

# *ecodefating*

## **LIFE PROJECT – ECODEFATTING LIFE13 ENV/IT/00470**

“Environmentally friendly natural products instead of chemical products in the degreasing phase of the tanning cycle”

### **DELIVERABLE - ACTION C.4 Report on environmental monitoring of pre- industrial defatting phase with natural products**



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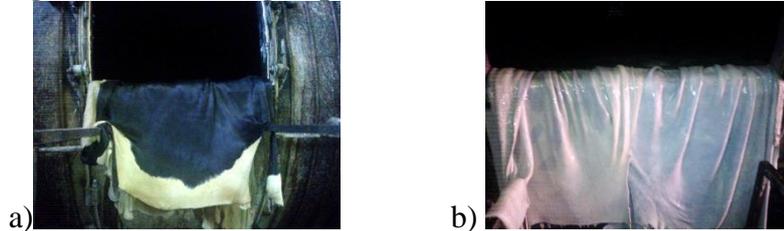
## 2. List of abbreviations, acronyms and symbols

°C	Celsius degree	ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
µg/L	<b>micro gram per litre</b>	ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
µm	<b>micro meter</b>	K	<b>Kelvin</b> (absolute temperature)
Al	<b>aluminum</b>	L (l)	<b>litre(s)</b>
As	<b>arsenic</b>	l/min.	<b>litre per minute</b>
B	<b>boron</b>	mg	<b>milligram(s)</b>
Ba	<b>barium</b>	mg/L(l)	<b>milligram(s) per litre</b>
Be	<b>beryllium</b>	micro-	<b>10<sup>-6</sup></b>
BOD	<b>biological oxygen demand</b>	ml	<b>millilitres</b>
ca.	<i>circa</i> ( <b>approximately</b> )	milli-	<b>10<sup>-3</sup></b>
Ca(ClO) <sub>2</sub>	<b>calcium hypochloride</b>	mm	<b>millimetre(s)</b>
Ca(OH) <sub>2</sub>	<b>calcium hydroxide</b>	m <sup>3</sup>	<b>cubic meter</b>
Cd	<b>cadmium</b>	Mn	<b>manganese</b>
Co	<b>cobalt</b>	MnSO <sub>4</sub>	<b>manganese sulphate</b>
COD	<b>chemical oxygen demand</b>	ms	<b>millisecond(s)</b>
conc.	<b>concentrated</b>	NaOH	<b>sodium hydroxide</b>
CO <sub>2</sub>	<b>carbon dioxide</b>	Ni	<b>nickel</b>
Cr	<b>chromium</b>	nm	<b>nanometer(s)</b>
Cu	<i>cyprium</i> (copper)	O <sub>2</sub>	<b>oxygen</b>
CVAA	<b>cold vapor atomic absorption</b>	Pb	<i>plumbum</i> (lead)
DMA	<b>direct mercury analyzer</b>	ppb	<b>parts per billion</b>
Fe	<i>ferrum</i> (iron)	ppm	<b>parts per million</b>
h	<b>hour</b>	Sb	<i>stibium</i> (antimony)
HCl	<b>hydrochloric acid</b>	Se	<b>selenium</b>
Hg	<i>hydrargyrum</i> (mercury)	Tl	<b>thallium</b>
H <sub>2</sub> O <sub>2</sub>	<b>hydrogen peroxide</b>	V	<b>Volt</b>
H <sub>3</sub> PO <sub>4</sub>	<b>phosphoric acid</b>	Zn	<b>zinc</b>
HNO <sub>3</sub>	<b>nitric acid</b>		

