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CONDUCTOMETRIC TESTS AND TOTAL CHROMIUM LEACHABILITY IN AQUEOUS SOLUTION, FROM TANNED LEATHER WASTE

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ABSTRACT. Tanning is the most important operation in leather processing, which turned the leather into a non-putrefying material. Tanning may be carried out with chromium salts (III) or with a variety of other tanning agents. In present days, tanning with chromium salts (III) is the most widely used technique in industrial processing of leather, almost 90 % of leather goods being processed by this method.

Taking into account the fact that the wastes from the leather and fur industry are framed by Commission Decision 532/2000 under code 04 01 08 (non hazardous), this study aim's to analyze the leachability of total chromium from tanned and dyed leather waste originated from leather processing industries, in order to establish the environmental risks of them. Leachability tests, conductometric tests and determination of the refractive index were carried for three types of tanned leather waste (G-gray, Bn-brown, Bk-black), at different temperatures.

The results shown that the values for the total chromium in leachate were higher than the maximum allowed concentration for the hazardous waste (MAC = 70 mg/kg). The leachability of total chromium increased at low temperatures (5-13°C) and at high temperatures (40-60°C).

In Romania an important amount of tanned leather waste reaches the municipal landfills. These results indicate that the leather waste can be disposed *only in special landfills for hazardous waste.*

Key words: *chromium, leather, waste, leachate, conductometric tests*

INTRODUCTION

Waste represents a particular challenge due to: the increasing quantities and types that by degradation and infestation represent a threat to the natural environment and human health, and also because of the important raw materials quantities that can be recovered and returned to the economic cycle. Leather industry has always been one of the most important industries of the European economy (Vișan et al., 2002). Worldwide, the largest amount of generated waste in the leather processing is in Asia (without China) and China (see figure 1). Generally it can be observed that the waste amounts generated in Asia (excluding China) and the Western Europe are approximately equal, specifying that it represents about half of the total waste worldwide generated.

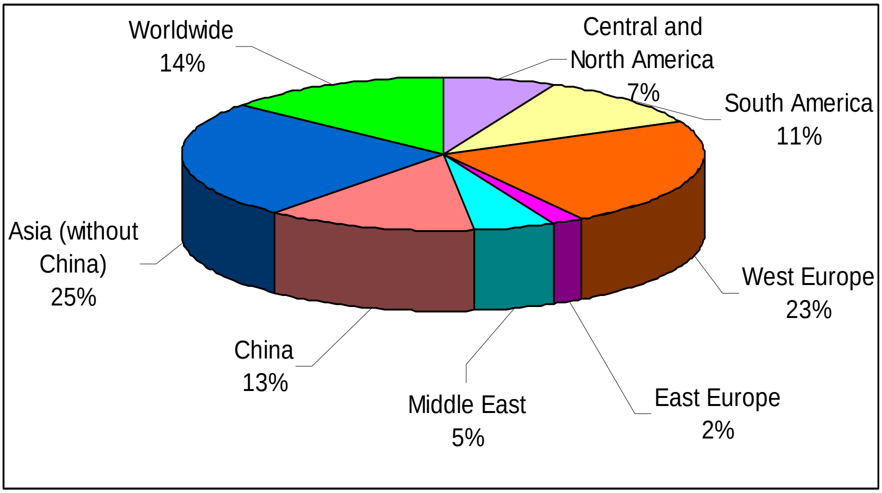

Fig. 1. *The worldwide waste quantity generated in the leather processing process (CTC, 2000)*

From figure 1 it can be observed large differences between the generated waste from Western Europe and Asia (excluding China), and the rest of the world. The largest quantities, 25% belong to Asia (without China) and the lowest amounts are recorded to Eastern Europe at a rate of 2%. Asia together with Western Europe, with a share of 61%, is generating more than half of the generated worldwide waste.

