

Characterization of tannery wastes Comparison of three leachability tests

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Abstract

12 samples from different tanning industries and corresponding to leather wastes and semi-processed leather trimmings and shavings have been characterized. The characterization includes the determination of moisture level, reactivity, analysis of dry sample, analysis of the effluent from the leachability test and toxicity test with *Photobacterium phosphoreum* and *Daphnia magna*. The leachability of Cr, Zn, Pb, Cd, Ni, Cu, Ba and phenolic compounds was evaluated by three different methods: the extraction procedure (EP) according to the Spanish legislation (very similar to the EP test from USEPA), the extraction procedure from the EEC proposal of Directive and the toxicity characteristic leaching procedure (TCLP) from the USEPA. © 1997 Elsevier Science B.V.

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1. Introduction

One of the main problems associated with the activity of tannery industries is the great amount of solid and liquid wastes (animal remains, hides and skins, shavings and trimmings, sludges, process effluents, etc.) generated. The most common way to manage these solid wastes is by disposing of them on controlled land sites. However, it is very difficult to characterize these solid wastes due to the great amount and variety of treatments used in the tannery industry.

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Due to the fact that chromium metal is the most important tanning agent, a great deal of research has been done to determine the content of chromium in tannery wastes and sludges and to establish whether the trivalent or the hexavalent chromium ion is present in the wastes [1–6]. Some other studies have been made in order to minimize the amount of tannery wastes [7,8], to treat them [9,10] and to use them [11–14].

However, chromium is not the only compound present in tannery wastes. As leather undergoes several different treatments, a great number of chemical compounds can be present in tannery wastes and there is the possibility that some of these wastes could be considered as hazardous or toxic.

Regulations about solid wastes are each time more and more restrictive and this has provoked a certain reticence from different types of industrial activities in accepting these regulations. In Spain, the basic law of hazardous and toxic wastes [15] lays down the requisites for a waste to be considered as hazardous or toxic. Moreover, the EEC proposes introducing further regulations [16]. On the other hand, the Regional Autonomous Government of the Valencian community has legislative powers regarding in environmental aspects and, in particular, the disposal of solid waste. The Valencian government is studying the disposal of solid wastes and the tannery industry has demanded special treatment for the wastes generated. For this reason, our Department is studying the characterization of tannery solid wastes from several industries for the Environmental Protection Agency of the Valencian government.

On the other hand, the characterization of these wastes requires the effluent composition obtained from a leachability test to be known. Due to the fact that in the regulations there is no single method to develop this leachability test, the different tannery wastes were tested with three different leachability methods in order to compare the results obtained.

2. Materials and equipment

A total of 12 samples, from 12 different tanning industries, all provided by the Environmental Agency of the Valencian Government, were analyzed. The samples were grouped into two categories (Table 1):

2.1. *Leather wastes*

Finished articles, with a great surface. Discarded leather articles with different colors. Four samples: L1, L2, L3 and L4. Sample L1 is colored blue, brown and white; sample L2 blue, brown and black; L3 brown, grey, blue, lilac and black; L4 white and brown.

2.2. *Shavings*

Semi-processed leather trimmings and shavings, colored blue. Eight samples: S5, S6, S7, S8, S9, S10, S11 and S12.

The analysis of the elements present in the samples was obtained by means of an electron microscopy with X-ray analyzer (JEOL JSM-840). X-Ray fluorescence analysis

Table 1
Description of waste samples

Sample		Color	Type	Origin
L1	1	Blue	Leather waste	Canals
	2	White	Leather waste	Canals
	3	Brown	Leather waste	Canals
L2	1	Blue	Leather waste	Paterna
	2	Brown	Leather waste	Paterna
	3	Black	Leather waste	Paterna
L3	1	Brown and blue	Leather waste	Paterna
	2	Grey	Leather waste	Paterna
	3	Brown	Leather waste	Paterna
	4	Black	Leather waste	Paterna
	5	Lilac	Leather waste	Paterna
	6	Blue	Leather waste	Paterna
L4	1	White	Leather waste	Paterna
	2	Brown	Leather waste	Paterna
S5		Blue	Shavings	Manises
S6		Blue	Shavings	Manises
S7		Blue	Shavings	Manises
S8		Blue	Shavings	Manises
S9		Blue	Shavings	Manises
S10		Blue	Shavings	Manises
S11		Blue	Shavings	Manises
S12		Blue	Shavings	Manises

