



Chemical and ecotoxicological characterization of solid residues produced during the co-pyrolysis of plastics and pine biomass

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ABSTRACT

A mixture of 70% (w/w) pine biomass and 30% (w/w) plastics (mixture of polypropylene, polyethylene, and polystyrene) was subjected to pyrolysis at 400 °C, for 15 min, with an initial pressure of 40 MPa. Part of the solid residue produced was subjected to extraction with dichloromethane (DCM). The extracted residue (residue A) and raw residue (residue B) were analyzed by weight loss combustion and submitted to the leaching test ISO/TS 21268-2 using two different leachants: DCM (0.2%, v/v) and calcium chloride (0.001 mol/L). The concentrations of the heavy metals Cd, Cr, Ni, Zn, Pb and Cu were determined in the eluates and in the two residues. The eluates were further characterized by determining their pH and the concentrations of benzene, toluene, ethylbenzene and xylenes (BTEX). The presence of other organic contaminants in the eluates was qualitatively evaluated by gas chromatography, coupled with mass spectrometry. An ecotoxicological characterization was also performed by using the bio-indicator *Vibrio fischeri*. The chemical and ecotoxicological results were analyzed according to the French proposal of Criteria on the Evaluation Methods of Waste Ecotoxicity (CEMWE). Residue A was not considered to be ecotoxic by the ecotoxicological criterion (EC_{50} (30 min) $\geq 10\%$), but it was considered to be ecotoxic by the chemical criterion ($Ni \geq 0.5$ mg/L). Residue B was considered to be ecotoxic by the ecotoxicological criterion: EC_{50} (30 min) $\leq 10\%$. Besides that, residue B was considered to be hazardous according to the European legislation (BTEX concentrations higher than 100 ppb). The results indicate that volatile organic contaminants can be present in sufficient amounts in these residues and their eluates to induce ecotoxicity levels. The extraction of the pyrolysis residue with DCM was an efficient method for removing lighter organic contaminants.

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1. Introduction

The main aim of this study was to perform the chemical and ecotoxicological characterizations of solid residues produced in the co-pyrolysis of plastics and biomass. In pyrolysis processes, the wastes are subjected to high temperatures in the absence of air or in an oxygen-deficient atmosphere, producing a mixture of hydrocarbons (in vapor and liquid fractions) that can be used as fuel or as feedstock in chemistry industries, and a carbon-rich solid residue (the solid fraction). Usually, the carbonaceous residue produced in the pyrolysis process is not considered economically interesting, and is usually disposed off in landfills. Therefore, it is important to evaluate the short, medium and long-term stability of these residues, namely to evaluate the possible leaching of toxic compounds and the ecotoxicity of the eluates. Therefore, in this work, leaching studies were conducted.

In the literature, it was not possible to find works dedicated to the chemical and ecotoxicological characterizations of solid residues (and their leachates) produced in the pyrolysis and/or co-pyrolysis of plastics and biomass. It was only possible to find recent works devoted to the chemical characterization of residues of pyrolysis produced from different wastes [1–4]. These studies have shown that submitting different types of wastes to pyrolysis may have a positive effect on the immobilization of heavy metals in the solid residues. However, given the high toxicity and high environmental mobility of heavy metals, it is advisable to monitor their release from the solid residues, because different pyrolysis conditions and different leachant solutions may affect the heavy metal mobility.

In many leaching studies [1–3,5–7], the information available about organic contaminants comes from the determination of parameters such as Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC), Non-Volatile Organics (NVO), Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD). These parameters are relatively easy to measure and provide an indication of the potential consumption of oxygen, but they do not

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elucidate about the identity of the organic compounds present in the wastes. The standardization of the leaching techniques dealing with the extraction of organic compounds is just beginning and the studies that have been carried out up to now were mainly developed for contaminated soils [8]. There are no standard leaching techniques applicable to residues with a high load of organic compounds.

The extraction and determination of organic compounds in materials with high organic content is a difficult task, because of the high diversity of possible organic contaminants that are present. These organic contaminants are usually characterized by different water solubilities, different molecular weights, different polarities and different volatilities. Therefore, it is necessary to develop specific analytical procedures that are adequate for the determination of volatile organic compounds and non-volatile organic compounds in those materials and in their leachates.

Several research works have described the release of organic compounds from different materials and residues: cement-based and stabilized materials [9], contaminated soils [10–12], paint residues of furniture factories [13], shredder residues [14,15], municipal solid waste incinerators fly ashes [15,16], varnish residue and urea resin waste [17], sewage sludge [18] and landfills [19–27].

It was not possible to find any studies dealing with the leaching of organic compounds from solid residues produced in the co-pyrolysis of biomass and wastes. Only previous works from DEECA-INETI [28–30] have shown that the DCM solvent is able to extract a large set of hydrocarbons from the solid residues produced in the pyrolysis of plastics or biomass.

The organic contaminants leached from a given material or residue are dependent on its composition and may include classes of compounds such as aromatic and polyaromatic hydrocarbons, aliphatic hydrocarbons, polychlorinated biphenyls and dioxins, among others. The aromatic hydrocarbons are usually benzene derivatives with different alkyl groups in the different positions of the aromatic ring and have in common the properties of being highly toxic, with a high to medium volatility and a low to medium water solubility. The lighter members of this group are benzene, toluene, ethylbenzene and xylene (usually referred as the BTEX group), and they have a particularly high environmental mobility. Some authors [13,19,20,23,24,27] have studied the presence of aromatic compounds in eluates from different wastes and found that the compounds of the BTEX group are always present in relatively high concentrations, giving a major contribution to the Total Organic Carbon content of the eluates.

In the present study, the determination of organic contaminants was focused on the volatile group because these are also commonly the compounds with lower molecular weight and higher water solubility.