The main goal in the leather industry is the production of the leather products, this sector representing 41% of all industrial uses for this material. In this context, Romania had an important tradition in leather processing and still has it.

The leather industry is using only 80% of the rawhide material, the rest of 20% representing the processing waste. A proportion of 25% of the rawhide represents the final product, 70% is represented by the solid waste, and 5% by the residual water. By tanning, from 1,000 kg of leather is obtained 600 to 700 kg of solid waste and 40-50 m^3 of wastewater (Vișan et al., 2002). Approximately 70% of the waste is recovered and for the rest are studying utilization possibilities (Vişan et al., 2002). In Romania, the total rawhide amount annually processed, about 11,000 tons of waste, is structured as follows: 5,500 tons / year of raw-hide waste; 3,500 tons / year of tanned and unfinished leather waste; 1,800 tons / year of tanned and finished leather waste; 200 tons / year of leather fur waste (Vișan et al., 2002).

The processed leather waste has a major impact on the environment because of the contained substances, mostly heavy metals. It is very important to not discard the processed leather waste in nature or to store it in open dump landfills; it is indicated to manage it properly through recycling and recovery thereof or by storage in compliant landfills. The open dump landfills, generally, due to lack of facilities and poor exploitation, generate impact and risk to the environment and public health. The main impacts and risks are: the changes in landscape and visual discomfort, air pollution, surface water pollution, changes in soil fertility and biocenosis composition of the neighboring land (Lixandru, 1999; Popița et al., 2013).Therefore, the waste from tanneries must be handled and stored so as to avoid leakage, odor problems and air emissions (BAT, 2013).

In the tannery process, generally, as tanning agent are used trivalent chromium (Cr III) compounds. But, some leather products may contain traces of hexavalent chromium (Cr VI), which is considered prioritary / hazardous substance (Directive 60, 2000; Directive 105, 2008; Regulation 1272, 2008). In tanning process, only Cr (III) compounds are used, but it may be possible sources of Cr (VI) as a contaminant: after UV exposure (at over 80°C) the fat-liquoring acids is possibly to lead to the oxidation of Cr (III); the formation of Cr (VI) may result in the process of the storage of fat-liquored leather at 35% humidity (Kolomaznik et al., 2008). Also, in the shoe production, the use of alkaline glues may contribute to the formation of Cr (VI) (Kolomaznik et al., 2008).

The oxidation of Cr (III) to Cr (VI), in basic solutions, occurs easily with the use of peroxides and hypochlorite. The oxidation of Cr (III) to Cr (VI), in acid solutions, occurs with the use of sulfuric acid. The oxidation occurs after the following equations (Eq. 1 and 2):

For an alkali medium:

$$2Cr_2O_3 + 8OH^- + 3O_2 \rightarrow 4CrO_4^{2-} + 4H_2O \quad (1)$$

For an acid medium:

$$2Cr_2O_3 + 3O_2 + 2H_2O \rightarrow 2Cr_2O_7^{2-} + 4H^+ \quad (2)$$

(Kolomaznik et al., 2008)

Cr (VI) usually exists in the form of $H_2Cr_2O_7$ and its salts and in the form of $Cr_2O_7^{2-}$. Both anions CrO_4^{2-} and $Cr_2O_7^{2-}$ are water soluble and their formation is pH dependent. Above pH=7 predominates the Cr (III) and below pH=6 predominates Cr (VI) (Frey and McGuire, 2004; Gode, 2007).

In case of the open dump landfills, it can occurs that the acid rain leach the Cr (III) compounds from the landfilled leather waste and the soluble salts can reach underground water sources and surface water streams. The underground water could reach a treatment water plant, where in the process of the sterilization of drinking water under strong oxidation conditions by ozone or by hypochlorite, the Cr (III) is converted into Cr (VI). The reaction with magnesium and calcium ions present in drinking water and generate magnesium and calcium chromate or dichromate salts which are carcinogenic. In this respect the calcium and magnesium chromate and dichromate salts which are elements presents in soil and drinking water, were classified as carcinogenic compounds (Kirk, 1992).

