out for each sample L<sub>RME/N</sub> y L<sub>RME/V</sub>, by using a10 ml Pyrex volumetric flask. This flask was previously washed with HCl (1:10) and rinsed with deionized water three times. Thereafter, it was weighted in a PW, ADAM ®analytical balance (accuracy ± 0.0001 g) at 25°C and the data were recorded. The flask were filled with each leachate sample to the marking and weighted again. The weight difference divided by the 10 mL was recorded as the density of each sample.
- *Electrolytic conductance*. This parameter was determined by employing a conductivity electrode with ACH HQ/40 d equipment. The electrode was immersed into the liquid sample (for L<sub>RME/N</sub> y L<sub>RME/V</sub>) to measure conductivity which is expressed in mS/cm.

#### Chemical characterization

- *COD*. The chemical oxygen demand was determined for each leachate sample by means of reactor digestion method. The reactor employed was a HACH DBR 200 at a temperature within the 148°C-150°C. Samples were diluted twice with deionized water in 1:10 proportion and a 1:20 proportion (final dilution factor of 2000). Diluted samples were added to vials containing silver sulphate, sulphuric acid, demineralized water, chromic acid and mercury sulphate. Blank was prepared using water instead of samples. Latterly, vials were mixed and placed indigesters. Passed 2 hours, the digester was withdrawn and cooled, until content measurement using the HACH DR/890colorimeter.
- *COT*.COT was determined by the direct method for high ranks (20-700 mg/L), according to THE PROCEDURES MANUAL (2013).
  - I. In a 50-ml Erlenmeyer flask, astir bar was placed before adding10 ml of the sample; 4 ml of pH 2 buffer solution were added and mixed for 10 minutes. Then persulfate powder was for the blank, buffer was replaced with deionized water.
  - II. To each sample vial,  $300\mu$ L of each leachate were added ( $L_{SHW/N}$  y  $L_{SHW/O}$ ), to blank,  $300\mu$ L of water. Then all the vials were mixed and sealed.
  - III. These vials were taken to the digester for 2 hours. After the temperature has dropped, COT was measured with the HACH DR/890 colorimeter.
- Metals. Metals were determined by using atomic absorption spectrophotometry. To 45 ml of each leachate's sample, 5 ml of H<sub>2</sub>SO<sub>4</sub>, 5 ml of H<sub>2</sub>O<sub>2</sub> and 5 ml of HCl were added and digested during one hour. Thereafter, 5 ml of H<sub>2</sub>O<sub>2</sub> and 5ml of HCl were added to each sample; then, 5 ml of H<sub>2</sub>O<sub>2</sub> to the L<sub>SHW/N</sub>. During the whole process, both samples were constantly mixed (2-rpm) and kept at 165 °C, throughout 3 hours. After this time, samples were filtrated through Whatman 40 paper to discard any suspended particles. Each sample was taken into a BGB 932plus atomic absorption spectrophotometer and measured according to NMX-AA-051-SCFI-2001. Cd, Cu, Fe, Hg, Pb and Ni concentration were calculated using an external standard calibration curve.

- Nitrogen. The nitrogen's determination comprises four determinations, these are the following:
  - I. Ammoniacal nitrogen was determined via the salicylate method (10031method) High Range, Test N tube.
  - II. Inorganic nitrogen, via the titanium trichloride reduction method of (10021method).
- III. Total nitrogen. Determined via the Persulphate Digestion Method (Method 10072).
- IV. Kjeldahl nitrogen. Calculated as stated in equation 1.

$$N_K = N_T - N_I - N_A \qquad \text{eq. (1)}$$

Where, N<sub>T</sub> refers to total Nitrogen, N<sub>I</sub> to inorganic nitrogen and N<sub>A</sub> to ammoniacal nitrogen.

### V. RESULTS AND DISCUSSION

#### 5.1 SHE's physical chemical characterization.

Physical characterizations of USW were carried out (Fig. 2); its amounts (TABLE 1) and USW organic matter characteristics were also determined (TABLE 2).