Besides organic characterization, an inorganic characterization was performed in the wastes and their leachates with the determination of the following heavy metals using atomic absorption spectrometry: Cd, Cr, Cu, Zn, Pb and Ni.

The toxicity of a waste or of its leachate can also be evaluated by using ecotoxicological tests wherein the purpose is to characterize the toxicity level of the sample regardless of its chemical composition. The results of these tests allow for the classification of the waste as ecotoxic or non-ecotoxic. In this study, the ecotoxicity of the leachates was determined with the bacterium *Vibrio fischeri*.

2. Materials and methods

2.1. Pyrolysis

A mixture of 70% (w/w) pine biomass and 30% (w/w) plastics (mixture of PP, PE and PS) was subject to pyrolysis in a 1 L autoclave, during 15 min at a temperature of 400 °C with an initial pressure

of 40 MPa, in the presence of nitrogen. The experimental conditions were selected according to previous studies about the effect of experimental conditions on the yields of pyrolysis products and their characteristics. Pyrolysis experiments were done to increase the production of liquid compounds.

The composition of the plastics mixture attempted to reflect the average composition found in the Portuguese Municipal Solid Wastes (MSW): 56% (w/w) polyethylene, 27% (w/w) polypropylene and 17% (w/w) polystyrene. These fractions of plastics were collected in a local recycling factory.

At the end of the assay, the reaction products were as follows: 15% (w/w) gases, 30% (w/w) solids and 45% (w/w) liquids. About 10% losses of the final pyrolysis products were determined. One part of the solid fraction was submitted to a Soxhlet extraction with dichloromethane (DCM). This part of the study was performed at INETI-DEECA and the methodology and the main results were described in previous works [28–30].

The residue extracted with DCM (residue A) and the residue not extracted (residue B) were submitted to the following analyses.

2.2. Methodology used to assess the ecotoxicity of the pyrolysis residues

The French Ministry of Environment proposed the Criteria and Evaluation of Waste Ecotoxicity (CEMWE) [31] to regulate the European classification of wastes defined in the Hazardous Waste Directive [32] under the code H14 (ecotoxic wastes). According to this methodology, the ecotoxicity of a residue shall be assessed through its chemical composition or its ecotoxicological characteristics. Both shall be performed on raw waste and on its leachate.

The chemical composition is used as a positive criterion; the presence of at least one pollutant in a concentration higher than the limits fixed on the CEMWE allows for the classification of it as ecotoxic. If the chemical characterization is inconclusive, that is to say, if all the chemical species have concentrations below the limit values, it cannot be concluded that the waste is not ecotoxic and the assessment of the ecotoxicity has to proceed with the ecotoxicological characterization. The positive criterion of the ecotoxicological analysis means that if at least one of the biological tests is positive, the residue shall be classified as ecotoxic. The negative criterion presumes that only the negative response to all of the ecotoxicological tests allows classifying it as non-ecotoxic.

The conceptual methodology that is applied in this work to assess the ecotoxicity of pyrolysis residues is slightly different from the French proposal (Fig. 1). The main difference is related with the importance that is attributed to the chemical and ecotoxicological

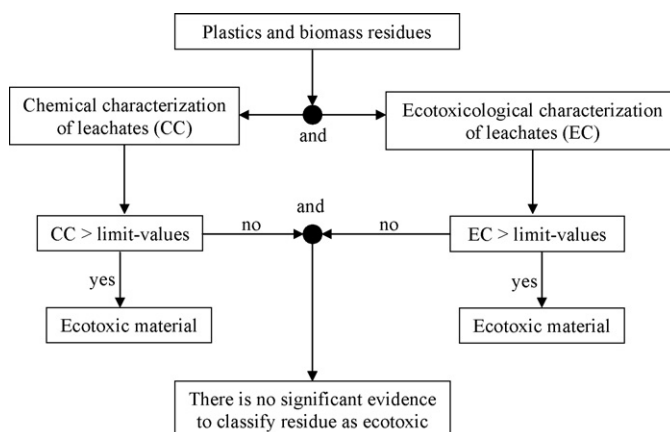


Fig. 1. Criterion applied to assess the ecotoxicity of pyrolysis residues.

characterizations. In this work, the chemical and ecotoxicological characterization was performed for all eluates and the results were then used to classify the waste using the criteria adopted for this study. This methodology enabled the obtaining of information on the contribution of each class of chemical contaminants to the ecotoxic characteristics of the waste and also to detect the eventual synergetic effects between chemical species that are present below their limit values.

2.3. Determination of the organic content in samples A and B

The organic content was determined by proximate analysis by measuring the weight loss associated with the combustion of the solid samples in a microwave muffle furnace. The samples were heated from room temperature ($25 \pm 1^\circ\text{C}$) until $550 \pm 1^\circ\text{C}$, with increments of 50°C . At each temperature stage, the samples were removed from the furnace, cooled to room temperature in a desiccator and weighed.

2.4. Determination of the content in heavy metals in samples A and B

The samples were placed in porcelain crucibles and digested with hydrogen peroxide 30% (v/v) in a heated bath at a temperature of 95°C and then digested with *aqua regia* (HCl:HNO₃, 3:1, v/v) at the same temperature.

Finally, a microwave acid digestion (HCl:HNO₃, 3:1, v/v) in closed PTFE vessels was used to complete the solubilization of the inorganic components of the sample.

The digested samples were filtrated and preserved in the conditions described in the standard ISO 5667-3 [33] until analysis.

A selected group of heavy metals were quantified in the digested samples using atomic absorption spectrometry (AAS): chromium was determined according to the standard ISO 9174 [34], and cadmium, copper, zinc, nickel, and lead were analyzed following the standard ISO 8288 [35].