of the samples was developed using a sequential automatic spectrophotometer (Phillips TW-1480). The liquid solutions from the TCLP leachability test were obtained using a Millipore zero head extractor and a Millipore rotatory agitator. pH determination in lixiviates was made with a Crison pH-meter (MicroPH 2001). The analysis of metal levels in the samples from the leachability tests was made with an inductively coupled plasma atomic emission spectrometer (Perkin-Elmer, Optima 3000). Colorimetric determination was made with a spectrophotometer (Shimadzu, UV 120-02). Toxicity determination with *Photobacterium phosphoreum* was developed using Microtox equipment (Mod. 500). The inhibition test was developed with *Daphnia magna* from our Department.

3. Experimental

To characterize the tannery wastes, the following treatment was applied to all the samples, irrespective of their origin or physical appearance.

3.1. Election of a representative sample

In order to obtain a representative sample, leather and shaving samples were reduced to an appropriate particle size (< 0.95 cm) using a pair of scissors or a razor blade. The representative sample was homogenized manually taking different portions of the original sample.

3.2. Determination of the moisture

The moisture was determined drying the sample at 105°C in an oven until constant weight.

3.3. Analysis of the characteristics of reactivity

The characteristics of reactivity of the sample were studied according to the EPA regulations [17].

3.4. Analysis of a dry sample by X-ray fluorescence and electronic microscopy

After measuring the moisture level, the dry sample was used to determine metals present. Two analytical techniques were used: a qualitative one, X-ray fluorescence, and a semi-quantitative one, electronic microscopy + X-ray spectrometer dispersive energy microanalysis. The first technique detects presence in the sample of elements whose atomic number is higher than that of magnesium. The second technique gives semi-quantitative information about the elements present in the point of the sample which has been studied. Because the information obtained corresponds to this particular point, each sample was studied in several points in order to obtain an average value. In this way, it was possible to know whether a certain metal was present in the sample or not.

3.5. Leachability test

The leachability test of the samples was carried out using three different methods: the extraction procedure according to the Spanish legislation [18], the extraction procedure according to the EEC proposal of legislation [16] and the TCLP procedure [19].

pH of the samples was measured at the beginning of the tests. Control of pH was carried out during the tests.

The extraction procedure in the Spanish legislation is analogous to the EPA extraction procedure toxicity [20]. The procedure uses de-ionized water as extractor fluid and the pH is modified by adding acetic acid to bring the pH down to 5.0 when necessary. Initially, the amount of water added is 16 times the amount of sample. In our case, acetic acid was not added because the pH remained lesser than 5.0 ± 0.2 during the test. Finally, an amount of water 4 times the amount of sample is added until a liquid/solid ratio = 20 is reached. The sample is agitated for 24 h and after this period the solid and the liquid phases are separated by filtration. Although no temperature control is established, the extraction must be carried out between 20 and 40°C (in our case, 25°C).

The extraction procedure from the EEC proposal of legislation uses a sample which contains, at least, 100 g in dry basis and is carried out at 20°C. The sample is introduced into a 2 l bottle and 1 l of de-ionized water is added. The bottle is closed and placed in a rotatory agitator for 24 h. After this period, the solid phase is separated by filtration or centrifugation. If the liquid phase is not clean, it is filtered again, using a 0.45 µm filter.

The TCLP method uses two different procedures, depending on whether volatile compounds are involved or not. In our case, the procedure when volatile compounds are not involved was used. The extraction fluid depends on the initial pH of the sample; in our case, all the samples had a pH < 5.0 and, therefore, extraction fluid number 1 was used. This fluid was prepared by adding 5.7 ml of glacial HOAc to 500 ml of water without interferents, then adding 64.3 ml of 1.0 M NaOH and diluting to a volume of 1 l. The sample and the extraction fluid were put into a borosilicate bottle and placed in a rotatory agitator (32 ± 2 rpm) for 18 h. After this period, the solid and the liquid phases were separated by a gradual vacuum filtration.

3.6. Analysis of the lixivate

Lixivate liquids from the three extraction procedures were analyzed using inductively coupled plasma atomic emission spectrometry (ICP) and UV-Vis. spectrophotometry.

Concentrations of Cr, Zn, Pb, Cd, Ni, Cu and Ba were measured by ICP using the method described in Standard Methods [21].