### 3. Introduction

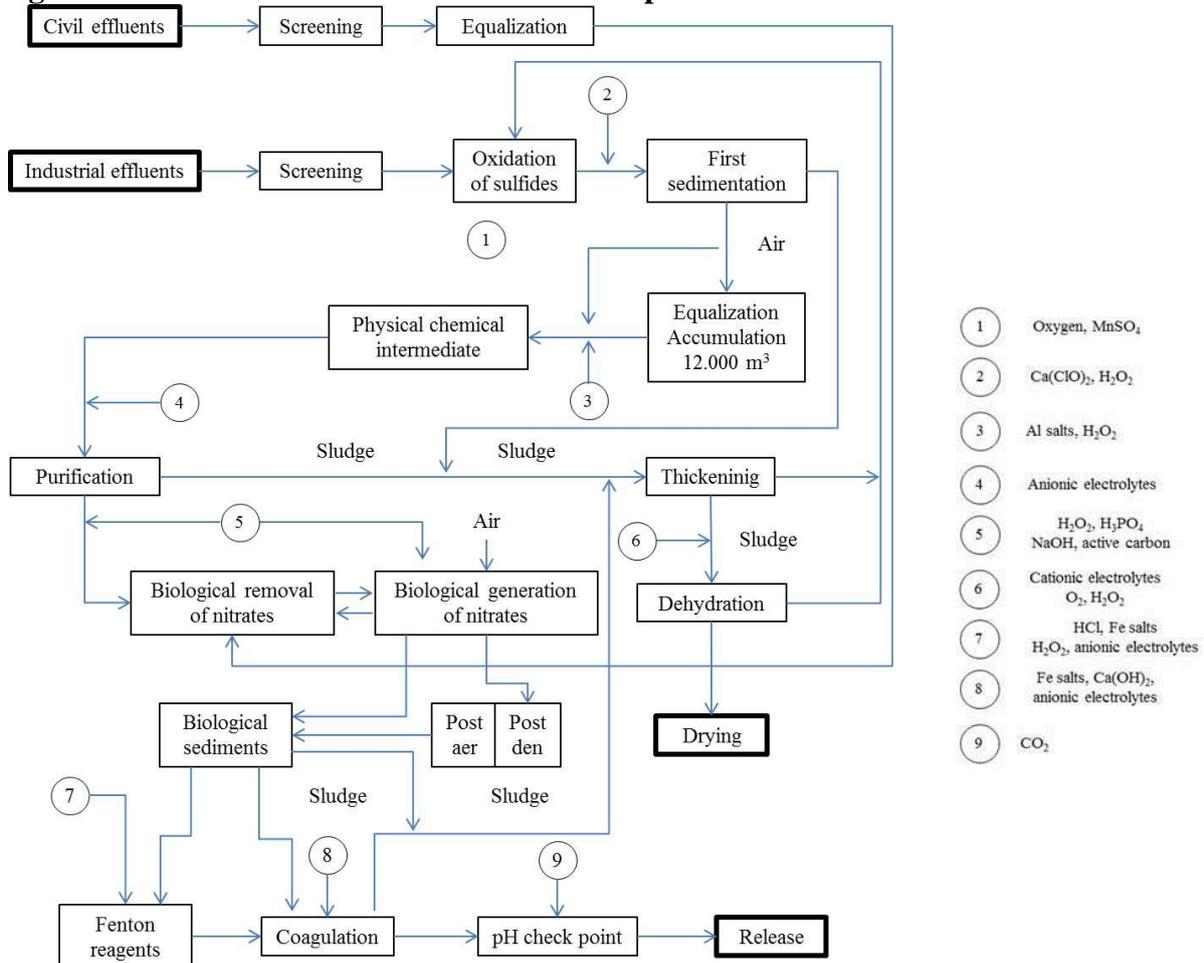
This report presents the results of the environmental impact of defatting wastewaters, coming from action B.3 at pre-industrial level (**Figure 3.1**).

**Figure 3.1 Defatting at pre-industrial level: a) before; b) after**



The defatting demonstrations were carried out on bovine and equine hides, as well as on calf-hides, representing the typical activity of a tannery during its production routine. In the case of the bovine and equine processing, the effluents were sampled after each stage involving the use of the defatting agent: soaking, liming and deliming. In the case of calf-hide processing the effluents were sampled at the end of the whole procedure. Even for the defatting at pre-industrial level, the defatting agent was EDF-20. The effluents were treated with activated sludge, to simulate the real biological oxidative conditions for water treatment inside a dedicated plant (**Figure 3.2**).

**Figure 3.2 Water treatment scheme in Cuoioedepur**



A further treatment with activated carbon was also introduced, to simulate the physico-chemical steps, that can be turned on either before or after the stage involving activated sludge. In addition, effluents from bovine and equine hide processing were also analysed for their heavy metal content, to compare the results with those obtained from the effluents after pig and ovine skin processing.