2.5. Leaching tests

The leaching methodology followed the standard leaching test ISO/TS 21268-2 [36]. This standard aims to mainly extract non-volatile organic and inorganic contaminants present in soils or soil materials. Since the solid residues of pyrolysis are granular materials, it was assumed that they would exhibit a similar leaching behavior to soils. Although this leaching standard is described as adequate to the determination of non-volatile contaminants, since the contact between the waste and leaching solution is performed in closed vessels, it should also allow for the sampling of volatile organic compounds.

The waste is mixed with the leaching solution in a single-stage batch test performed at an L/S ratio of 10 L/kg, at a constant temperature of $20 \pm 2^\circ\text{C}$. The containers (capped glass bottles) were shaken in a roller-rotating device at 10 rpm, for a period of 24 ± 0.5 h. The leachants used were the following: a calcium chloride solution with a concentration of 0.001 mol/L (according to the standard ISO/TS 21268-2 [36]) and a DCM solution of 0.2% (v/v).

The choice of a DCM solution as a leachant was an attempt to simulate a leaching situation wherein a mixture of water and organic solvents can occur, leading to the extraction of higher amounts of organic compounds from the residues. This could be the case of a landfill where large amounts of solvent-rich wastes were being disposed off. The concentration chosen to the DCM aqueous solution was the highest concentration that could be used without promoting a significant toxic effect in the bacterium used in the ecotoxicological assay (20% inhibition effect on the luminescence of *V. fischeri*).

Table 1

Codes used for the different eluates obtained.

Eluate code	Type of eluate
1	Residue A (previously extracted with DCM) leached with CaCl ₂ 0.001 M solution
2	Residue B (not extracted) leached with CaCl ₂ 0.001 M solution
3	Residue A (previously extracted with DCM) leached with DCM 0.2% (v/v) solution
4	Residue B (not extracted) leached with DCM 0.2% (v/v) solution

At the end of the leaching test, the mixtures were allowed to settle for 15 min and the eluates were filtrated over fiber glass filters GF/C Whatman. Blank tests were performed with both leaching solutions.

The eluates were divided into sub-samples to be used in the different chemical and ecotoxicological analyses. The samples used in heavy metals determinations were preserved according to the international standard ISO 5667-3 [33]. For the ecotoxicological characterization and the determination of organic contaminants, the eluates were preserved at a temperature of $4 \pm 1^\circ\text{C}$.

Table 1 shows the codes used for the different eluates obtained.

2.6. Determination of BTEX and other volatile benzene derivatives

The concentration of BTEX compounds in the eluates was evaluated by headspace static sampling and gas chromatography with flame ionization detection (GC-FID).

The headspace sampling was performed using the following optimized experimental conditions: equilibration time, 30 min; extraction temperature, 60°C ; headspace volume and eluate solution volume, 25 mL; sample volume, 0.5 mL.

The sample was injected in a TRACE™ GC 2000 Series gas chromatograph equipped with a split-splitless injector, a RTX®-VMS with $75 \text{ m} \times 0.53 \text{ mm} \times 3 \mu\text{m}$ capillary column and a flame ionization detector (FID). The carrier gas was hydrogen at 3 mL/min; the injector was operated in the splitless mode with a splitless time of 0.5 min and split flow of 50 mL/min; the injector and detector temperatures were, respectively, 150 and 220°C ; the oven temperature program was as follows: 32°C (hold for 7 min), up to 80°C at a rate of $10^\circ\text{C}/\text{min}$, up to 150°C at a rate of $50^\circ\text{C}/\text{min}$ (hold 10 min).

A stock standard solution with a concentration of 1 g/L of each component of BTEX in methanol was prepared. Standard solutions with the concentrations of 50, 100, 150, 200, 250 and 300 ppb of BTEX were prepared by dilution of an appropriated amount of the stock standard solution in each of the leaching solutions. These standard solutions were analyzed as described above and calibration curves were constructed for each analyte in both leaching solutions.

The range of concentrations chosen is the range where the FID detector gives a linear response for these analytes and includes the related limit-value of 100 ppb defined in the European legislation [37] for BTEX compounds in eluates.

Other volatile benzene derivatives present in the eluates were identified by headspace sampling and gas chromatography hyphenated with mass spectrometry. Identification was performed by comparison of the retention times and mass spectra of the compounds with standards. Some organic contaminants were tentatively identified by the comparison of their mass spectra with references from the Wiley and NIST spectra libraries.

The equipment used in the GC-MS experiments was a Focus gas chromatograph and a Polaris Q mass spectrometer. The separation column used was a TR-V1 with $30 \text{ m} \times 0.25 \text{ mm} \times 1.4 \mu\text{m}$. The carrier gas was helium at 1.5 mL/min; samples were injected, at 60°C , in the splitless mode with a splitless time of 1 min and a split flow of 50 mL/min; the interface and ion source were kept at 220°C ; the oven temperature program was as follows: 32°C (hold 5 min),

heating ramp up to 100 °C (5 °C/min), heating ramp up to 250 °C (10 °C/min) and finally heating ramp up to 280 °C (50 °C/min, hold 1 min).

2.7. Determination of inorganic parameters in eluates: pH and heavy metals

The pH of the eluates was determined according to standard ISO 10523 [38].

The heavy metals Cd, Cr, Cu, Ni, Pb and Zn were quantified in the eluates using atomic absorption spectrometry according to the standards ISO 8288 [35] and ISO 9174 [36].

2.8. Ecotoxicological characterization of leachates

The ecotoxicological parameter analyzed in the eluates was the luminescence inhibition of the bacterium *V. fischeri* ("Azur Environmental Microtox® system") according to ISO 11348-3 [39]. Blank tests were performed with both leaching solutions in order to determine the threshold luminescence inhibition caused by these solutions.