Leather processing generates substantial amounts of solid and liquid waste (skins, grease, dust, manure, sludge). In the literature, there are numerous studies (Yilmaz et al., 2007; Alptekin et. al., 2012; Nogueira et. al., 2011; Famielec and Wieczorek-Ciurowa, 2011) on tanned leather waste treatment for recycling and recovery. Most of these studies are related to the extraction of chromium from the waste to be reused in the tanning process (Yilmaz et al., 2007).

For leather processing, the reference documents for best available techniques (BAT - Best Available Techniques) are covered by the Directive 2010/75/EC (Directive 75, 2010). In the European legislation, as well as in the Romanian one, the waste from the leather industry, fur and textiles are listed and coded under Chapter 04 "Wastes from the leather, fur and textile industries" (Decision 532, 2000; GD 856, 2002).

It must be noticed that the leather waste, containing chromium salts isn't framed as hazardous waste; this waste is coded at code 04 01 08: "waste tanned leather (blue sheeting, shavings, cutting, buffing dust) containing Chromium". Only the codes marked with an asterisk (*) are considered as a hazardous waste (Decision 532, 2000; GD 856, 2002).

In this respect the present study mainly aims to analyze the leaching of the total chromium from leather waste originated from leather processing industry and comparing with the Maximum Allowed Concentration from leaching waste legislation. Also we determinate the conductometric parameters (pH, TDS, EC, salinity) in order to monitor the behavior of leather waste in the environment.

MATERIALS AND METHODS

In this study was used tanned leather waste from a shoe factory, which has been tested in different conditions of temperature and over different periods of time, to observe the leachability of the total chromium. We have used three different types of waste leather with different colors and textures (figure 2).

a b c

Fig. 2. *Waste leather type black-**Bk** (a), waste leather type brown-**Bn** (b) and waste leather type gray-**G** (c)*

Conductometric tests, the refractive index determination and leachability tests for total chromium were made for each type of waste leather for 5 days at 4 different temperatures: 5-13°C (outside temperature at the determination moment), 22-25°C (indoor temperature), 30-40°C and 40-60°C.

Conductometric tests (pH, total dissolved solids - TDS, electrical conductivity - EC, salinity) were performed with a portable multiparameter WTW Multi 350i. The refractive index was determinate with a digital refractometer Reichert AR 200. The total chromium concentration was analyzed with an Atomic Absorption Spectrometer (AAS) ZEEnit 700 (Analytic Jena) by flame absorption.

Leather waste was collected from a shoe factory, from the leather waste bins located inside of the company's perimeter. These wastes were taught to a sanitation company to transport them to the municipal open dump landfill waste. Leather waste was sorted by colors and/or different textures. For this study, were chosen three types of waste leather with different colors and textures to track the behavior, over time, of certain parameters in the leachate, in order to evidence if the different pigments influence the chromium leachability. The cutting step of the chosen leather waste types was made using mechanical shears by cutting small pieces with the length and width of about 1 cm.

In order to perform the leachability study was chosen, in accordance with the OM 95, 2005 (2 L/kg), the ratio scrap leather waste/distilled water and leather waste + sand/distilled water (OM 95, 2005). The vessels were filled with distilled water in which was immersed the leather waste and were subjected to various temperature conditions for 8 hours/day, 5 days, for each sample. Conductometric tests were carried out daily, at the temperatures presented above, after the 8 hours period accomplished.

After the completion of the conductometric experiment, the 2 phases (liquid/solid) were separated, the leachate was collected, acidified with concentrated nitric acid (HNO_3) to a pH = 2 and filtered in order to analyze the concentration of the total chromium.

The analysis of the total chromium from the leachate was performed by using the Atomic Absorption Spectrometry ZEEnit 700 (Analytic Jena) by flame atomic absorption method.