#### 4. Treatment of effluents from the pre-industrial demonstration with activated sludge

The activated sludge was collected from the water treatment plant CuoioDepur consortium, which is one of the two main infrastructures in S. Corce sull'Arno, dealing with the purification of tanneries' and civil effluents. Industrial wastewaters from tanneries flow down to the water plant in dedicated sewer pipes, that are separated from those collecting wastewaters of civil activities. The industrial pipes are publicly inaccessible and are inspected by authorized technical personnel on a three to six month period. Activated sludge is a biological consortium of several microorganisms in the form of a water suspended flocculent biomass, including friendly bacteria, protozoa, amoebas, fungi and others. The microorganisms of the sludge are at the basis of biological oxidation; their role is to use the organic substances present in the wastewater and degrade them to smaller and less dangerous compounds, that in part are used by microorganisms themselves for their nourishment and reproduction. The sludge was collected as a semisolid watery mixture in a plastic tank directly on site and it was kept under a constant flow of air for 24-28 h. In this way the microorganisms of the biomass remained under aerobic activities, ensuring the complete metabolism of the exogenous substances present in the liquid phase at the time of collection and thus, the assessment of the degradation activity of the pollutant content in tannery wastewater from new sources. The air purge was necessary to avoid any possible anaerobic mechanism of self-survival, inducing the microorganisms to keep themselves alive through a form of cannibalism (**Figure 4.1**).

**Figure 4.1 Activated sludge under air purge**



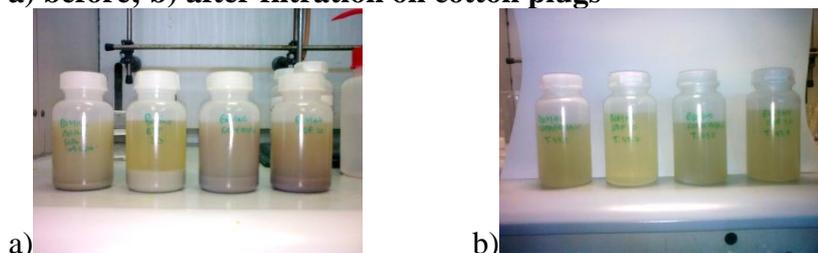
The monitoring action of wastewater treatment started with the preparation of the samples, to be put into contact with the activated sludge. Aliquots of 50 mL were taken from the separate phase of soaking, liming and deliming, having care to collect them as homogeneous as possible (**Figure 4.2**).

**Figure 4.2 Preparation of samples for treatment with activated sludge**



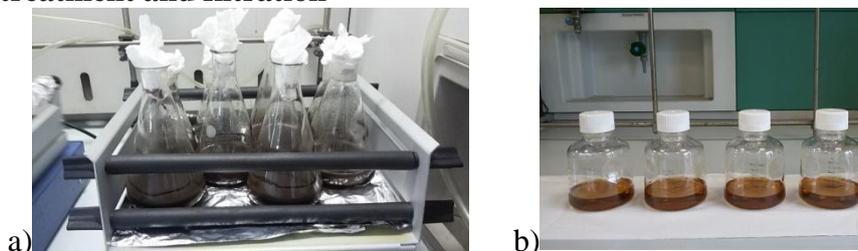
This operation was carried out for the effluents coming from the defatting of bovine and equine hides with EDF20 and with the commercial product Polause-SG50 for comparison purposes. The samples were diluted with tap water in 1:1 ratio to a total volume of 400 ml and filtered on cotton by gravity. In the case of the effluent from the defatting of bovine hides with EDF20 a gross suspension of muddy material was observed and this could be removed by simple filtration on a cotton plug by gravity, recovering a clear filtrate. In the other three cases, the muddy solid was too fine to stay on the filter. Therefore, after a first filtration on cotton the filtrate was allowed to settle at 4 °C and then subjected to a second filtration on a nylon 0.45 µm filter (**Figure 4.3**).

**Figure 4.3 Wastwaters from bovine and equine hide defatting: a) before; b) after filtration on cotton plugs**



In the case of effluents from calf-hide processing the samples were not filtered. The tests were performed on 50 mL aliquot of wastewater, brought into contact with 30 mL of air purged activate sludge. The resulting mixtures were shaken in open air for 48 h and then filtered on cellulose membranes having porosity of 0.45 µm, to remove the sludge biomass (**Figure 4.4**).

