

# Chromium stabilization of tannery sludge by co-treatment with ladle furnace slag

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## Abstract

Hazardous solid wastes may pose a serious risk to human health and to the environment, if not managed appropriately and disposed of safely. In this study, the effective stabilization of tannery sludge, a toxic industrial solid waste produced from the physico-chemical treatment of tannery wastewaters, was examined by the addition of ladle furnace slag (LFS), another industrial solid waste. Moreover, the simultaneous addition of organoclay (a commercially available chemical additive) and LFS for the stabilization of tannery sludge was also examined. The tannery sludge was mixed with LFS and water, as well as with LFS, organoclay and water at different ratios. The mixtures were left for one week ageing and then subjected to the standard leaching test EN 12457-2. Chromium and dissolved organic carbon (DOC) in tannery sludge (the major control parameters of this waste) were found to exceed the respective non-hazardous and hazardous waste limit concentration values respectively, according to the EU Directive 2003/33/EC. The leachates from the tannery waste stabilized with LFS, presented chromium concentrations below the regulation limit for disposal, even in landfills for non-hazardous wastes; however, DOC cannot meet the respective limit value. On the other hand, the leachates of this waste stabilized with LFS and organoclay, presented both chromium and DOC concentrations below the regulation limits for disposal in landfills for non-hazardous wastes. The ecotoxicity of original, as well as of stabilized waste was also evaluated by applying the standard *Microtox* procedure.

**Keywords:** tannery sludge; stabilization; ladle furnace slag; organoclay; leaching test

## 1. Introduction

The process of leather tanning consists of the transformation of animal skin to leather. Chromium salts, specifically the trivalent ones, are the most widely used chemicals in tanneries [1]. The tannery process results to the production of relatively large quantities of wastewaters. The dissolved chromium(III) and other spent (not-consumed) chemicals, which are present in these wastewaters, are mainly removed through the physico-chemical precipitation technique, using inorganic coagulants (and/or lime), before the wastewater is allowed to enter the subsequent biological treatment process. The precipitated (coagulated) solids, including chromium as well as some other co-precipitated organic etc. compounds, are discharged as sludge [2].

The chromium level in this tannery sludge is sufficiently high and its direct landfilling is not allowed, because chromium may be re-dissolved and hence, percolate through the soil during the wet season, resulting to soil and groundwater pollution [1]. The contamination of soils and water sources by chromium poses a serious health threat for humans, plants and animals, noting that the long-term exposure to trivalent chromium is known to cause allergic skin reactions and cancer [2–4].

The process of stabilization converts hazardous substances to more stable chemical forms, which are much less soluble, mobile and therefore, toxic, by using various additives. As a result, wastes can be subsequently safely disposed with minimizing the risk of releasing toxic substances, which could pollute soil, water or groundwater resources [5]. Various stabilizing agents, such as cement, hydrated lime, phosphoric compounds and pozzolanic materials, like fly ash, have been successfully used in different stabilization/solidification processes [4, 5]. These stabilizing additives can decrease the leaching of trace elements mainly through their adsorption to mineral surfaces, the formation of stable complexes with organic ligands, the surface precipitation and ion exchange [6].

However, the high cost of traditional stabilizing additives has prompted the development of alternative materials that are more cost-effective and also, environmentally acceptable. Nevertheless, the examination of tannery sludge stabilization by using alternative materials is rather limited. The main methods, which were proposed and applied for the stabilization of this industrial waste, included the encapsulation in cement matrix by the addition of cement, lime and/or fly ash, as well as the incorporation of tannery waste into a glassy matrix after the addition of specific reagents and the application of thermal treatment at least at 700°C [2–4]. Thus, the co-treatment of ladle furnace slag (another problematic industrial waste) is examined in this study as alternative material, in order to stabilize chromium in tannery sludge with additional benefits, including the reduction of treatment and disposal cost.

Ladle furnace slag (LFS), also known as basic slag or refining slag, is produced in the final stage of steelmaking process, specifically during steel refining in ladle furnaces. A considerable amount of slag is recovered as a by-product, representing about 1/3 of the total amount of slag usually produced in electric arc furnaces. Presently, this

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slag is generally treated as waste and dumped in specific-type landfills. LFS contains mainly calcium aluminosilicates and some Fe oxides [7, 8].