Month	Total	Collected days	Generating	Average
2013	collected (kg)		average daily	generation
			(kg)	per day per
				trade (kg)
March	25929.96	7	3704.28	142.47
April	26779.97	7	3825.71	147.14
Total		14		





ГАBLE 2. USW	organic matter	caracterization
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Determination	March 2013	April 2013	
pH	4.13±0.74	4.28±0.63	
Moisture, humidity	62.91±0.10	65.64±6.06	
Ashes	2.5825±0.93	3.25±1.62	
C/N	14.75±4.22	13.47±6.8	
Organic Matter	25.43±7.29	23.25±10.95	

FIGURE 2. USW material content.

The organic matter was found to be main residue, holding a 43.09% of the total mass of USW, followed by pre-printed paper with 11%. According [5] to 4,145,000 kg per day are collected, 37.56% of it is organic matter, which is of household origin. The food was of mall could explain the difference with our results. Moreover, our results are in agreement with those reported by [19], on the Quebec's Generation study, which report a 40% of organic matter. Because of this high organic matter content, compost seems to be the most adequate of disposal of these wastes. The humidity content in the samples ranks from62.91% to 65.64%. The data provided by Tchobanouglous, for humidity content in organic matter from business premises, varied from 38.8% and 78.7%, depending upon the type of mixture (for instance, fruit or processed meat). In that previous study, ashes level was 4.2% - 4.9% for food residues with no mixing. Our slightly smaller result may be due to the homogeneity of the samples.

Buenrostro, in 2012, carried out a study for the chemical parameters' determination of a closed landfill; where the pH's results showed a behaviour predominantly basic (8.04 a 8.96), this for buried wastes 20 years ago, except for residue of 10 years, since these last showed a pH of 5.87. Humidity recorded average values of 31 through 51%. The average a shes' content was of 26.8% (for 20-year-old wastes) and of 49.4% (for 10-year-old wastes).

#### $L_{SHW}$ 'sphysical-chemical characterization.

The leachate's pH ranks between 5.08 and 8.05 (Table 3). According to [7] this could be explained by the biological activity within it In keeping mind with this, it is not surprising that the older leachate had a lower pH than the "fresh" sample. Although is a simplistic explanation, further studies would be needed to determine all the parameters involved in pH changes throughout the maturation or ageing of the leachate.

Suspended solids content of both samples of leachate appeared to be quite different. Nevertheless, others authors have reported high variability in this parameter. [20] found leachates taken from household wastes in Hong Kong with more than 5,000 mg/L. In France, [21] found 13 mg/L of suspended soils. This variability would depend upon the qualitative and quantitative composition of the material of the waste originating the leachate and the microbial activity that could biodegrade or indirectly affect it.

The density was higher than water's due to the amount of organic matter that leachates with held. As for zeta potential<sup>1</sup> and particle size there has been no results reported. The values for zeta potential of the  $L_{RME/N}$  would be interpreted for light stability (-21 to 30 mV). Thus, the  $L_{RME/V}$  would present an incipient agglomeration (-11 a -20 mV) [22].

Lou *et al.* (2009) studied leachates from Laogang landfill of Shanghai, and reported a turbidity of  $1,749\pm5$  NTU; in our work, old leachate sample has a much smaller turbidity value that, while the "fresh" sample has a higher value ( $7,200\pm2$ ). In the latter, a high concentration of suspended solids was found, which could explain the higher turbidity.

Respecting physical parameters (Table 1), the  $L_{SHW/N}$ 's COD was of 6,407.5±18 mg/L and for the  $L_{SHW/O}$  was of 581.5±18 mg/L. In studies reported on the bibliography, the observed found rank for leachates is of 100 mg/L-70,900mg/L. In Cod's reported results for leachates from Salonica Mayor, Greece; a 70,900 mg/L concentration was found (2003) and another study carried out near Marsella (Francia), with a leachate sample over more than 10years of storage, the COD's concentration was of 100 mg/L (2002) [23]; [21]. In results of 2007 by Lou Z. &Zhao Y. In Laogang landfill of Shanghai, this team found that the leachate's COD was of 54,651 mg/L [24]. Thereby, the COD found in the  $L_{SHW}$ , takes place within the aforementioned rank of100 mg/L–70,900mg/L; anyhow, the  $L_{SHW/N}$  do present an load of dissolved organic matter. The main reaction that is carried out in the COD's determination is performed through the organic matter's oxidation present in the  $L_{RME}$ 's sample. The dichromate ion ( $Cr_2O_7^{-2}$ ) reacts with the current oxidizable compounds in the sample, reducing the ion  $Cr_2O_7^{-2}$  into green chromic ion ( $Cr^{3+}$ ), consequently, the Ag<sub>2</sub>SO<sub>4</sub> with catalyser is required and the HgSO<sub>4</sub> acts to with draw the chloride's interference (Baird , 2001). The actual reaction is depicted as the following:

$$Cr_2 O_7^{2-} + 14H^+ + 6e^{-} \xrightarrow{Ag_2 SO_4} 2Cr^{3+} + 7H_2 O \tag{1}$$