2.9. Reagents

Pure dichloromethane was purchased from Fischer Scientific. CaCl₂ powder was obtained from Merck with a purity of 95%. Methanol was supplied by Fluka (99.8% grade). The aromatic standards were purchased from: Panreac (Benzene and toluene, 99.5%), Fluka (ethylbenzene, >99%), Acros Organics (m/p/o-xylenes, 99%), Aldrich (cumene 98%, propylbenzene 98%, 4-ethyltoluene 90%, tert-butylbenzene 99%, 1,2,4-trimethylbenzene 98%, 1-methylpropylbenzene 99%, butylbenzene 99%, 1,4-diethylbenzene 96% and 1,2,4,5-tetramethylbenzene 98%).

V. fischeri was supplied in lyophilized form by Azur Environmental Systems.

3. Results and discussion

3.1. Weight loss by combustion

Residues A and B lost more than 99% of their initial weight (Fig. 2), when heated up to 450 °C, which indicates that they were mainly composed of organic matter.

Residue A did not present a significant initial weight loss (from 25 °C to 200 °C), while residue B suffered a weight loss higher than

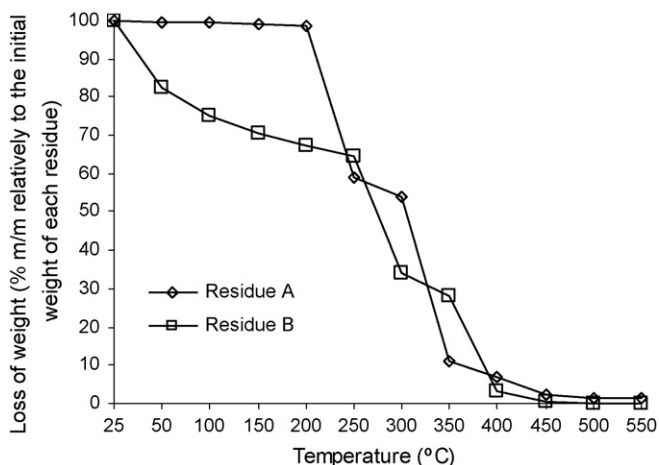


Fig. 2. Loss of weight (% m/m relatively to the initial weight of each residue), by combustion in a microwave furnace up to 550 °C.

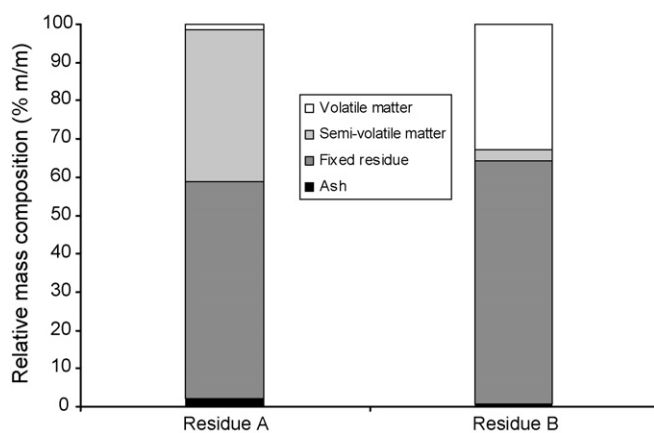


Fig. 3. Relative mass composition (% m/m relatively to the initial weight of each residue).

30% (w/w) in the same temperature range. Between 200 °C and 450 °C both residues lost weight at a similar rate until stabilizing at a steady value of less than 1% of their initial weight. Both residues presented a stable residual weight between 450 °C and 550 °C.

This behavior indicates that the residues had identical contents of non-volatile organic compounds, but the pre-treatment of residue A with DCM removed the organic fraction with volatility temperatures between 25 °C and 200 °C.

The composition of the residues A and B is shown in Fig. 3, in terms of the volatility of their components (volatile, semivolatile, non-volatile organic matter and ashes). Volatile organic compounds were those volatilized up to 200 °C. The weight loss registered between 200 °C and 250 °C were attributed to semivolatile compounds, while the weight decrease observed from 250 °C to 450 °C was assigned to the volatilization and combustion of heavy organic compounds denominated fixed carbon. The residue non-combusted above 450 °C is considered to be mainly composed of ashes.

The extraction with DCM was, therefore, an efficient process for the removal of the volatile organic fraction from these residues, and thereby reducing their toxic load but not affecting the semivolatile and non-volatile fractions. The low content of volatile organic matter in residue A is attributed to the volatiles that remain after extraction with DCM. The high content of semivolatile compounds in residue A is mostly due to a concentration effect resulting from the removal of light organic compounds. It can be seen that residue A presents a low content in the remaining volatile matter after DCM extraction.

3.2. Contents of some heavy metals in the solid wastes

Table 2 shows the content of some heavy metals in residues A and B and in the pine biomass. Table 3 shows the qualitative content of metals in the plastics used in the pyrolysis.

Both residues showed detectable amounts of the metals Cr, Ni and Zn, while the concentrations of metals Cd, Cu and Pb were

Table 2
Heavy metals content in the pyrolysis solid residues and in the raw pine biomass (mg/kg).

Metals (mg/kg)	Residue A	Residue B	Pine biomass
Cd	<0.54	<0.54	<0.20
Cr	102	4.98	1.10
Cu	<0.25	<0.25	0.90
Ni	91.1	44.1	1.00
Pb	<12.3	<12.3	0.20
Zn	57.0	47.2	2.60

Table 3
Qualitative metal content in the plastics determined by XRF.