The objective of the present work includes the examination of tannery waste stabilization by using LFS, in order to both stabilize chromium, as well as the rest organic compounds content and the evaluation of stabilization process effectiveness, by using the EN 12457-2 standard leaching test. Additionally, the stabilization of chromium and organic compounds content by using the combination of LFS and specific organoclay as additives was also examined. The classification of stabilized waste according to EU Directive 2003/33/EC, as well as the potential toxic effect, by using common ecotoxicity tests, was also examined.

## 2. Materials and methods

### 2.1. Tannery sludge

The tannery sludge is produced in the specific wastewater treatment plant, accepting wastewaters from the tanneries cluster in the industrial area of Thessaloniki in Northern Greece. The tannery sludge contains mainly trivalent chromium, organic matter, proteins, fats and salts, such as chlorides and sulfates [3, 9] and it was air-dried (up to about 10% moisture) - it is hereafter called “tannery waste”.

### 2.2. Ladle furnace slag

A typical composition of LFS, regarding the oxide compounds content, is given in Table 1. LFS sample with about 1.5% moisture, originated from an electric arc furnace process, was delivered by AEIFOROS S.A. in Thessaloniki.

**Table 1.** Typical composition of LFS according to AEIFOROS S.A.

% wt.						
Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	MgO	MnO	SiO <sub>2</sub>	LOI
9.0	55.0	5.5	7.0	2.0	17.0	4.5

### 2.3. Organoclay

Organoclay is a commercial product produced (and received) by CETCO S.A. It is a semi-granular adsorption media, effective in removing oils, greases and other high molecular weight/low solubility organics.

### 2.4. Stabilization process

The stabilization of tannery waste was studied by using different ratios of tannery waste and LFS, i.e. ratios of 50: 50, 40: 60, 30: 70 and 20: 80. Additionally, the tannery waste stabilization was examined by using different ratios of tannery waste, LFS and organoclay, i.e. ratios of 30: 50: 15, 35: 45: 20, 35: 40: 25, 30: 55: 15, 30: 50: 20 and 30: 45: 25. Homogenization of these mixtures was achieved using the addition of sufficient deionized water to be saturated and the resulting (homogenized) mixtures were left for 7 days for aging. The final stabilized products had about 11–14% moisture.

### 2.5. Leaching test

The evaluation of chemical toxicity was performed by the application of EN 12457-2 standard leaching test. Table 2 shows the basic characteristics of the EN 12457-2 leaching test. The stabilized products were subjected to leaching test after 7 days. The classification of examined wastes was based on the Council Directive 2003/33/EC, regarding the acceptance of wastes at landfills.

**Table 2.** Basic characteristics of the EN 12457-2 leaching test [10].

EN 12457-2	
Particle size	Granular, < 4 mm
Mass of sample	100 g
Leaching solvent	Deionized water, 1000 mL
Liquid/Solid ratio, L/S (L/kg)	10
Time per stage	24 h
Way of mixing	Rotational, 10 rpm

Measurements of pH and electric conductivity (EC) were carried out in the leachates by using a Crison multi-meter. Total Cr concentrations were determined by a Perkin Elmer Atomic Absorption Spectrometer (AAS Analyst 400), whereas the Zn, Se, Pb, Ni, Mo, Cu, Cd, Ba and As concentrations were determined by using a Perkin Elmer Inductively Coupled Plasma–Atomic Emission Spectrometer (ICP-AES 40). DOC was determined with a TOC-V<sub>CSH</sub> E 200 V Shimadzu analyzer and fluoride, chloride and sulfate anions were measured with a Metrohm Ionic Chromatographer (883 Basic IC Plus).

## 2.6. Ecotoxicity test

The toxicity assessment of resulting leachates after the application of aforementioned standard leaching procedure took place by using the common photobacterium *Vibrio fischeri*. Microtox test was based on the bioluminescence inhibition measurement of marine bacteria *Vibrio fischeri*, with exposure times of them to leachates set at 5, 15 and 30 min (standard procedure) and by using the Microtox M500 Analyzer (SDI). The pH of leachates was adjusted to 8.0 with HCl. The toxicity of leachates was evaluated, following the 81.9% basic test protocol, i.e. with sample concentration 81.9%.