RESULTS AND DISCUSSIONS

The results showed a correlation between the total chromium concentration in the leachate, and the changes of the conductometric measured parameters during the analysis time (5 days) and the different temperatures.

The conductometric parameters determination

Conductometric tests (pH, TDS, EC and salinity determination) and the refractive index determination were made for three types of waste leather (**G**-gray, **Bn**-brown, **Bk**-black) for 5 days at 4 different temperatures: 5-13°C (outside temperature at the determination moment), 22-25°C (indoor temperature), 30-40°C and 40-60°C.

In figure 3 is presented the pH variation for the three waste leather types (gray-**G**, black-**Bk** and brown-**Bn**), depending on analysis time and temperature.

From figure 3 it can be seen that the samples with leather brown waste **Bn** had a basic pH=7-8, at all temperatures, which slowly decrease or remain constant during the analysis period of 5 days.

Note that the blank had a pH = 5.2. The samples **G** and **Bk** were acidic at a pH=3-4 and remained acidic with slow modifications during the analysis period of 5 days.

The EC (electroconductivity) variation for the three waste leather type (gray-**G**, black-**Bk** and brown-**Bn**), depending on analysis time and temperature is presented in figure 4.

The figure 4 show that the **Bk** type of waste leather had the highest values at high temperatures (40-60°C), but also at outside indoor and 30-40°C temperatures. The **Bn** type had the highest values at temperatures of 30-40°C and also at indoor temperatures. As can be seen the **Bn** type values are lower at higher temperatures than at indoor temperatures. The **G** type had the lowest values at all temperatures.

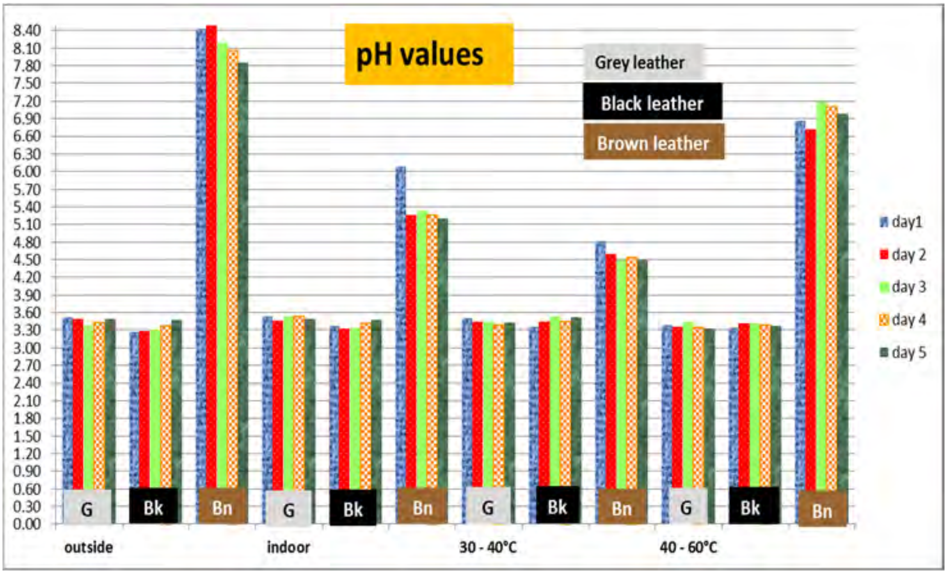

Fig. 3. *The pH variation for the three waste leather type (gray G, black Bk and brown Bn), depending on analysis time and temperature*