Concentration of phenolic compounds was determined by a colorimetric method [22]. The method detects all the *ortho*- and *meta*-phenolic compounds and some of the *para*-phenolic compounds. It is based on the reaction, in the presence of potassic ferrocyanide, of the 4-aminoantipyrine with those phenolic compounds that can be distilled with vapor. The resulting aqueous solution is colored and its absorbance can be measured at 500 nm.

Determination of hexavalent chromium was made using the colorimetric method of the diphenylcarbazide [21]. This is the most reliable and sensitive method, as Rutland et al. [3] indicated in their article about the problems associated with hexavalent chromium determination. Precautions to be taken pointed out by these authors have been considered. In the method, Cr^{VI} reacts with diphenylcarbazide in an acidic solution and a red-violet colored solution is obtained, whose absorbance can be measured at 540 nm.

3.7. Toxicity determination

Toxicity determination in the lixivate liquid was carried out with *P. phosphoreum* [23] and *D. magna* [24].

In the test of bioluminescence, the lixivate is put in contact with a culture of *P. phosphoreum*, a bacteria emitting light and measuring the loss of emitting power because of the action of the toxic substances present in the lixivate. The result is expressed as the concentration which causes the emitting power to decrease by 50% (EC₅₀) after 15 min of exposure. The pH during the test was kept between 6 and 8 to ensure that the toxicity is only due to the substances present in the lixivate and not to

the effect of the pH on the bacteria. Zinc sulphate, with a EC_{50} between 0.5 and 2.5 ppm of Zn^{2+} , was used as a control standard.

In the inhibition test, the lixivate is put in contact with a certain number of organisms (*D. magna*) bred in the laboratory, observing the percentage of organisms immobilized after a certain period of time. The conditions used in the test were:

- Species: *D. magna* which were less than 72 h old.
- Origin: Science Faculty, Alicante University.
- Temperature: $20 \pm 1^\circ C$.
- Breeding method: As described in [24].
- Feeding: *Chlorophicea* or green algae *Scenedesmus quadricauda*.
- Concentration tested: 750 mg l^{-1} .
- Origin of the reconstituted river water: Distilled water with 0.2 g l^{-1} of sodium bicarbonate, 0.224 g l^{-1} of calcium chloride and 0.026 g l^{-1} of potassium sulphate; pH 7.9.
- Lighting: 16 h with fluorescent lamp and 8 h of darkness.
- Test duration: 24 and 48 h.

According to the Spanish regulations [18], the lixivate from the EP procedure is toxic if $EC_{50} < 750 \text{ mg l}^{-1}$. As the number of *D. magna* available was not enough, the test was carried out using only a concentration of 750 mg l^{-1} . To check the test, a standard of potassium dichromate (1.2 ppm) whose EC_{50} (between 0.9 and 1.5 ppm) is known together with a blank solution was used.

Table 2 shows a comparison between some different criteria for considering a waste

Table 2
Limits in different legislations for considering a waste as toxic

	EP toxicity test (USA)	EP toxicity test (Spanish legislation)	Spanish legislation on content in waste	EEC proposal of directive
Operating conditions of leachability	pH ≤ 5 ; $20 < T < 40^\circ C$	pH ≤ 5 ; $20 < T < 40^\circ C$		$20^\circ C$ water
Mass ratio extracting mixture/sample	1:20	1:20		1:10
As	5.0 ppm		0.01%	0.2–1 ppm
Ba	100.0 ppm			
Cd	1.0 ppm		0.01%	0.1–0.5 ppm
Cr ^a	5.0 ^a ppm		Cr ^{VI} < 0.01%	0.1–0.5 ppm
Cr ^{VI}				
Pb	5.0 ppm			0.4–2.0 ppm
Hg	0.2 ppm			0.02–0.1 ppm
Se	1.0 ppm			
Cu				2–10 ppm
Ag	5.0 ppm			
Zn				2–10 ppm
Ni			0.01%	0.4–2.0 ppm
Phenols				20–100 ppm
EC_{50} <i>P. phosphoreum</i>		3000 mg l^{-1}		
EC_{50} <i>D. magna</i>		750 mg l^{-1}		

^a This limit does not apply if only Cr^{III} is present.

as toxic. In accordance with the US legislation, any waste that exceeds the limits indicated for the components outlined in Table 2 must be considered as toxic. The Spanish legislation considers the EP test for studying the EC_{50} of *P. phosphoreum* and *D. magna*; when these values of EC are less than those indicated in Table 2, the waste must be considered as toxic. In addition, the Spanish legislation considers a waste as toxic when the concentration of carcinogen compounds [25] is greater than 0.01% in the waste. According to the EEC legislation [26], a waste is considered as toxic when the concentration of carcinogen and very toxic compounds in the waste is greater than 0.1%, the concentration of toxic compounds is greater than 3% and the concentration of harmful compounds is greater than 25%. On the other hand, there is a proposal for a directive relating to the disposal of wastes [16] where a waste would be considered as toxic when the concentration in the effluent from a leachability test with water exceeded the limits indicated in Table 2. Note that the limits established by the proposal are lesser than those from the EPA and this can be considered as logical taking into account that no acid is added in the European test.