## 3. Results and discussion

### 3.1. Characterization of raw wastes

The major physico-chemical characteristics of leachates produced from the raw wastes, i.e. from LFS and tannery waste, by using the standard leaching test EN 12457-2 are presented in Table 3. The leachate of tannery waste was slightly alkaline with pH value 8.5, in accordance also with the respective literature [1, 9, 11], while the EC value was 4.1 mS/cm. The pH value of LFS leachate is highly alkaline, i.e. 12.8, as it was observed also in similar studies [7]. The presence of free lime (CaO) and magnesia (MgO) in LFS increases the respective pH value in the range of 10–13 [12]. The high pH value is due to the hydrolysis of lime that yields free hydroxyl ions. The leachates of highly alkaline materials present also high conductivity values. Additionally, the LFS leachate contains also significant calcium cations' concentration, resulting in the EC value of 12.8 mS/cm.

**Table 3.** Physico-chemical analysis results of leachates obtained from LFS and tannery waste, by using EN 12457-2 standard leaching test (L/S 10 L/kg), in comparison with the respective limit values of Council Directive 2003/33/EC [13].

L/S 10 L/kg	Tannery waste	LFS	Inert waste	Non-hazardous waste	Hazardous waste
pH	8.5	12.8	-	-	-
EC (mS/cm)	4.1	10.5	-	-	-
<b>mg/kg of dry substance</b>					
As	0.02	0.04	0.5	2	25
Ba	2.5	30	20	100	300
Cd	nd	0.02	0.04	1	5
Cr total	<b>42*</b>	1.7	0.5	10	70
Cu	0.8	nd	2	50	100
Mo	0.09	0.06	0.5	10	30
Ni	1.9	0.03	0.4	10	40
Pb	nd	nd	0.5	10	50
Se	nd	0.05	0.1	0.5	7
Zn	2.3	0.2	4	50	200
DOC	<b>3,700</b>	50	500	800	1,000
F <sup>-</sup>	nd	25	10	150	500
Cl <sup>-</sup>	6,050	90	800	15,000	25,000
SO <sub>4</sub> <sup>2-</sup>	9,450	185	1,000	20,000	50,000

nd: not detected

\*Value exceeding the regulation limit for disposal in **non-hazardous waste** landfills.

\*\*Value exceeding the regulation limit for disposal in **hazardous waste** landfills.

The chemical analysis of tannery waste leachate reveals the presence of high chromium concentration (42 mg/kg), i.e. above the maximum permissible limit for disposal in non-hazardous waste landfills (which is 10 mg/kg). Trivalent chromium is the dominant oxidation state of Cr in tannery waste [11], noting that hexavalent chromium was not formed during tannery industry process, as the presence of relatively high organic matter concentrations does not favour the oxidation of trivalent chromium [3, 4]. In addition to chromium, a number of other potentially toxic elements were also present in the leachate, including As, Ba, Cu, Mo and Zn; however, the concentrations of these toxic metals

were below the permissible limit concentration values, regarding waste acceptable in inert waste landfills (Table 3), apart from Ni concentration (1.9 mg/kg), which is above the respecting limit value (0.4 mg/kg). Cd, Pb and Se were not detected in this leachate.

The further characterization of tannery waste showed rather high concentration of Dissolved Organic Carbon (DOC, 3,700 mg/kg), which was higher, than the respective limit value for waste acceptable even in hazardous waste landfills (1,000 mg/kg), due to the initial high organic content of this waste, which has been also previously reported [11]. The concentrations of chloride and sulfate anions in the obtained leachate, i.e. 6,050 mg/kg and 9,450 mg/kg respectively, were below the permissible limit values for disposal in non-hazardous waste landfills (which are 15,000 mg/kg and 20,000 mg/kg, respectively). Hydrated calcium sulfate was also formed during the precipitation of tannery waste from the reaction between chromium sulfate and calcium hydroxide [3]. However, fluoride anions were not detected in the leachate.