Qualitative class	Plastics			Pine
	PE	PP	PS	
Major metals	Titanium (Ti)	Calcium (Ca)	None metal was detected	Manganese (Mn), chromium (Cr), nickel (Ni), zinc (Zn)
Minor metals	Lead (Pb), calcium (Ca), magnesium (Mg)	Lead (Pb), zinc (Zn), titanium (Ti), calcium (Ca), potassium (K), aluminum (Al)	Iron (Fe), aluminum (Al), magnesium (Mg), sodium (Na)	Copper (Cu), lead (Pb), calcium (Ca)
Trace metals	Zinc (Zn)	Strontium (Sr), chromium (Cr), potassium (K)	Titanium (Ti), zinc (Zn)	Aluminum (Al), iron (Fe), potassium (K), sodium (Na), magnesium (Mg), mercury (Hg)

Table 4
pH values and heavy metals content in eluates (mg/kg).

Parameter	Eluate 1	Eluate 2	Eluate 3	Eluate 4
pH	6.0	6.2	5.7	6.2
Cd (mg/kg)	<0.12	<0.12	<0.12	<0.12
Cr (mg/kg)	<1.15	<1.15	<1.15	<1.15
Cu (mg/kg)	<0.11	<0.11	<0.11	<0.11
Ni (mg/kg)	30.6 ± 8.02	<1.03	32.7 ± 1.68	<1.03
Pb (mg/kg)	<5.00	<5.00	<5.00	<5.00
Zn (mg/kg)	5.45 ± 1.48	1.76 ± 0.71	5.43 ± 0.71	2.58 ± 1.09

below the respective detection limits. Cr, Ni and Zn are also the metals that were detected in higher content in the pine biomass and were subjected to a magnification factor in the solid residues due to the pyrolysis process.

The higher concentrations of these metals in residue A can also arise from a concentration effect due to the removal of the light organic fraction during DCM extraction.

3.3. Chemical analysis of the eluates

3.3.1. pH and heavy metals

The pH values and concentrations of heavy metals in the eluates are shown in Table 4.

Table 5
Analytical performance of HS-GC-FID for BTEX determination in eluates.

Analyte	Regression equation	Correlation coefficient, R^2	Detection limit (ppb)	Quantification limit (ppb)
CaCl ₂ solution 0.001 M ^a				
Benzene	$y = 65099x + 8E+05$	0.9951	21.9	73.1
Toluene	$y = 94414x + 1E+06$	0.9948	22.6	75.4
Ethylbenzene	$y = 201465x + 4E+06$	0.9959	17.6	58.8
m/p-Xylene	$y = 187461x + 2E+06$	0.9949	19.6	65.4
o-Xylene	$y = 72361x + 7E+05$	0.9934	25.7	85.5
DCM solution 0.2% (v/v) ^b				
Benzene	$y = 53399x + 9E+05$	0.9946	23.1	76.9
Toluene	$y = 78389x + 1E+06$	0.9943	23.7	79.0
Ethylbenzene	$y = 167419x + 4E+06$	0.9945	23.4	78.1
m/p-Xylene	$y = 154734x + 3E+06$	0.9948	22.8	75.9
o-Xylene	$y = 59479x + 8E+05$	0.9952	21.7	72.4

^a Linear calibration range 50–300 ppb to benzene, toluene and o-xylene and 50–250 ppb to ethylbenzene and m/p-xylenes.

^b Linear calibration range 50–300 ppb.

Table 6
Validation of the analytical method for BTEX quantification.

Analyte	Precision ^a (R.S.D.%) CaCl ₂ aqueous solution 0.001 M		Precision ^a (R.S.D.%) DCM aqueous solution 0.2% (v/v)	
	LOQ	2 × LOQ	LOQ	2 × LOQ
Benzene	9.6	9.2	6.8	10.6
Toluene	5.2	10.0	2.8	8.2
Ethylbenzene	11.4	6.0	6.0	3.6
m/p-Xylenes	8.0	6.5	12.7	10.5
o-Xylene	6.7	5.7	4.5	16.3

LOQ, limit of quantification.

^a Five replicates.

All the eluates showed similar pH values (from 5.7 to 6.2) similar to the pH of the leaching solutions (CaCl₂ solution presented a pH value of 6.3 and the DCM solution presented a pH value of 5.9), which means that there was not a significant leaching of acidic or basic components of the residues.

All the metals analyzed were present in those concentrations below the detection limits, except for Ni and Zn, which also appeared in significant quantities in the solid residues. Ni and Zn were easily released from the residues to the eluates.

The solid residues also had high concentrations of Cr (especially residue A) but this metal was not detected in the eluates. This suggests that the chromium detected in the residues should be Cr(III), which has low solubility at neutral pH values.

3.3.2. BTEX quantification

An analytical method for the determination of BTEX in the eluates using GC-FID was developed and validated. Calibration curves were constructed for these analytes, in both CaCl₂ and DCM leaching solutions and the corresponding detection and quantification limits were evaluated (Table 5). All correlation coefficients were above 0.993 and the limits of quantification were quite below 100 ppb for all analytes in both solutions, but slightly lower in the CaCl₂ solution. This can be explained by the salting-out effect of CaCl₂ that promotes the releasing of the analytes from the aqueous

Table 7
BTEX concentrations in the eluates (ppb).

Eluates	Concentrations (ppb), mean \pm S.D. (n=3)				
	Benzene	Toluene	Ethylbenzene	m/p-Xylenes	o-Xylene
1	<21.9	<22.6	<17.6	<19.6	<25.7
2	<21.9	511 \pm 9	277 \pm 2	<19.6	49 \pm 2
3	<23.1	<23.7	<23.4	<22.8	<21.7
4	197 \pm 7	726 \pm 14	382 \pm 4	<22.8	73 \pm 4

solution to the headspace vapor phase. In the DCM solution, the presence of the organic solvent in the aqueous phase decreases its ionic strength, thus contributing to a higher dissolution of the analytes. This behavior is evidence of the important matrix effect that influences the determination of BTEX compounds in such complex aqueous samples.

The precision of the method was evaluated at two concentration levels (LOQ and 2 \times LOQ) and varied from 2.8 to 12.7% R.S.D. (Relative Standard Deviation), for the different analytes in both leaching solutions (Table 6).