4. Results and discussion

4.1. Moisture of the samples

Table 3 shows the moisture content of the samples. It can be observed that leather wastes have a lower level of moisture (18–25%) than shavings (45–57%).

4.2. Reactivity of the samples

No sample has shown any kind of reactivity: instability, reactivity with water, emission of gases or detonation.

Table 3
Moisture of the samples

Sample	Moisture (wt%)
L1	22.02
L2	24.96
L3	17.95
L4	21.99
S5	56.40
S6	51.77
S7	52.83
S8	45.27
S9	56.12
S10	50.37
S11	54.23
S12	51.12

Table 4
Relation of elements detected by XRF in the samples

Sample	Elements
L1	Al, S, Ca, Cl, Cu, Cr, Sr, P, Fe, Pb, K, Si, Zn, Ti, Br, W
L2	Al, S, Ca, Cl, Cu, Cr, Sr, P, Fe, Pb, K, Si, Zn, Ti, Br, W, Co
L3	Al, S, Ca, Cl, Cu, Cr, Sr, P, Fe, K, Si, Zn
L4	Al, S, Ca, Cl, Cr, Sr, P, Fe, K, Si, Ni, Ti, Zr
S5	Al, S, Ca, Cl, Cr, P, Fe, K, Si, Ti, Br
S6	Al, S, Ca, Cl, Cr, P, Fe, Si
S7	Al, S, Ca, Cl, Cr, Sr, P, Fe, K, Si, Ti
S8	Al, S, Ca, Cl, Cr, Sr, P, Fe, K, Si, Zn, Ti, Br
S9	S, Ca, Cl, Cu, Cr, P, Fe, Si, Zn, Ti, Br
S10	Al, S, Ca, Cl, Cr, Sr, P, Fe, Si, Zn, Ti, Br
S11	S, Ca, Cl, Cu, Cr, Sr, P, Fe, Si, Zn, Ti
S12	Al, S, Ca, Cl, Cr, Sr, P, Fe, K, Si, Zn, Ti

Table 5
Wt% (on dry solid) of elements determined by SEM–EDX

Sample	Na	Si	S	Ca	Cl	Cr	Mg	P	Al	Ti	K	
L1	1	0.76	0.25	6.44	0.67	1.37	3.54	0.13	0.26	1.19	nd	0.23
	2	0.94	1.10	6.87	0.36	3.90	2.89	0.12	0.24	0.87	4.52	0.22
	3	0.60	0.20	4.60	0.33	0.84	4.60	0.10	1.60	0.10	0.05	0.10
L2	1	1.19	0.51	3.79	1.21	6.43	5.12	0.11	0.12	0.31	nd	0.25
	2	0.30	1.29	3.33	1.55	0.66	4.84	0.15	0.68	1.16	nd	0.80
	3	2.30	3.52	5.02	2.60	1.22	6.12	0.52	0.31	0.73	nd	0.51
L3	1	0.82	0.37	4.49	1.11	4.48	3.58	0.16	1.31	0.81	nd	0.21
	2	0.34	0.27	4.90	0.94	0.85	4.07	0.19	1.90	0.27	nd	nd
	3	0.60	0.50	5.25	1.28	2.52	4.69	0.20	0.45	0.45	nd	nd
	4	1.31	0.34	4.59	0.78	1.56	1.82	0.71	1.03	0.45	nd	0.28
	5	0.34	0.27	4.34	0.78	0.61	4.54	0.12	1.63	0.30	nd	nd
	6	1.18	0.39	4.48	1.17	1.56	4.73	0.28	1.57	0.34	nd	0.35
L4	1	0.83	1.08	2.37	0.95	0.45	1.81	0.08	0.24	1.33	3.33	0.08
	2	0.43	0.48	3.89	0.87	0.92	5.25	0.05	0.50	0.32	0.04	0.10
S5	5.01	0.16	6.17	1.28	10.18	5.50	0.75	nd	nd	nd	0.07	
S6	3.95	0.10	6.13	3.52	9.42	5.13	0.56	nd	nd	nd	0.02	
S7	2.53	0.11	5.28	0.36	6.84	8.58	nd	nd	nd	nd	nd	
S8	4.65	0.34	10.85	10.72	12.35	4.97	nd	nd	0.10	nd	nd	
S9	2.80	nd	2.78	0.25	10.21	3.20	nd	nd	nd	nd	nd	
S10	2.27	nd	4.92	1.62	8.19	6.64	nd	nd	nd	nd	nd	
S11	3.99	0.25	3.49	0.36	11.15	5.18	nd	nd	nd	nd	nd	
S12	3.16	0.08	5.35	0.09	5.91	5.02	nd	nd	nd	nd	nd	