LFS leachate contains trace amounts of elements potentially mobile and toxic to the environment; however, As, Cd, Mo, Ni, Se, Zn were released in relatively small concentrations in the leachate, i.e. below the respective limit values for wastes acceptable in inert waste landfills (Table 3). Cu and Pb were not detected in the leachate, while Ba and Cr concentrations (i.e. 30 mg/kg and 1.7 mg/kg, respectively) were below the maximum permissible limit values for disposal in non-hazardous waste landfills (which are 100 mg/kg and 10 mg/kg, respectively).

Low value of DOC was observed in the leachate of LFS (50 mg/kg), i.e. below the limit value for waste acceptable in inert waste landfills (500 mg/kg). In addition, low values of chloride and sulfate anions were observed, i.e. 90 mg/kg and 185 mg/kg respectively, also below the respective limit values for wastes acceptable in inert waste landfills (800 mg/kg and 1,000 mg/kg, respectively). Fluoride anions' concentration in the LFS leachate was 25 mg/kg and did not exceed the limit value for waste acceptable in non-hazardous waste landfills (which is 150 mg/kg); fluoride anions were attributed to the composition of LFS, in which calcium fluoride (as fluorite) exists [14].

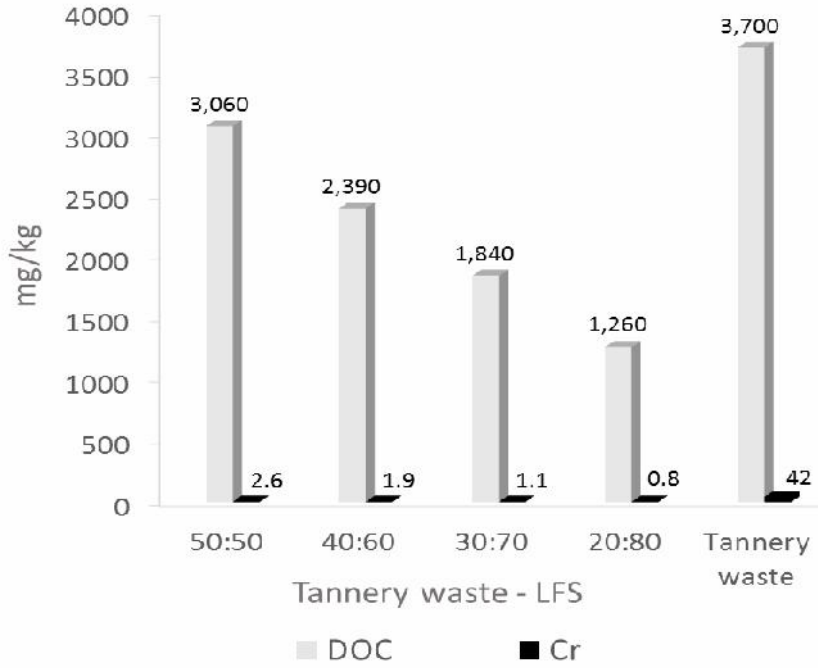
According to these results, the concentrations of total chromium and DOC in the leachate of tannery waste are considerably high and therefore, this waste cannot be accepted, even at specific landfills for hazardous wastes. On the other hand, LFS is acceptable even in non-hazardous waste landfills, according to Council Directive 2003/33/EC. Inorganic materials, such as this waste (LFS), are highly alkaline and could be used as effective additives for the immobilization of heavy metals in contaminated solid wastes or soils. LFS is a material capable of activating lightly pozzolanic properties [8, 12]. Due to these properties, LFS might be a suitable additive for the stabilization of tannery waste and therefore, its appropriateness was further examined, noting that there are not relevant studies, according to our current knowledge.

### 3.2. Stabilization of tannery waste

The standard leaching test methods are used in order to assess: (a) whether land disposal of a specific waste is an appropriate method of management, (b) the effectiveness of (eventually) applied waste treatment process, and (c) the environmental impact of wastes. When water passes through a solid waste, certain ingredients can be dissolved, considering that the pH value is a critical parameter, controlling the leachability especially of metals.