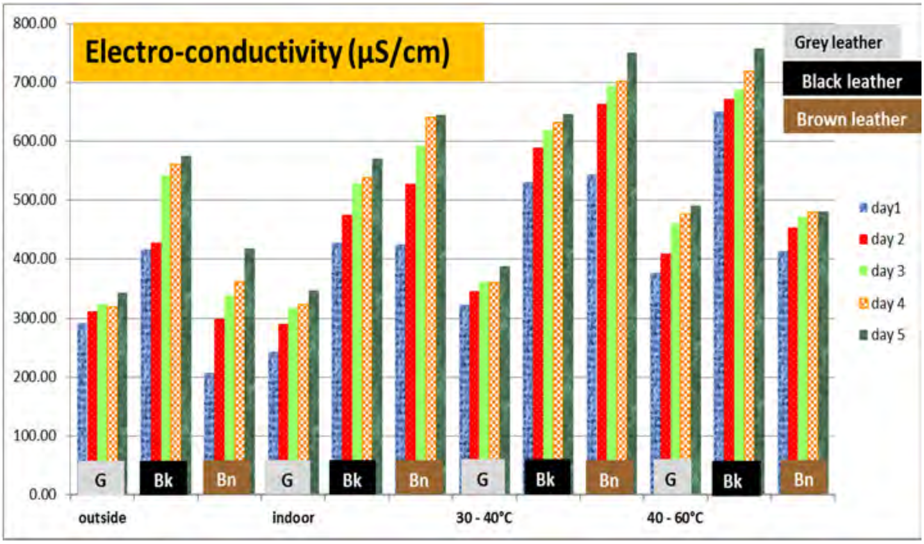

Fig. 4. *The EC variation for the for the three waste leather type (gray-**G**, black-**Bk** and brown-**Bn**), depending on analysis time and temperature*

TDS variation for the three waste leather type (gray-**G**, black-**Bk** and brown-**Bn**), depending on analysis time and temperature is presented in figure 5.

Figure 5 show, as in the case of EC, that the waste leather type **Bk** had the highest values at the highest temperature (40-60°C). The **G** type had the lowest values at all temperatures. During the 5 days, all the waste leather types presented increases, proportional with the analysis time. Note that the **Bk** type had higher values at outside temperatures and indoor temperature, in contrast with the other types of waste leather **G** and **Bn**. That means that the temperature is an important factor in the leaching waste leather process. High levels of TDS in water can indicate the presence of a wide range of pollutants.

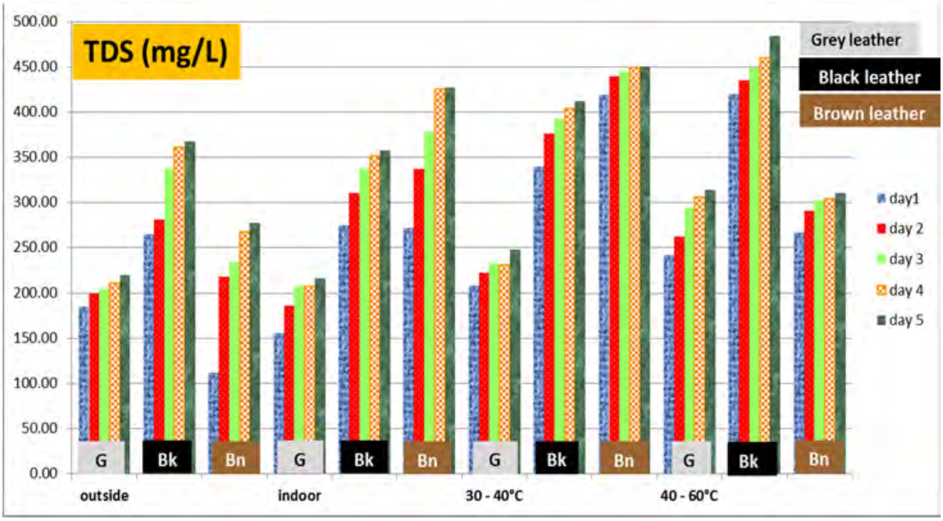

Fig. 5.*TDS variation for the three waste leather type (gray-**G**, black-**Bk** and brown-**Bn**), depending on analysis time and temperature*

Figure 6 offers information about the salinity variation for the three waste leather type (gray-**G**, black-**Bk** and brown-**Bn**), depending on analysis time and temperature.