**Figure 4.4 Wastwaters: a) with activated sludge; b) after 48 h treatment and filtration**



The COD and BOD analyses of the five samples, expressed in mg O<sub>2</sub>/l, showed fluctuating results before and after the treatment with sludge (**Table 4.1**).

**Table 4.1 Analyses of effluents before and after treatment with sludge**

Effluent	Product	Before treatment			After treatment		
		COD	BOD	BOD/COD	COD	BOD	BOD/COD
		mg O <sub>2</sub> /l			mg O <sub>2</sub> /l		
Bovine	EDF-20	1360	562	0.41	573	115	0.20
	SG50	1466	665	0.45	337	80	0.24
Equine	EDF-20	1441	542	0.38	567	129	0.23
	SG50	1794	649	0.36	573	137	0.24
Calf-hide	EDF-20	1546	104	0.07	8365	2100	0.25

It could be said that the effluents from equine hide processing had a higher polluting chemical content than that observed in the effluents from the bovine one. One of the reasons may be found in the work procedure of equine hide processing, which had a higher degree of complexity and also involved the use of thioalcohol derivatives in the liming stage, to remove hair from the hides. However, in general the estimated biodegradability of the effluents, expressed as BOD/COD ratio, showed an acceptable level of rate, oscillating around 0.4 which is indicative for an average speed of biodegradation. Nonetheless, it was found quite surprising that after the sludge treatment of the effluents the biodegradability of the supernatants decreased by 50% on average from the original values, despite that the COD content had been reduced to about 20-30% of the original values. A reasonable explanation of this unexpected trend is associated to the absence of any pre- or post-treatment phase of the effluents such as sedimentation, flocculation, oxidation of sulfides and biological generation of nitrates, that implement the treatment of wastewaters with activated sludge. The oxidation of sulfides is fundamental to achieve the purification of wastewaters, since sodium sulfide ( $\text{Na}_2\text{S}$ ) and sodium hydrosulfide ( $\text{NaHS}$ ) are the reducing agents of choice, to convert raw hides into a malleable and soft material before entering the tanning stage to become leather. Sulfides are responsible for the deterioration of the purification process, inducing poor oxygenation and the generation of toxic waste. This rationale is also consistent with the results of the treatment of effluents from calf-hide processing, showing the same rate of biodegradability for the supernatant after treatment. In this case the high level of COD and consequently of BOD, could be attributed to some residual sludge in the supernatant. The next treatment of the supernatants with active carbon (0.2 g / 50 ml of sample) confirmed the good work done by the activated sludge, since the value of the COD dropped below the threshold limit of the instrument (ca. 50 mg/l  $\text{O}_2$ ) for the effluents from both bovine and equine hide processing. In the case of effluents from the defatting of calf-hides the COD was remarkably reduced by 98% of the original value.

**Table 4.2 COD of effluents after contact with carbon**

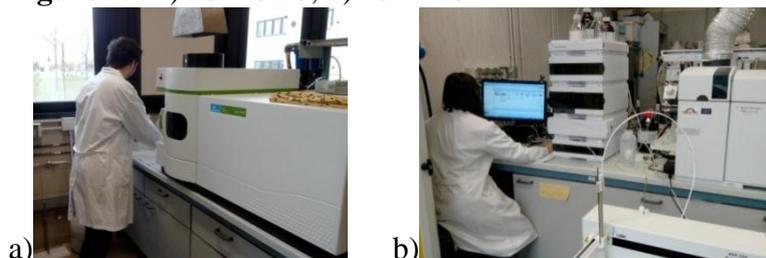
Effluent	Product	COD (mg $\text{O}_2$ /l)	
		After sludge	After carbon
Bovine	EDF-20	573	< 50
	SG50	337	< 50
Equine	EDF-20	567	< 50
	SG50	573	< 50
Calf-hide	EDF-20	8365	180

These results cleared out the importance of wastewaters pre-treatment before entering into the tanks containing activated sludge, whose adaptability was efficacious towards the new defatting agent.