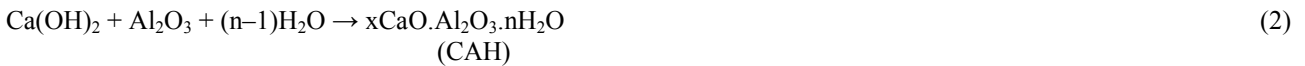
The co-treatment of tannery waste with LFS increased the pH from about 8.5 (initially) in the tannery waste leachate up to 12.5 for the stabilized products, because during the leaching procedure some alkali species were transported into the aqueous phase, resulting to pH increase. The values of EC were also high enough, i.e. about 7.8–8.9 mS/cm. The presence of metals in leachates is mainly dependent on the chemical complexes that are formed in the solid phase between the LFS and the tannery waste, as well as on their speciation in the formed complexes. It has been shown that an increase in pH results to an increase in the fixation of metals by the surface of solids [15]. Low (acidic) pH values can cause more intense reactions and can transport dissolved constituents from the solid phase into the leachates, whereas high (alkaline) pH values in most cases can reduce the solubility of various components, including metals [4].

The total chromium concentrations, as well as the DOC concentrations in the leachates of stabilized products obtained with LFS addition are presented in Figure 1 in comparison with the total chromium and DOC concentrations in the leachate of single (tannery) waste. Total chromium concentrations in the leachates of stabilized products (0.8–2.6 mg/kg) are less, than those mentioned in the Council Directive 2003/33/EC for disposal in non-hazardous waste landfills (which is 10 mg/kg). Steel slag has been successfully used to stabilize/solidify soil contaminated with Cr(III) and Cr(VI) and the leaching of both Cr(III) and Cr(VI) species was found to decreased substantially with the increase of slag content [12]. On the other hand, DOC concentrations in the leachates of stabilized products (1,260–3,060 mg/kg) were found to be higher than that mentioned in the guidelines for disposal even in hazardous waste landfills (1,000 mg/kg). As it was expected, DOC concentrations were decreased, as the mass ratio of LFS was increasing and the tannery waste mass ratio was accordingly reduced. However, the reduction of DOC values was higher than the expected values, considering only the dilution of tannery waste with the LFS addition. High pH (alkaline) values can increase the transportation of dissolved constituents from the solid phase into the leachates, i.e. can favour the leaching of organic compounds.



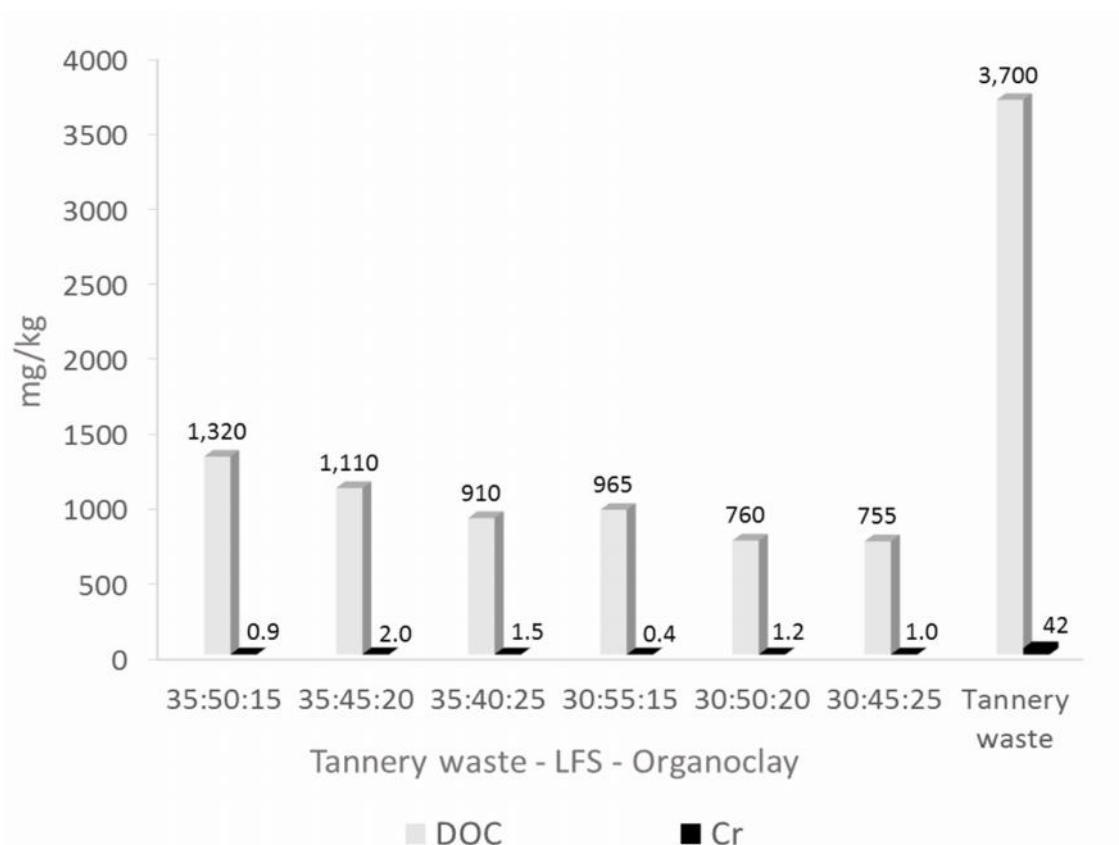
**Figure 1.** Total chromium and DOC concentrations in the leachates (mg/kg) obtained for various Tannery waste–LFS mass ratios.