The validated method was used to determine the concentrations of BTEX compounds in the four eluates (Table 7). Triplicate analyses were performed for each determination.

No BTEX compounds (or other volatile organic compounds) were detected in eluates 1 and 3 obtained from residue A, which confirms that the extraction of the residue with DCM was an efficient method for the removal of volatile organic contaminants.

Eluates 2 and 4 showed a contamination with toluene, ethylbenzene and o-xylene in concentrations from 49 ppb to 726 ppb with predominance of toluene. Toluene and ethylbenzene were also the compounds detected in the liquid fractions with the highest concentrations [28]. Eluate 4 had higher concentrations of the analytes that were detected in the eluate 2 and also had benzene at a concentration of 197 ppb. As stated before, eluates 2 and 4 were obtained by leaching residue B with a CaCl₂ solution and a DCM solution, respectively. The results obtained in this work show that the presence of organic solvents in the leaching solution causes a substantial increase in the amounts of organic contaminants leached from the residues. This was to be expected given the decrease in the ionic strength of the leachant when variable amounts of less polar molecules are dissolved in the aqueous leaching solution. This behavior should be taken into account in the design of leaching standards or there is the risk that the organic loads of leachates produced in real landfills (often containing considerable amounts of solvent impregnated materials) can be grossly underestimated.

3.3.3. Identification of other volatile organic contaminants

Other volatile organic contaminants were also identified in the eluates by performing their analysis using headspace sampling and gas chromatography coupled with mass spectrometry. The conditions used in the static headspace sampling are the same used in the analysis of BTEX by GC-FID but the chromatographic conditions had to be adjusted to the specific characteristics of the GC-MS technique.

Besides for the confirmation of the presence of BTEX, several other aromatic hydrocarbons (PAHs, furans and other benzene derivatives) and other organic compounds such as phenolics were also detected (Table 8). These organic compounds are typical components of the liquid fraction obtained from the co-pyrolysis of plastics and biomass [28], so it is expected that they can occur as contaminants of the solid residue resulting from that respective process. The relative concentration of each detected compound decreases as the retention time increases because the headspace is enriched in the lighter compounds present in the eluate. The use of a volatile-specific sampling technique produces samples with higher

Table 8
List of the organic compounds detected in the eluates.

Name	Relative concentration (%)				
	R.T. (min)	Eluate 1	Eluate 2	Eluate 3	Eluate 4
Benzene ^a	9.12		2.05		1.75
Toluene ^a	13.73	1.35	41.0	0.64	32.4
Ethylbenzene ^a	17.62	1.81	33.6	0.55	31.3
m/p-Xylenes ^a	17.93	0.10	2.54		1.50
o-Xylenes ^a	18.96		2.48		1.17
Cumene ^a	19.86	0.31	9.12	0.08	4.27
Propylbenzene ^a	20.77		1.49		0.73
4-Ethyltoluene ^a	20.98		0.82		0.39
3-Ethyltoluene ^b	21.17		0.08		0.03
2-Ethyltoluene ^b	21.56		0.5		0.17
tert-Butylbenzene ^a	21.79		0.01		0.05
1,2,4-Trimethylbenzene ^a	21.90		0.43		0.16
1-Methylpropylbenzene ^a	22.23		0.19		0.10
1-Methyl-4-(1-methylethyl)benzene ^b	22.52		0.07		0.03
Trimethylbenzene (isomer) ^b	22.70		0.20		0.06
2-propenylbenzene ^b	22.83		0.15		
1-propenylbenzene ^b	23.06		0.49		0.14
Butylbenzene/1,4-Diethylbenzene ^a	23.27		0.20		0.07
1-butenylbenzene ^b	24.09		0.20		0.08
1,2,4,5-Tetramethylbenzene ^a	24.60		0.03		0.01
Methylphenol (isomer) ^b	24.71		0.08		0.07
3-Methylbenzofurane ^b	24.76		0.12		0.11
4-etenyl-1,2-dimethylbenzene ^b	25.14		0.06		0.04
Dimethylphenol (isomer) ^b	25.35				0.05
1-Methylpropenylbenzene ^b	25.40		0.11		0.05
Dimethylphenol (isomer) ^b	26.23		0.06		0.08
Naphthalene ^b	26.40		0.14		0.23
Trimethylphenol (isomer) ^b	26.60		0.07		
Trimethylphenol (isomer) ^b	26.90		0.02		0.04
Trimethylphenol (isomer) ^b	27.41		0.04		0.08
2,3,5,6-Tetramethylphenol ^b	27.95		0.01		0.04
Methylnaphthalene ^b	28.47		0.05		0.15

R.T., retention time.

^a Compound identified by co-injection of standards.

^b Compound tentatively identified by comparison with the spectra of NIST and Wiley libraries and by comparison between isomer molecular structures.

concentrations of the compounds that can more easily be liberated from the eluate by the processes of volatilization and/or diffusion.

The compounds detected in higher relative concentration, besides BTEX, were cumene and propylbenzene, which are two volatile aromatic hydrocarbons.

It was possible to detect several aromatic compounds in eluates 1 and 3 namely toluene, ethylbenzene, m/p-xylenes and cumene (Fig. 4).

Eluates 2 and 4 were much more contaminated (Fig. 5), as the GC-FID analyses had already indicated and it was possible to detect several other compounds at sufficient high concentration to enable the acquisition of elucidative mass spectra. Once again the salting-out effect of the CaCl₂ favours the headspace sampling from the eluate 2 that, therefore, releases higher amounts and a greater variety of organic compounds into the vapor phase. Some differences in the qualitative composition of the samples obtained from the eluates 2 and 4 are probably a result of the specific interactions of each leachant solution with the residue.