### 5. Determination of metal content in defatting effluents from action B.3

As already pointed out in the deliverable C.3, the monitoring of metals is a fundamental indicator to control the quality of any incoming material and processes. The analysis of Al, As, B, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Be, Ba, Sb, Tl, Pb, Se and Cd metal was carried out in semi quantitative fashion, using the Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (**Figure 5.1**).

**Figure 5.1** a) ICP-OES, b) ICP-MS.



ICP-MS measurements were carried out with a quadrupole Agilent 7700 spectrometer, equipped with a collision cell system. Samples were introduced into the plasma by an auto sampler Agilent ASX-520. The instrument was fitted with a MicroMist Agilent standard nebulizer for 7700 and a Scott-type double-pass glass spray chamber cooled to 4°C. A solution of 10 µg/L of iridium in 2% HNO<sub>3</sub> was used as internal standard, according to the conditions of the instrument (**Table 5.1**).

**Table 5.1 Instrumental parameters for the Agilent 7700 ICP MS**

<b>Operating conditions</b>	
<b>Radiofrequency power</b>	1550 W
<b>Plasma flow rate</b>	15.0 L/min
<b>Carrier flow rate</b>	1.05 L/min
<b>Helium</b>	4.5 mL/min
<b>Octapole bias</b>	-18.0 V
<b>Octapole RF</b>	200 V
<b>KED</b>	3.5 V
<b>Sampling depth</b>	8 mm
<b>Acquisition parameters</b>	
<b>Dwell time</b>	300 ms
<b>Number of sweeps</b>	300

ICP-OES measurements were carried out with an Optima 8000 ICP-OES Spectrometer. ICP-OES is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions, emitting electromagnetic radiation at wavelengths characteristic of a particular element. It is a flame technique with a flame temperature ranging from 6000 to 10000 K. The intensity of the emission is indicative of the concentration of the metal within the sample. Approximately 350 mg of unknown sample were placed in a Teflon container with 2 ml of 69% HNO<sub>3</sub>, 1 ml of 30% H<sub>2</sub>O<sub>2</sub> and 6 ml of conc. HCl at room temperature for 1 h. After that, the mixture was put in a microwave digester for 30 min at 180 °C. The liquid was then transferred in 50 ml flasks and analysed. Mercury content was determined by Milestone Direct mercury analyser DMA-80 (**Figure 5.2**).

**Figure 5.2 DMA-80**



The technique associated to the DMA-80 instrument does not require any sample preparation and delivers comparable results to those obtained with Cold Vapor Atomic Absorption (CVAA) or ICP-MS instruments, that however do require sample preparation, often turning tedious, costly, and time-consuming. The DMA-80 combines the techniques of thermal decomposition, catalytic conversion, amalgamation, and atomic absorption spectrophotometry. Controlled heating stages are implemented to first dry and then thermally decompose the sample, which is confined inside a quartz tube. A continuous flow of oxygen carries the products of decomposition through a catalyst bed, where all mercury species are reduced to elemental Hg and driven to a gold amalgamator where the mercury is selectively trapped. The system is purged with argon gas and the amalgamator is subsequently heated, releasing all mercury vapors to the single beam, fixed wavelength atomic absorption spectrophotometer. The intensity of the absorption is measured at 253.7 nm and it is proportional to the content of mercury in the sample.

The analyses were carried out on effluent samples, taken after rehydration of the hides before their soaking and after the last delimiting stage of the work process, before the hides entered into tanning. Effluents from the use of both EDF20 and the commercial product SG50 were screened. The total metal content found was quite low in the effluents from bovine hide processing and most of the metals were below the detection limit. Even more important was the low content of mercury, which was only 5% of the 1 ppb threshold limit (**Table 5.1**).