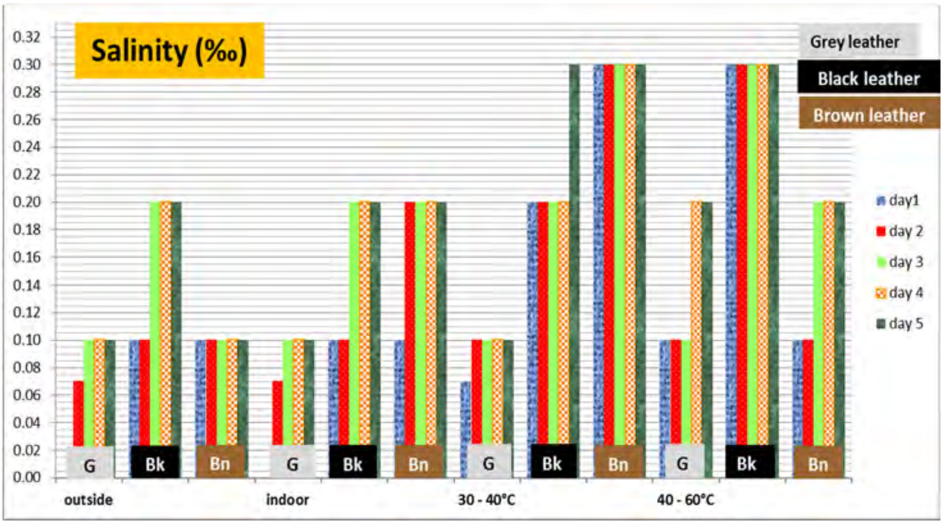

Fig. 6. *Salinity variation for the for the three waste leather type (gray-**G**, black-**Bk** and brown-**Bn**), depending on analysis time and temperature*

As can be seen in figure 6, the **Bk** type of waste leather had the highest values at high temperatures (40-60°C), but also at outside indoor and 30-40°C temperatures. The **Bn** type had the highest values at temperatures of 30-40°C and the **G** type had the lowest values at all temperatures. It can be observed that the salinity generally had a gradual increase grows after the first day of experiment. The increasing of salinity was pronounced at low temperatures.

Figure 7 represents the refractive index variation for for the three waste leather type (gray-**G**, black-**Bk** and brown-**Bn**), depending on analysis time and temperature.

From figure 7 it can be seen that the refractive index increased proportional with the analysis time and has the highest values at outdoor temperatures, for all types of leather. The highest values belong to the **G** waste leather type. The refractive index decreased with the increasing of the temperature. The higher was the refractive index; the cleanest was the water in which the leather was immersed. This is related with the lowest values of the **G** type for the: salinity, TDS and EC values.