<sup>&</sup>lt;sup>1</sup>Z potential: a commonly used measurement in **colloid chemistry**. This one shows the necessary potential in order to penetrate the ionic layer surrounding a particle, so that it destabilizes the particle. Thereupon, we can tell that the zeta potential is regarded as a electrostatic potency amidst the layers around a particle.

Parameter	L <sub>SHW/O</sub> (2 years storage)	L <sub>SHW/N</sub> (storage for 2 days)	Leachate concentration data reported by the authors
pH*	$3.79 \pm 0.01$	$7.81 \pm 0.01$	5.08 a 8.05 (Renou <i>et al.</i> , 2008)
Turbidity*(NTU)	174.5±2	7200±2	1749±5 (Lou <i>et al.</i> , 2009)
Suspended Solids* (mg/L)	195±18.2	4,850±18.2	
Particle Size* (nm)	560±76	$\begin{array}{ccc} 1253 & 191.1 \pm \\ \pm 320 & 30.8 \end{array}$	
pZ (mV)	-24.5	-18.2	
Density (g/mL)**	$1.0102 \pm 0.0001$	$1.0225 \pm 0.0001$	
Electrolytic conductivity (mS/cm)	4.78	16.26	25-350 (Kjeldsen <i>et al.</i> ,2002)
COD* (mg/L)	581.5±18	6407.5±18	100 - 70, 900 (Tabet <i>et al.</i> , 2002; Tatsi <i>et al.</i> , 2003; Ziyang & Youcai , 2007)
TOC*(mg/L)	98±8	3163.3±8	182-9870 (Tabet <i>et al.</i> , 2002; Tatsi <i>et al.</i> , 2002; Lou <i>et al.</i> , 2009).
Fe (mg/L)	3.59	35.08	2-5500 (EPA, 1995)
Cu (mg/L)	2.90	0.89	0.05-0.348 (Kjeldsen <i>et al.</i> , 2002)
Hg (mg/L)	0	0	0-0.2 (EPA, 1995)
Ni (mg/L)	0.52	0.17	0-13 (EPA, 1995)
Cd (mg/L)	1.005	0.868	0-0.05 (Kjeldsen <i>et. al.</i> , 2002)
Pb (mg/L)	1.96	0.21	0-12 (Kjeldsen et. al., 2002)
NH <sub>3</sub> -N* (mg/L)	3±5	50 ±5	0.2-13,000 (Kjeldsen et. al., 2002)
Inorg. N* (mg/L)	1.65	57.75	13-5,000 (Lo I. 1996; Tabet <i>et al.</i> , 2002)
Total N (mg/ L)	12.8±0.5	490±0.5	
Kjeldahl N (mg/L)	8.15	382.25	5-13,000 (Lo L 1996: Tabat at al. 2002)

**TABLE 3**. *L<sub>RME</sub>*'s physical-chemical features.

\*In a single lab, using a standard solution with the apparatus for each determination, a single operator acquires a standard deviation for each test (equipment's accuracy).

\*\*Heavy equipment's sensitivity.

--- No ranks reported.

In case of the TOC, Lou *et. al.*, [25] reported a TOC concentration of 9,870 mg/L for fresh leachates and, for mature leachates, the concentration was of 182 mg/L. In this manner, the results upon this work are below of the reported by these authors (amid  $98\pm83$  mg/L for  $L_{SHW/O}$  and  $163.3\pm8$  mg/L for  $L_{SHW/N}$ ). The  $L_{RME/N}$  concentration is much smaller than the highest reported TOC's concentration, but this still has a great quantity of susceptible substances to be oxidized by chemical means, since the COD and TOC were shown as elevated ones et al [23]; et al [21]; et al [25]. The TOC from  $L_{RME}$  sample is digested by persulphate and acid in order to generate CO<sub>2</sub>. During the digestion, the carbon dioxide is spread in the pH indicator reagent inside of the

ampulla. The carbon dioxide adsorption in the indicator shapes up the carbonic acid, which changes the pH of the indicator solution, which, in turn, varies the colour. The general reaction is depicted below:

$$K_2Cr_2O_7^{2-}$$
 + organic matter  $\rightarrow H_2O$  +  $CO_2$  +  $Cr^{+3}$  (2)