nd: not detected.

Table 6

Ratios (mol of Na + 2 mol of Ca)/(mol of Cl), (3 mol of Cr)/(2 mol of S) and (mol of Na + 2 mol of Ca + 3 mol of Cr)/(mol of Cl + 2 mol of S) by SEM-EDX

Sample		$\frac{\text{mol Na} + 2 \text{ mol Ca}}{\text{mol Cl}}$	$\frac{3 \text{ mol Cr}}{2 \text{ mol S}}$	$\frac{\text{mol Na} + 2 \text{ mol Ca} + 3 \text{ mol Cr}}{\text{mol Cl} + 2 \text{ mol S}}$
L1	1	1.72	0.51	0.61
	2	0.53	0.39	0.42
	3	1.80	0.92	0.99
L2	1	0.62	1.25	0.97
	2	4.87	1.34	1.63
	3	6.69	1.12	1.67
L3	1	0.72	0.73	0.73
	2	2.58	0.76	0.90
	3	1.27	0.82	0.90
	4	2.18	0.37	0.61
	5	3.13	0.96	1.09
	6	2.50	0.97	1.18
L4	1	6.59	0.70	1.17
	2	2.40	1.24	1.35
S5		0.98	0.82	0.89
S6		1.31	0.77	0.99
S7		0.66	1.5	1.19
S8		2.12	0.42	0.99
S9		0.46	1.06	0.69
S10		0.78	1.24	1.04
S11		0.61	1.37	0.92
S12		0.85	0.86	0.86

4.3. Analysis of the dry samples

Table 4 shows the elements detected by X-ray fluorescence (XRF). Table 5 shows the results obtained by scanning electron microscopy + X-ray spectrometer dispersive energy microanalysis (SEM-EDX). Leather samples were grouped and analyzed according to their colors. The average percentage of Cr in the leather wastes ranged from 1.8 to 6.1% (mean value 4.1%, sample standard deviation 1.3%), whereas in the shavings it ranged from 3.2 to 8.6% (mean value 5.5%, sample standard deviation 1.6%). A considerable percentage of Ti was detected in two samples (L1₂ and L4₁) which had a white color. Elements such as Si, Mg, P and Al were detected in all the leather samples.

Table 6 shows the ratios obtained by SEM-EDX: (mol of Na + 2 mol of Ca)/(mol of Cl), (3 mol of Cr)/(2 mol of S) and (mol of Na + 2 mol of Ca + 3 mol of Cr)/(mol of Cl + 2 mol of S). These ratios, obtained by a semi-quantitative method, seem to indicate the presence of sodium, chloride, chromium and sulphate in the stoichiometric relation corresponding to NaCl, CaCl₂ and Cr₂(SO₄)₃. Chemicals NaCl and CaCl₂ are used in the tannery industry, but the chromium salt used is CrOHSO₄. However, it is possible that the retention of chromium and sulphate are close to the ratio mol of Cr/mol of S equal to 2/3, corresponding to Cr₂(SO₄)₃. As can be seen, the values of the ratio (mol of Na + 2 mol of Ca + 3 mol of Cr)/(mol of Cl + 2 mol of S) are those

Table 7

Final pH in the lixiviates obtained by the extraction procedure according to the Spanish legislation (A), the extraction procedure according to the EEC proposal of legislation (B) and the TCLP procedure according to the USEPA legislation (C)

Sample	pH(A)	pH(B)	pH(C)
L1	3.9	3.8	4.7
L2	4.3	4.3	4.9
L3	3.9	4.0	4.4
L4	4.3	4.4	4.9
S5	3.5	3.5	4.3
S6	3.8	3.8	4.6
S7	3.8	3.9	4.6
S8	3.7	3.6	4.5
S9	3.8	3.4	4.6
S10	3.9	4.0	4.6
S11	3.8	3.9	4.5
S12	3.3	3.3	4.6

closest to 1, indicating the presence of the products previously mentioned. In this analysis, only the majority elements (Na, Cl, Cr, S) have been considered. Ratios different to unity can be due to the presence of other chemicals (Al, Mg, K, Ti, Ca) in salts, acids and bases.