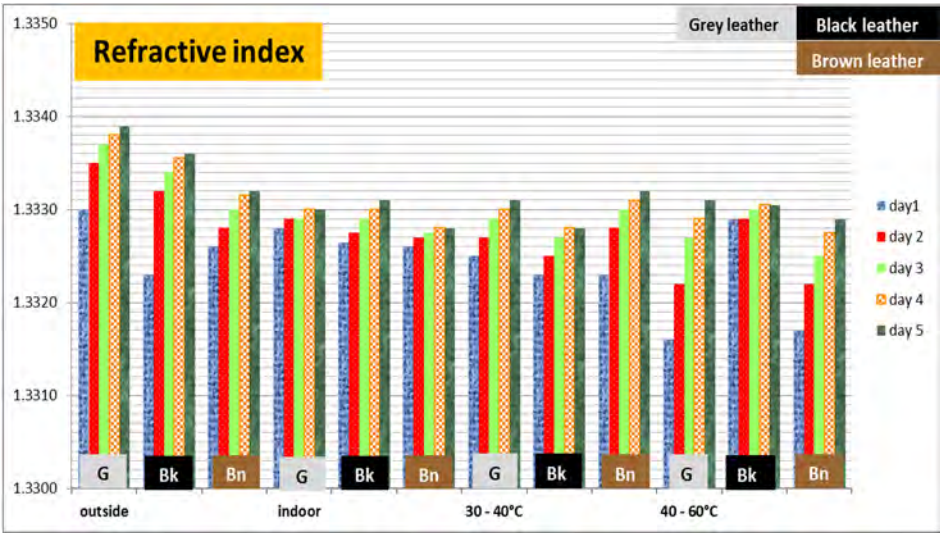

Fig. 7. *Refractive index variation for the for the three waste leather type (gray-**G**, black-**Bk** and brown-**Bn**), depending on analysis time and temperature*

Total chromium analysis

The total chromium concentration was analysed from the leachate of the three types of leather waste: gray-**G**, brown-**Bn** and black-**Bk**.

Figure 8 presents the values of the total chromium concentration in the leachate for the three types of leather waste.

From figure 8, it can be seen that all the samples at all the temperatures range, shown a significant increase of the total chromium concentration in leachate, over the maximum allowed concentration MAC = 70 mg/kg (OM 95, 2005, table 4.1 hazardous waste leachability). That means that the samples are characterized by a hazardous character and represents a serious problem for the environment.

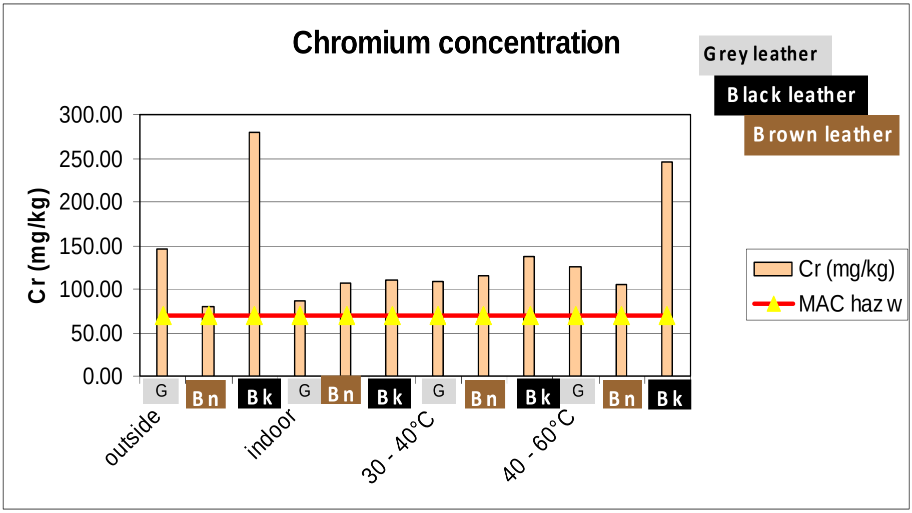

Fig. 8. *The total chromium concentration in the leachate for the for the three types of leather waste: gray-**G**, brown-**Bn** and black-**Bk***

In this respect the **Bk** type had the highest values at outside temperatures, followed by the values at temperatures between 40-60°C. It is interesting to note that for the total chromium concentration increases above the MAC not only at outside-low temperatures, but also at temperatures higher than 40°C. This behavior may be characteristic for this type of leather waste if reach on the open dump landfills and leach in natural condition (winter and summer temperatures). In contrast with other analyzed leather waste types (gray, brown), the total chromium concentration in leachate are much higher for black leather waste, probably resulting due to the absorbed chromium salts in the tanning process. The **G** type had the following highest values after the **Bk** type at the same range of temperatures (low and high).