3.4. Ecotoxicity tests

The ecotoxicological data obtained in the eluates are shown in Table 9. The luminescence inhibition of *V. fischeri* was evaluated for an exposure period of 5, 15, and 30 min.

Eluates 2 and 4 have shown the highest toxicity. Concentrations of 0.53% and 1.27% (v/v), has induced a 50% of luminescence inhibition to *V. fischeri*, probably due to the presence of higher contents of

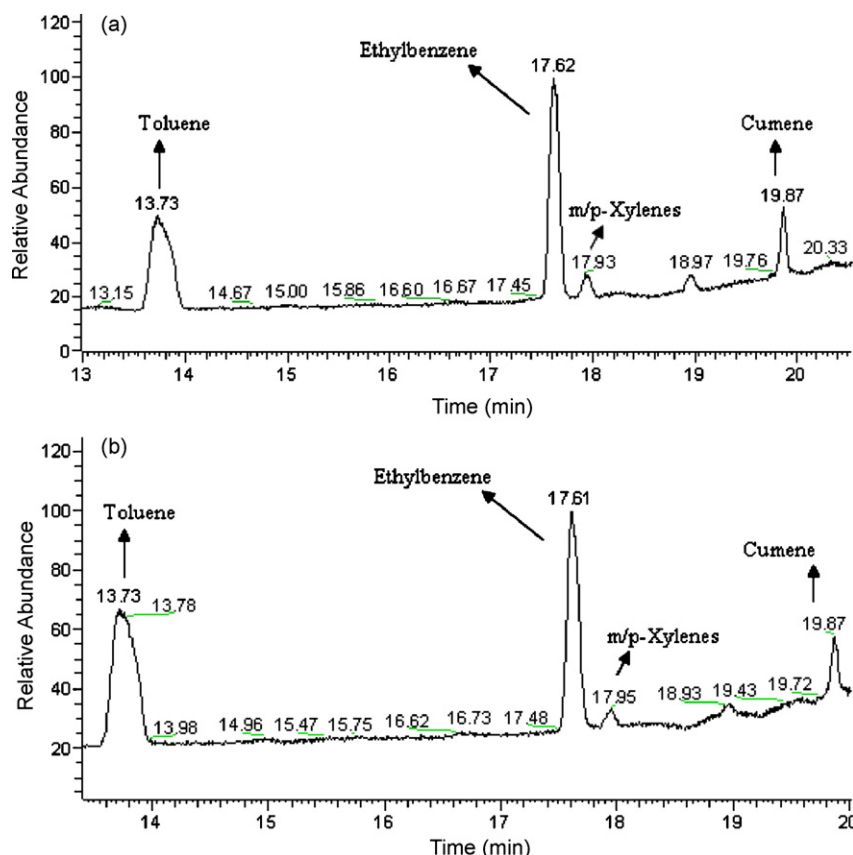


Fig. 4. GC-MS chromatogram of (a) eluate 1 and (b) eluate 3, where it can be observed the presence of toluene, ethylbenzene, xylenes, and cumene.

Table 9

Ecotoxicity of eluates to *Vibrio fischeri* bacterium, for exposure periods of 5, 15, and 30 min.

Eluate	Effective concentration, EC ₅₀ (%) (v/v)		
	5 min	15 min	30 min
1	>99	>99	70.4
2	1.03	1.27	1.08
3	>99	>99	73.6
4	0.62	0.53	0.56

organic compounds, as residue B was not previously extracted with DCM, as it happened with residue A from which were obtained eluates 1 and 3. Therefore, no significant toxicity was detected in eluates 1 and 3. Only for an exposure period of 30 min was it observed that there was a 50% luminescence inhibition for concentrations of approximately 70% (v/v).

The high toxicity levels of eluates 2 and 4 seemed to be mainly associated with the high concentrations of organic contaminants such as BTEX. Eluate 4 obtained with the DCM solution has shown the highest toxicity. This behavior can be associated with a higher organic load that was already mentioned in the chemical analysis, but also with the toxicity of the DCM present in the leaching solution that by itself induced a 20% luminescence inhibition.

3.4.1. Chemical criteria for the classification of the solid residues

The CEMWE [28] French proposal defines limit values for the heavy metals included in this work. The concentrations of those metals are expressed in mg/L of leachate and the corresponding limit values are shown in Table 10.

The French proposal includes limit values for some organic compounds but not for BTEX.

Comparing the chemical characterization of the eluates with the limit values as defined in the CEMWE proposal, it can be observed that:

- All eluates have shown values of Cd, Cr, Cu, Pb and Zn below the limit-value defined in the proposal;
- Eluates 1 and 3 have shown Ni concentrations higher than the limit-value established in the French proposal; these eluates have been produced from residue A, so we can classify this residue as ecotoxic.
- Eluates 2 and 4, resulting from the leaching of residue B, presented all the inorganic parameters below the limit values fixed in the proposal; according to this proposal we classify residue B as non-ecotoxic.

Eluates 2 and 4 have shown values for BTEX above 100 ppb, the limit-value defined in the European legislation for each BTEX analyte [36]. According to this European Decision, inert residues are those with BTEX limit values below 100 ppb. Therefore, according to 2003/33/CE Council Decision, residue B is a non-inert residue.

Table 10

Heavy metals concentrations in eluates and limit values as defined in the French proposal CEMWE [28] (mg/L).

Metals	Eluate 1	Eluate 2	Eluate 3	Eluate 4	CEMWE ^a
Cd	<0.01	<0.01	<0.01	<0.01	0.2
Cr	<0.12	<0.12	<0.12	<0.12	0.5
Cu	<0.01	<0.01	<0.01	<0.01	0.5
Ni	3.06	<0.10	3.27	<0.10	0.5
Pb	<0.50	<0.50	<0.50	<0.50	0.5
Zn	0.55	0.18	0.54	0.26	2.0

^a Maximum values admissible for non-ecotoxic residues (mg/L).