**Table 5.1 Heavy metals in effluents from bovine hide defatting**

Before soaking					Before tanning				
metal	ICP-OES		ICP-MS		metal	ICP-OES		ICP-MS	
	EDF20	SG50	EDF20	SG50		EDF20	SG50	EDF20	SG50
Al	-	11.80	-	11.83	Al	2.61	-	2.64	-
As	-	5.49	-	5.48	As	4.83	2.87	4.81	2.79
B	-	-	-	-	B	-	-	-	-
Ba	2.07	0.75	-	0.75	Ba	2.07	1.97	2.09	1.86
Be	-	-	-	-	Be	-	-	-	-
Cd	-	-	-	-	Cd	-	-	-	-
Co	-	-	-	-	Co	-	-	-	-
Cr	2.13	2.01	2.11	2.04	Cr	49.40	11.6	49.39	11.63
Cu	-	-	-	-	Cu	9.81	-	9.78	-
Fe	14.60	20.90	14.58	20.90	Fe	108.5	21.3	108.6	21.42
Mn	0.68	1.88	0.68	1.87	Mn	2.21	1.98	2.21	1.99
Ni	-	-	-	-	Ni	-	-	-	-
Pb	1.94	-	1.94	-	Pb	0.78	-	0.78	-
Sb	1.33	2.28	0.43	2.28	Sb	1.33	1.24	1.32	1.21
Se	-	1.05	-	1.05	Se	0.19	1.95	0.16	1.99
Tl	-	-	-	-	Tl	0.22	-	0.22	-
V	8.18	-	8.19	-	V	-	-	-	-
Zn	-	0.74	-	0.69	Zn	-	-	-	-
metal	before soaking		before tanning						
Hg*	EDF20	SG50	EDF20	SG50					
	0.05	0.05	0.05	0.05					

\*: ppb

Similar results were obtained from the analyses of the effluents from the equine hide processing (**Table 5.2**).

**Table 5.2 Heavy metals in effluents from equine hide defatting**

Before soaking					Before tanning				
metal	ICP-OES		ICP-MS		metal	ICP-OES		ICP-MS	
	EDF20	SG50	EDF20	SG50		EDF20	SG50	EDF20	SG50
Al	-	2.61	-	2.59	Al	-	11.82	-	11.79
As	5.49	-	5.50	-	As	2.87	4.83	2.88	4.83
B	-	-	-	-	B	-	-	-	-
Ba	-	2.01	-	2.00	Ba	1.56	-	1.56	-
Be	-	-	-	-	Be	-	-	-	-
Cd	-	-	-	-	Cd	-	-	-	-
Co	-	-	-	-	Co	-	-	0.04	-
Cr	2.01	2.13	2.01	2.11	Cr	11.90	47.60	11.94	47.59
Cu	-	-	-	-	Cu	4.32	-	9.79	-
Fe	21.40	14.83	21.37	14.85	Fe	21.30	98.40	21.34	98.37
Mn	1.70	0.86	1.70	0.85	Mn	2.01	1.20	2.03	1.18
Ni	-	-	-	-	Ni	-	-	-	-
Pb	1.94	-	-	-	Pb	0.78	-	0.78	-
Sb	2.31	0.43	2.30	0.42	Sb	2.35	1.27	2.35	1.27
Se	1.43	0.97	1.44	0.95	Se	-	-	-	-
Tl	-	-	-	-	Tl	-	0.13	-	0.13
V	7.40	8.34	7.42	8.33	V	-	-	-	-
Zn	-	-	-	-	Zn	-	0.74	-	0.73
metal	Before soaking		Before tanning						
Hg*	EDF20	SG50	EDF20	SG50					
	0.05	0.05	0.05	0.05					

\*: ppb

## 6. Conclusions

The purification of defatting wastewaters from the demonstration action B.3 using activated sludge, showed the compatibility of the effluents with the standard biological oxidizing process, which is routinely adopted within water treatment plants. The removal of suspended solids before treatment has determined relatively low level of CODs, that however were reduced by 60-70% by the sludge. The low levels of BODs after treatment indicated the presence of residual chemical species low to undergo biodegradation. In this case, the absence of chemical and physico-chemical treatments leave chemical species in the effluents difficult to undergo degradation, such as sulfides. The metal analyses of the effluents showed very low values, indicating that the defatting process was reliable without adding any extra pollutant and affecting the quality of both the finished products (the leather) and the by-products (the wastewaters). Even in this case, the metal analysis was confirmed its important role as indirect environmental monitoring tool. In some cases, Fe and Cr were detected as the most abundant metals, as the result of work processes carried out with metal based equipment (*i.e.*, steel) releasing inevitably traces of those elements. In any case, the general trend of these analyzes highlighted the presence of only few metals and in specific cases far below the legal limits required both for drinking water and for the water to industrial use, confirming the goodness of the process.