Regarding the metals concentration in leachates, the Environmental Protection Agency (1995), reports ranks for Fe of 2-5,500 (mg/L), Hg of 0-0.2 mg/L, Ni of 0-13 mg/L and Pb of 0-12 mg/L. Kjeldsen *et. al.*, [19], mention the rank for the Cu, to be of 0.05-0.348 (mg/L). In the case of this study, the  $L_{RME}$  comprise a higher concentration with regards of the forenamed authors, but not as near as the maximum allowable limit. Except for Cd, the authors manage a rank of 0-0.05 (mg/L). At the present study, it is important to mention that the Cd is found in a higher concentration than the reported rank and surpasses the sewage dump's maximum allowable limit stated in NOM-052-ECOL-1993. The Pb also surpasses the maximum allowable limit [26]; [19]; [3].

The Total Nitrogen is a crucial compound in order to preserve life in aquatic ecosystems. The NOM-001-ECOL-1996, specific as Total Nitrogen's rank for sewage of 15 mg/L- 25 mg/L [27]. When this limit is exceeded, the main consequence becomes the water eutrophication and hence the aquatic species' death. In the case of  $L_{SHW}$ ; the  $L_{SHW/O}$  presents a Total Nitrogen's concentration of 12.8±0.5 mg/L which ranks with in the commonly established by NOM-001. However, the  $L_{RME/N}$  has a concentration of 490±0.5 mg/L, so that it surpasses this limit. Some performed leachates studies in China and France have reported that the Nitrogen Kjeldahl has a rank of 5-13,000 mg/L. Kjeldsen *et. al.* [19], reported the expected rank of Ammonia Nitrogen in leachates, to be of 50-2200 mg/L. In this study, the Kjeldahl Nitrogen of the  $L_{SHW}$ 's fits within the reported ranks by the foregoing authors, in contrast with the Ammonia Nitrogen that stays above the value. The previous results show the importance of having controlled landfills that comply with the specifications of the NOM-083-SEMARNAT-2003 [20]; [23]; [3].

It is worth mentioning that amidst the  $L_{RME/N}$  and  $L_{RME/N}$ , there are some variations in determined parameters upon study. The variation of turbidity is remarkable; the  $L_{RME/N}$  presents the higher one due to undegraded organic matter. Turbidity is linked to the quantity of suspended solids because if high turbidity is observed, this quantity will be high, the COD and TOC will also increase. Moreover, a high density is mingled due to the suspended solids quantity and the particle sizes that the antecedent solids contain. The variation of metals concentration in the  $L_{SHW}$  is, in turn, noteworthy; it is reckon that the soils' precipitation and adsorption are vital to the metals immobilization. Hence it is the cause of low concentration in  $L_{SHE/O}$  [28]. Thereupon, the wastes contain oil and organic matter that, before they were taken to the landfills, are part of processes such as the irrigation of vegetables. Vegetables can have a meaningful adsorption capacity; this means that the irrigation water can be an important factor to the variation of the prior metals' concentration.

#### VI. CONCLUSIONS

The leachates are components highly polluting, and the main source of their appearance is wastes' decomposition in non-controlled landfills. The dissolved organic matter represents the component with the highest pollution degree; therefore it causes the COD, TOC and Suspended Solids to rise in  $L_{SHW/N}$  mainly. The  $L_{SHW/O}$  hold smaller content, not less important, though. Mingling these parameters the Total Nitrogen is deduced, which can be a potential contaminant for aquifers or shallow waters in a long-term. The  $L_{SHW/N}$  comprises Ni, Fe and Cd concentrations that may represent potential contaminant hence it affects the ecological homeostasis. The  $L_{SHW/O}$  can be within the required specifications, however, more studies are needed in order to assure whether it is time effect or the season in which they were collected.

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