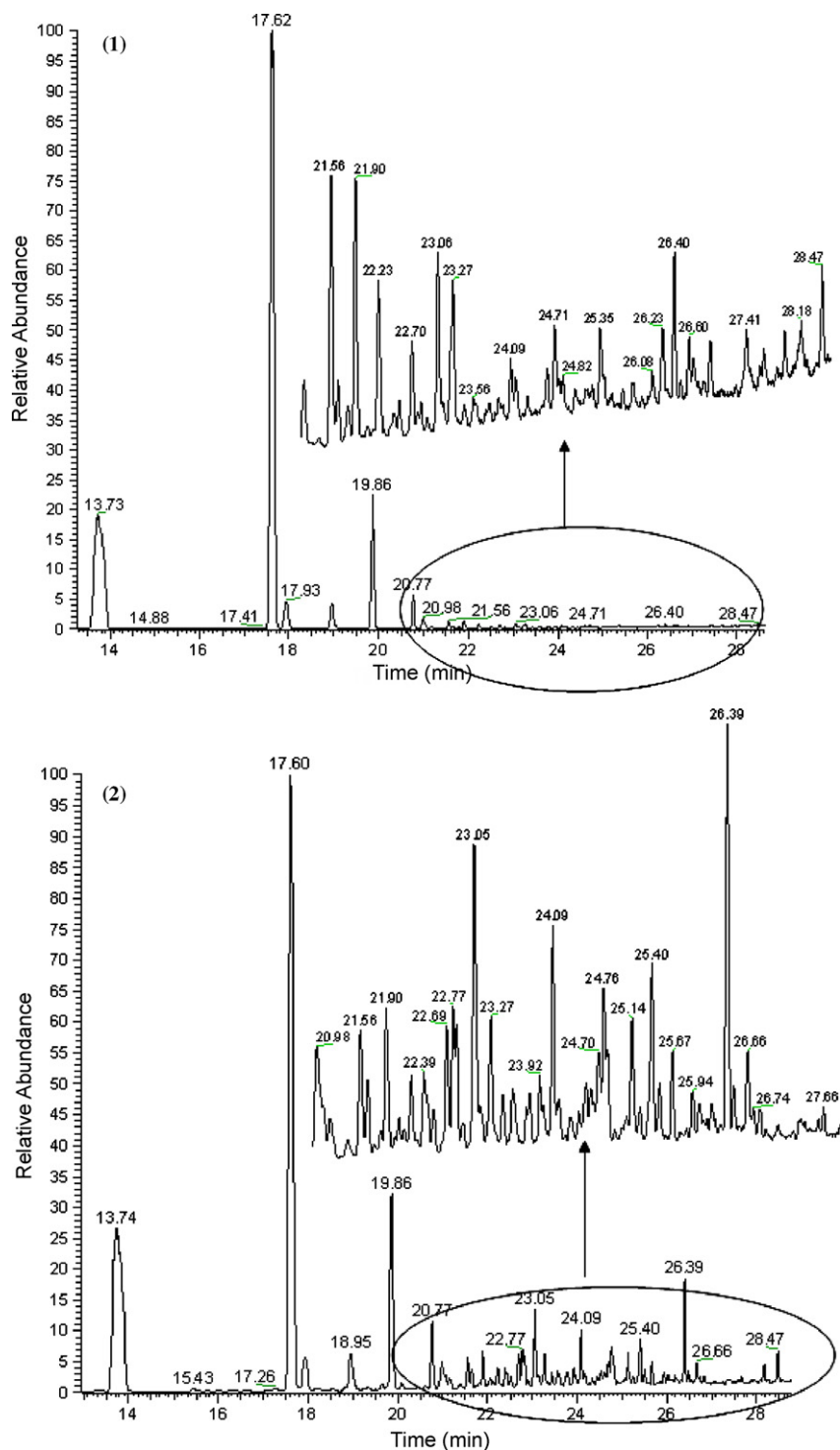


Fig. 5. GC-MS chromatogram of (1) eluate 2 and (2) eluate 4, where it can be seen a high content in volatile compounds.

3.4.2. Ecotoxicological criteria for the classification of the solid residues

The ecotoxicological limit-value defined in the French proposal [28] for bio-indicator *V. fischeri* is EC_{50} (30 min) $\leq 10\%$ (v/v). Comparing the results of the ecotoxicological characterization with this limit-value, it can be observed the following:

- Eluates 1 and 3 have shown values above 10%, making it in turn possible to conclude that the residue A is not ecotoxic.

- Eluates 2 and 4 have shown EC_{50} values below 10%, being possible to classify residue B as ecotoxic waste.

4. Conclusions

The extraction of pyrolysis solid residues with an appropriate organic solvent is an efficient method for the reduction of their content in organic contaminants and, therefore, a reduction on their ecotoxicity. The resulting extraction solvent has, however, to

be submitted to an industrial treatment in order to recover both solvent and the organic compounds.

The solvent used in this work, DCM, showed a good capacity for the removal of volatile organic compounds but the weight loss experiments showed that the residue extracted with DCM still contained a reasonable amount of non-volatile organic matter.

The chemical analysis by GC-FID and by GC-MS showed that these residues are contaminated with relatively high concentrations of volatile organic compounds, namely BTEX with a high ppb range. These concentrations are above the legislated values admissible for eluates of industrial residues. Residue A was not classified as ecotoxic by the biological criteria but is considered ecotoxic by the chemical criteria. The toxicity of residue A is associated with the presence of the heavy metal Ni.

Residue B was classified as ecotoxic by both chemical and biological criteria and its toxicity was attributed to the presence of organic contaminants. Residue B was also classified as a non-inert residue according the 2003/33/CE Council Decision.

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