It can be seen a closely correlation between the pH range (figure 3) and the total chromium concentration values. The **Bk** and **G** types had acidic pH (3-3.5) at outside and high temperatures (40-60°C) and the total chromium values were higher than for the **Bn** type which had a basic pH range (7-8.5) at the same temperatures. If we correlate the obtained values with the pH dependence of the chromium species, Cr (III) and Cr (VI), we can conclude that the **Bk** and **G** type may contain mainly Cr (VI) compounds and the **Bn** type may contain mainly Cr (III) salts.

It is very known that a particular importance has the speciation between the Cr (III) and Cr (VI), because of the carcinogenic action of the Cr (VI) compounds. The Cr (III) and Cr (VI) compounds are accessible to the population due to their presence in many consumer products. The primary ways for exposure are: inhalation, ingestion in the case of Cr (III) and absorption through the skin in case of Cr (VI). The higher solubility and the reaction with cell membrane of the Cr (VI) compounds, than the Cr (III) compounds represent a problem for the human health (Kolomaznik et al., 2008).

CONCLUSIONS

The experimental results obtained from the conductometric tests and analysis of the total chromium concentration highlighted the following:

- The present study shows a strong link between the conductometric tests (pH, EC, TDS, salinity, refractive index) performed for three different types of tanned leather wastes (**G**-gray, **Bn** -brown and **Bk**-black), with the analysis time and the temperature.
- Each type of leather waste had a different behavior depending on temperature and analysis time, maybe because of the different composition with substances, originated from the tanning process (the tanning being done differently according to the leather color and texture).
- The **Bk** type presented the following: an acidic pH ranged between 3-3.5, for all temperatures; higher TDS and EC values at higher temperatures (both 40-60°C and 30-40°C), at ouside temperatures had the highest values in contrast with the other two types **G** and **Bn**; highest values for salinity at highest temperatures (40-60°C), at ouside temperatures had the highest values in contrast with the other two types **G** and **Bn;** the refractive index had higher values for the outside temperatures which for the conductometric parameters valuest were lower and the lower values for the highest temperature range at higher values of the conductometric parameters.

- The **Bn** type presented the following: a basic pH ranged between 7-8.5, for all temperatures; higher TDS and EC values at high temperatures (30-40°C), at ouside temperatures had low values in contrast with the other two types **G** and **Bk**; highest values for salinity at high temperatures (30-40°C), at ouside temperatures had the low values as the **G** type in contrast with **Bk** type**;** the refractive index had higher values for the outside temperatures which for the conductometric parameters valuest were lower and the lower values for the highest temperature range at higher values of the conductometric parameters.
- The **G** type presented the following: an acidic pH ranged between 3-3.5, for all temperatures; lowest TDS and EC values at all temperatures; lowest values for salinity at all temperatures**;** the refractive index had higher values for the outside temperatures which for the conductometric parameters valuest were lower and the lower values for the highest temperature range at higher values of the conductometric parameters.
- Total chromium concentration in the leachate for all three types of leather waste exceeded the MAC for hazardous waste leachability (OM 95, 2005, table 4.1 hazardous waste leachability).
- The **Bk** type had the highest values for the total chromium concentration at outside temperatures and at the highest temperature (40-60°C), followed by the **G** type which had high values at outside temperatures.
- The tanned leather waste is framed in the specific legislation as a non-hazardous waste at code 04 01 08: “waste tanned leather (blue sheeting, shavings, cutting, buffing dust) containing Chromium”, but it should be considered as a hazardous waste, as regards the behavior in aqueous solution, under different conditions of temperature.
- The tanned leather waste cannot be landfilled in municipal landfills, due to the higher concentration of total chromium in leachate.

Because of the higher values of the total chromium analyzed concentration, a particular importance has the speciation between the Cr (III) and Cr (VI), because it is known that the Cr (VI) compounds have carcinogenic action. In this respect further studies regarding the speciation will be developed.

In conclusion is necessary to find new recycling methods for the tanned leather waste, because it requires landfilling in special authorized landfills for hazardous waste.

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