4.4. Leachability tests

Three different leachability tests have been carried out with all the samples: the extraction procedure according to the Spanish legislation (A), the extraction procedure according to the EEC proposal of legislation (B) and the TCLP procedure according to the USEPA legislation (C).

Table 7 shows the final pH of each test. No great variations of pH were observed during the tests. In the case of the extraction procedure according to the Spanish legislation it was not necessary to add acetic acid because pH was always lesser than 5.0. Therefore, the only difference in practice with the extraction procedure according to the proposal of the EEC was the liquid/solid ratio.

Table 8 shows the concentration (ppm) of several metals (Cr, Ba, Pb, Zn, Cd, Cu and Ni) analyzed in the three lixivate liquids obtained from each sample. Data in the table are mean values from two or three analyses. In four samples (S7, S8, S9 and S10), the leachability tests and the corresponding analyses were repeated some months later, with very similar results.

Cr is the metal with the greatest concentration. As no Cr^{VI} was detected in any sample when the diphenylcarbazine method was used, concentrations in Table 8 must be considered as Cr^{III}. Therefore, according to the USEPA legislation, the samples should have been classified as non hazardous if only chromium had been analyzed. Table 9 shows a comparison between our data and those obtained by Menden and Rutland [2]. A great similarity in both leather and shaving samples can be observed.

Table 8

Concentration (ppm) of elements in the lixiviates obtained by the extraction procedure according to the Spanish legislation (A), the extraction procedure according to the EEC proposal of legislation (B) and the TCLP procedure according to the USEPA legislation (C)

Sample	L1	L2	L3	L4	S5	S6	S7	S8	S9	S10	S11	S12	
Cr	A	2.56	2.96	14.6	22.9	39.1	78.0	33.4	23.7	5.86	22.9	35.4	61.5
	B	1.68	1.22	14.7	14.7	35.8	59.8	52.3	12.8	5.05	11.4	28.0	51.6
	C	6.56	28.9	48.4	65.0	228	254	197	162	168	250	183	317
Ba	A	nd	0.16	0.20	0.18	0.30	0.12	0.56	0.14	0.18	0.76	0.36	0.16
	B	nd	0.005	0.02	0.005	0.11	0.10	0.08	0.12	0.17	0.28	0.09	0.09
	C	1.01	0.36	0.54	0.26	0.21	0.26	0.23	0.16	0.24	0.16	0.16	0.14
Pb	A	0.40	0.46	0.20	0.24	0.68	0.76	0.30	0.78	0.42	0.28	0.40	0.60
	B	0.08	0.15	0.14	0.15	0.41	0.49	0.20	0.38	0.25	0.21	0.34	0.44
	C	0.09	0.21	0.19	0.32	0.59	0.74	0.42	0.54	0.56	0.57	0.48	0.78
Zn	A	0.90	0.14	0.28	nd	0.30	0.24	0.38	0.32	0.04	0.16	0.16	0.66
	B	0.66	0.11	0.20	0.04	0.32	0.32	0.42	0.51	0.33	0.42	0.35	0.39
	C	1.28	0.39	0.87	0.34	0.44	0.51	0.55	0.39	0.47	0.63	0.48	0.55
Cd	A	nd	0.02	0.02	nd	0.06	0.06	0.02	0.06	0.02	0.02	0.04	0.04
	B	nd	0.008	0.009	0.007	0.02	0.03	0.01	0.02	0.01	0.01	0.02	0.01
	C	0.004	0.012	0.012	0.012	0.04	0.048	0.031	0.037	0.039	0.042	0.036	0.046
Cu	A	0.016	nd	0.08	0.06	nd	0.04	0.02	0.08	0.08	nd	0.04	0.02
	B	0.01	0.01	0.01	0.06	0.04	0.06	0.02	0.08	0.01	0.02	0.04	0.01
	C	0.005	0.015	0.023	0.057	0.04	0.07	0.027	0.049	0.034	0.024	0.039	0.012
Ni	A	0.28	0.28	0.20	0.32	0.36	0.44	0.24	0.42	0.42	0.18	0.22	0.06
	B	0.02	0.05	0.05	0.04	0.16	0.013	0.08	0.12	0.08	0.07	0.11	0.05
	C	0.028	0.08	0.058	0.065	0.19	0.20	0.13	0.17	0.27	0.16	0.17	0.12

nd: not detected.