Aluminosilicates and Fe oxides existing in LFS possess variable charge surfaces, where specific adsorption of metals may take place [12]. Due to its specific mineralogical composition, LFS can develop certain cementitious and hydraulic/pozzolanic properties, considering also that both hydration of calcium silicates and carbo-hydration processes are expected to take place upon exposure to usual environmental conditions [8]. The solubility of silica and alumina increases at alkaline pH values, making these elements available for reaction with free calcium, originating from LFS; therefore, the cementitious hydrates CAH and CSH compounds are formed, according to the following equations [2, 4]:



It is most likely that chromium is transformed to the respective calcium–chromium minerals, or immobilized into the stable calcium silicate hydrate phase (CSH) by the applied stabilization treatment [4].

The co-treatment of tannery waste with LFS and organoclay increased the pH values of stabilized products up to 12.7. EC values were also increased up to about 7.8–9.5 mS/cm. Figure 2 presents Cr and DOC concentrations in the respective leachates for each examined proportion of tannery waste with LFS and organoclay. Mixing tannery waste with LFS and organoclay in the 30: 50: 20 ratio was resulting to the production of stabilized solid waste, acceptable for disposal even in non-hazardous waste landfills, i.e. having DOC 760 mg/kg and total Cr 1.2 mg/kg, in comparison with the respective EU regulation limits (which are: total Cr 10 mg/kg and DOC 800 mg/kg). More specifically, Cr leaching potential was found to decrease by about 90%, while DOC leaching potential by about 32%, i.e. beyond the expected reduction from the simple dilution by the mixing application. The organophilic surface properties of organoclay additive are consisted mainly from covalently linked organic moieties. The adsorptive capacity of organoclay reduces the required final protective cap thickness, as compared to in-situ applied sand caps. This adsorptive capability can provide an appropriate sub-aqueous chemical isolation of contaminated waste or soil sample, mitigating the organic contaminant transport into the water.



**Figure 2.** Total chromium and DOC concentrations in the leachates (mg/kg) for various Tannery waste–LFS–Organoclay mass ratios.

Metal concentrations in the leachate of stabilized tannery waste with LFS and organoclay addition at mass ratio 30: 50: 20 are presented in Table 4. As, Ba, Cu, Mo, Ni and Zn metals were released in detectable amounts in the leachate, although these concentrations did not exceed the respective limit values for disposal in non-hazardous waste landfills. Cd, Pb and Se metals were not detected in the leachate. The high pH value of LFS favours both the adsorption of heavy metals and their surface precipitation, resulting to their stabilization. It has been observed that LFS has a significant capacity to sorb especially Pb, Cu and Ni metals [7].