Table 9

Comparison with Cr data from Menden and Rutland [2]

	This work Cr (ppm)			Menden and Rutland Cr (ppm)		
	EP	TCLP	TCLP/EP	EP	TCLP	TCLP/EP
Leather						
Mean	10.8	37.2	4.62	11.2	40	5.44
Range	2.56–22.9	6.56–65.0	2.56–9.77	2.20–48.6	5.71–148	1.20–11.2
Std. Dev.	9.8	25.2	3.45	10.2	31.7	2.44
<i>n</i>	4	4	4	17	27	15
Shavings						
Mean	37.5	219	6.15 ^a	43.4	139	4.33
Range	5.86–77.96	162–317	3.26–10.9 ^a	8.49–140	71.2–246	1.49–10.7
Std. Dev.	22.8	52.8	2.37 ^a	35.3	51.8	2.02
<i>n</i>	8	8	7	21	21	21

^a Sample S9 with a TCLP/EP ratio = 28.7 was not considered.

Table 10

Weight percentage of Cr solubilized in the lixiviates obtained by the extraction procedure according to the Spanish legislation (A), the extraction procedure according to the EEC proposal of legislation (B) and the TCLP procedure according to the USEPA legislation (C)

Sample	% extraction (A)	% extraction (B)	% extraction (C)
L1	0.14	0.05	0.36
L2	0.11	0.02	1.08
L3	0.75	0.38	2.48
L4	1.30	0.42	3.68
S5	1.42	0.65	8.27
S6	3.04	1.67	9.90
S7	0.78	0.61	4.58
S8	0.95	0.26	6.53
S9	0.37	0.16	10.51
S10	0.69	0.17	7.52
S11	1.37	0.54	7.06
S12	2.45	1.03	12.65

No other metal analyzed exceeded the levels proposed in the legislation for considering a waste as toxic [19] except Pb. The level of Pb in three samples (S5, S6 and S12) was slightly higher than the limit established in the EEC proposal [16] and therefore these three samples should be considered as hazardous.

When comparing the three tests, no general rule can be established. The three extraction procedures differentiate on two factors: the liquid/solid ratio (10:1 or 20:1) and the extracting agent (water or a mixture of acetic acid and sodium hydroxide), which conditions the final pH of the sample. In our case, tests A and B used the same extracting agent and had similar pH (Table 7), and therefore the liquid/solid ratio was the only difference. Tests A and C used the same liquid/solid ratio, but the extracting agent and the pH were different. Tests B and C used a different liquid/solid ratio, extracting agent and pH. In some cases (Cu, Ni, Cd), the most severe extraction was obtained in the majority of the samples when the leachability test according to the Spanish legislation was used. This would indicate a combined effect of the liquid/solid ratio and the pH in order to obtain a most severe extraction. This effect of the liquid/solid ratio was previously observed in a paper about characterization of ceramic sludges [27]. In other cases (Cr, Zn) the most severe extraction was obtained when the TCLP test was used, indicating that the extracting agent and the pH were the controlling factors.

Table 10 shows the percentage of extraction of Cr in the three lixiviates as compared with the Cr detected by SEM–EDX (taking into account the moisture of the sample):

$$\% \text{ Extraction} = \frac{(L/S) \times (\text{Cr concentration})}{[1 - (\% \text{ moisture}/100)] (\% \text{ Cr by SEM-DEX})}$$

Information in this table, only serves as a guide because SEM–EDX data are semi-quantitative. Only a small quantity of chromium present in the sample is extracted during the leachability tests. In general, Cr is more easily extracted in shavings than in

Table 11

Concentration (ppm) of phenols in the lixiviates obtained by the extraction procedure according to the Spanish legislation (A), the extraction procedure according to the EEC proposal of legislation (B) and the TCLP procedure according to the USEPA legislation (C)

Sample	Phenols (ppm) (A)	Phenols (ppm) (B)	Phenols (ppm) (C)
L1	2.56	1.24	1.33
L2	1.58	0.44	0.37
L3	2.64	0.55	0.71
L4	6.00	1.87	2.10
S5	1.05	1.07	1.04
S6	0.32	0.19	0.13
S7	3.42	2.16	2.05
S8	3.80	2.22	1.55
S9	42.40	20.15	17.61
S10	3.26	1.15	0.92
S11	1.52	1.15	1.02
S12	2.60	1.21	1.06

leather wastes. When the TCLP method is used the percentage of Cr extracted ranges between 0.36 and 3.68% for leather wastes and between 4.58 and 12.65% for shavings. Results with the other two methods are similar although Cr is less vigorously extracted than with the TCLP method (the percentage of Cr extracted ranges between 0.02 and 1.30% for leather wastes and between 0.14 and 3.04% for shavings).

Table 11 shows the concentration (ppm) of phenolic compounds in the three lixivate liquids obtained from each sample. These concentrations are very small, except the concentration in sample S9 (42.4, 20.15, and 17.61 ppm, respectively), which is close to or at about the lower limit established for considering the waste as toxic from the point of view of its disposal on landsites [16].

Table 12

Toxicity values (EC_{50}) (ppm) by *P. phosphoreum* in the lixiviates obtained by the extraction procedure according to the Spanish legislation (A), the extraction procedure according to the EEC proposal of legislation (B) and the TCLP procedure according to the USEPA legislation (C)

Sample	EC_{50} (ppm) (A)	EC_{50} (ppm) (B)	EC_{50} (ppm) (C)
L1	74203	85997	29195
L2	21135	> 450000	414075
L3	28022	35994	18011
L4	52493	77348	82940
S5	37472	12269	5470
S6	10990	7279	4417
S7	18842	10075	31636
S8	329174	375349	240502
S9	27385	22356	13033
S10	14001	45677	26764
S11	4222	2035	4780
S12	23546	16474	23395

4.5. Toxicity determination

Table 12 shows the results of the test of bioluminescence with the three lixivate liquids. Only sample (S11) had a value of EC_{50} of *P. phosphoreum* close to 3000 ppm, the limit in the Spanish legislation. To identify the presence of toxic organic compounds in the sample, an extract with *n*-hexane was analyzed by GC + MS, showing the presence of aromatic compounds with a similar structure to that of benzothiazole (95.9% probability) and of 1,2-benzene-dicarboxylic acid, butyl-2-methyl-propylester (94.6% probability). The first is considered as harmful and a derivative compound, 2-(thiocyanomethylthio)-benzothiazole, is used in the tannery of skins [25], whereas compounds with a similar structure to 1,2-benzenedicarboxylic acid, butyl-2-methyl-propylester are considered as toxic in the lists of the EPA.

In the inhibition test, in all the samples, none or only one *Daphnia* was immobilized and therefore, it was tested that the EC_{50} with *D. magna* was more than 750 mg l^{-1} , which is the limit indicated in Spanish legislation [18].

5. Conclusions

With respect to the characterization of the samples, the following conclusions can be reached.

The moisture percentage was notably greater in shaving samples than in leather waste samples.

No reactivity was detected in any sample.

From the SEM–EDX analysis, the average percentage of Cr in leather samples was 4.1%, whereas in shaving samples it was 5.5%. A high percentage of Ti was detected in two white colored samples.

The analysis of the lixivate liquids obtained with 3 different leachability tests showed that no metal exceeded the level to consider a waste as toxic, except the level of Pb in three samples which was greater than the lower limit according to the EEC proposal. These three samples would therefore be considered as hazardous.

No Cr^{VI} was detected in the lixivates of any sample and therefore the concentration of Cr corresponds to Cr^{III} . Consequently, the samples should be considered as no toxic.

Only one sample had an EC_{50} with *P. phosphoreum* close to the toxicity limit according to the Spanish legislation. The chemical which causes this toxicity could be benzothiazole (95.9% probability) or 1,2-benzenedicarboxylic-acid, butyl-2-methyl-propylester (94.6% probability).

No toxicity with *D. magna* was detected in any sample.

When comparing the three leachability tests, the following conclusions can be reached:

There is no single leachability test that always extracts the greatest amount of any of the analyzed compounds.

There is no single factor which can be considered responsible for the strength of the attack.

In general, the results are quite reproducible with the three leachability tests.

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