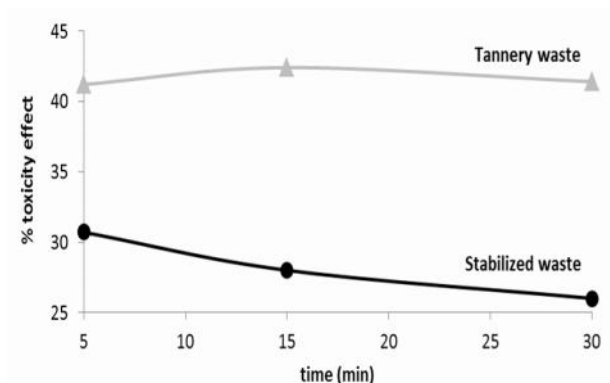
**Table 4.** Selected toxic metals (mg/kg) in the leachate (using L/S: 10 L/kg) of stabilized tannery waste with LFS: tannery waste: organoclay = 30: 50: 20 (mass ratio)

mg/kg (dry substance)								
As	Ba	Cd	Cu	Mo	Ni	Pb	Se	Zn
0.02	1.7	nd	2.4	0.03	1.5	nd	nd	0.25

nd: not detected

### 3.3. Ecotoxicity test

The toxicity effect of leachate obtained from tannery waste, when using the photobacterium *Vibrio fischeri* did not exceed 43%. The bioluminescence inhibition was found 41.2%, 41.4% and 42.4% for 5, 15 and 30 min exposure time, respectively (Figure 3). The sensitivity of *Vibrio fischeri* against the heavy metals, such as As, Ba, Cu, Se and Zn, at the concentrations range usually detected in these leachates' types, is rather low, or insignificant for most examined cases [16]. However, the other physicochemical characteristics, such as hardness (Ca, Mg), nutrients, bioavailability of metals and the interactive effects among the different constituents may also influence the resulting ecotoxicity of a relevant sample [17]; noting that a gradual reduction of toxicity effect, almost linear, during time is typical of organic compounds. The percentage effect of leachate from the stabilized waste under the optimized conditions (i.e. tannery waste: LFS: organoclay, 30: 50: 20, mass ratio) on *Vibrio fischeri* reached 31%, as the bioluminescence inhibition was found 30.7%, 28.0% and 26.0% for 5, 15 and 30 min exposure time, respectively (Figure 3). This curve is typical of behavior for several heavy metal compounds, i.e. the percentage toxicity effect is reduced during time.



**Figure 3.** Toxicity effect (%) of the leachates from the original tannery waste, as well as from the stabilized one (conditions: tannery waste: LFS: organoclay, 30: 50: 20 as mass ratio) on *Vibrio fischeri* in accordance with time response.

#### 4. Conclusions

There is a demand in tannery industry for an efficient, environmentally sound and low-cost process, which could allow the disposal of rich-chromium sludge/solid waste, produced by the physico-chemical wastewater treatment. Another industrial solid waste, i.e. LFS, was examined as an alternative amendment material for the stabilization of this hazardous (tannery) waste to achieve an integrated management.

The degree of stabilization achieved by LFS was satisfactory, as far as the concentration of chromium is concerned. In accordance to the Council Directive 2003/33/EC, the leachates of stabilized waste with LFS had chromium concentration values below the respective limit values for disposal at landfills for non-hazardous wastes. However, the presence of high organic compounds leaching potential remains a problem in this method. On the other hand, mixing tannery waste with LFS and organoclay in 30: 50: 20 mass ratio, resulted in a stabilized solid waste, which fulfils the regulation concentration limit for disposal even at non-hazardous waste landfills, i.e. DOC 760 mg/kg (with limit value 800 mg/kg) and Cr 1.2 mg/kg (with limit value 10 mg/kg).

Additionally, apart from the physicochemical analysis of tannery waste, as well as of the stabilized product, the evaluation of potential environmental hazard of these wastes was achieved by using the photobacterium ecotoxicological test. Specifically, the toxicity effect of original tannery waste leachate on *Vibrio fischeri* was up to 42%, while that of the respective stabilized waste was found lower, i.e. between 26 to 31%.

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