Characterization of chars produced in the co-pyrolysis of different wastes: Decontamination study

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ABSTRACT

The present work is devoted to the study of the decontamination of chars obtained in the co-pyrolysis of plastics, biomass and tyre wastes. The chars were extracted with several organic solvents of different polarities either individually or in sequence. The ability of each selected extractant to remove toxic pollutants was evaluated by comparing the extraction yields and by characterizing the crude extracts with a combination of chemical analysis and toxicity bioassays. Also, the mineral composition of the treated and non-treated chars was assessed. The results obtained in this study indicate that hexane is the more efficient extraction solvent to be used in the organic decontamination of chars obtained in the co-pyrolysis of plastics, tyres and biomass. A sequential extraction with solvents of increasing polarity can provide a better decontamination of the raw pyrolysis char than any individual extraction. The compounds removed from the char during the decontamination process are mainly aliphatic hydrocarbons and aromatic hydrocarbons, therefore a material that may be upgraded to be used as a fuel and/or as raw material for the organic chemical industry.

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1. Introduction

The interest in the upgrading of wastes such as plastics, biomass and tyres is growing since high amounts of these wastes are presently generated. A range of complementary options can be developed to address each different waste stream with the best environmental and economic approach.

World's annual production of plastic materials has reached around 230 million tonnes in 2009 with Europe representing 24% of the global plastics production [1]. At present, over 1 billion tyres are sold worldwide each year and subsequently just as many falls into the category of end of life tyres [2]. Also, biomass wastes are produced in huge amounts from different sources (agriculture, cleaning forests and wood processing industries) and recovery routes have to be developed for these wastes in order to reclaim its organic content in an energetic useful way [3].

The traditional strategies for solid waste transformation and disposal include landfilling or incineration. Thermal treatment of wastes, by gasification or pyrolysis, is considered to be one of the best treatment methods since it allows the energetic and chemical valorization of the wastes and minimizes the discharge of pollutants into the environment [4].

In the pyrolysis process, the wastes are converted into a hydrocarbon mixture (vapour and liquid fractions) that can be used as fuel or as feedstock in chemistry industries, and a carbon-rich solid by-product (char) that can be used as carbon black or alternatively upgraded to activated carbon [5]. These chars may contain a wide range of toxic substances including heavy metals and organic compounds distributed by a porous structure [6]. Therefore, they have a toxicity potential that must be assessed in order to define their safe reutilization or disposal.

The present work is devoted to the study of chars obtained in the co-pyrolysis of plastics, biomass and tyre wastes. The composition of these chars is not yet well studied and only recently Bernardo et al. [7–9] provided some information about the characterization and risk assessment of these materials.

The main conclusions of these studies were that, globally, the chars must be classified as hazardous and ecotoxic materials, but when submitted to a treatment with an appropriate organic solvent an efficient reduction of their content in organic contaminants was achieved and, therefore, a reduction on their ecotoxicity was observed.

In this study, the use of several halogenated and non-halogenated solvents with different polarities, was examined for the solubilization/desorption of inorganic and organic contaminants from the char's matrix. The ability of each selected extractant to remove toxic pollutants was determined by comparing the extracts yield and thoroughly characterizing the different extracts obtained.

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A chemical fractionation of the crude solvent extracts obtained was performed in order to separate the organic compounds into different classes: aliphatic, aromatic and polar constituents. Up to now, studies concerning the chemical fractionation of extracts in different organic classes by solvents extraction have been applied, mostly to the characterization of coal/petroleum tars and related material [10–14] as well as to biomass tars [15–17]. This type of approach applied to the characterization of pyrolysis chars has not been reported before, in particular, with a detailed analysis of the individual organic compounds.

There are no specific methods or standards indicated for the analysis of pyrolysis chars. However, the common procedures used in the chemical fractionation of petroleum wastes, for example the method recommended by EPA [18], can be adapted taking into account the physical and chemical similarities between petroleum wastes and pyrolysis chars contaminants.

In this work, another tool will be used to evaluate the efficiency of the extraction procedure in removing toxic substances from the pyrolysis chars: bioassays in the different solvent extracts obtained as well as in each of the organic fractions obtained. The so called bioassay-directed fractionation (BDF) is a valuable technique that aims to establish a causal link between chemical substances and biological effects in environmental samples by combining chemical and biological techniques. The toxicity measurement of the chemical fractions has the advantage of giving a global response to all toxic compounds that are present. The BDF approach has been mainly used in aqueous samples [19–21], air particulates [22] and contaminated sediments/soils [23–25]. To the author's knowledge, this is the first time that BDF is applied and used in the characterization of pyrolysis chars.

The results will allow the choice of an efficient solvent to be used in the decontamination of the pyrolysis chars.

2. Materials and methods

2.1. Pyrolysis chars

The char samples were obtained in the co-pyrolysis of a waste mixture composed of 30% (w/w) pine biomass, 30% (w/w) used tyres and 40% (w/w) plastics. The mixture of plastics was 56% (w/w) polyethylene, 27% (w/w) polypropylene and 17% (w/w) polystyrene, simulating the composition of the plastic fraction present in Portuguese municipal solid wastes (MSWs). Pyrolysis experiments were carried out in a 1 L autoclave (Parr Instruments) with an initial nitrogen pressure of 0.41 MPa during 15 min at a temperature of 420 °C. At the end of the assay, the reaction products were as follows: 10% (w/w) gases, 60% (w/w) liquids and 25% (w/w) solids. About 5% losses of the final pyrolysis products were determined.

More information about the pyrolysis installation and experiments can be found in previous papers [8,26,27].

The chars obtained were a carbonized particulate residue impregnated with the oily condensates.

2.2. Chars extraction: solvents selection

The pyrolysis chars were submitted to a soxhlet extraction according to an adaptation of the EPA 3540C method [28]. Several organic solvents with different polarities were used: hexane, dichloromethane, a mixture of 1:1 (v/v) of hexane:acetone and ethanol. Also, a sequential extraction of hexane, mixture of 1:1 (v/v) hexane:acetone and ethanol was performed with the aim of achieving a higher extraction yield. Extraction was performed during 16 h at a rate of 4 cycles/h.

The solvents were eliminated from the crude extract solutions using a vacuum rotary evaporator. All extracts were equilibrated to room temperature and weighed to determine the extraction yields.

2.3. Determination of the organic matter content in the raw and extracted chars

The relative mass composition of chars based on the volatility of their components (volatile, semivolatile, non-volatile organic matter and ashes) was determined by measuring the progressive weight loss associated with the combustion of the solid samples in a microwave muffle furnace. The samples were heated from room temperature (25 ± 1 °C) until 600 ± 1 °C with increments of 50 °C, remaining 10 min at each temperature stage. At the end of each heating stage, the samples were removed from the furnace, cooled to room temperature in a desiccator and weighed.

It was considered that volatile organic compounds were those that were lost at temperatures up to 200 °C. The weight loss registered between 200 °C and 350 °C was attributed to semi-volatile compounds, while the weight decrease observed from 350 °C to 550 °C was assigned to losses of heavy organic compounds (fixed carbon). The residue non-combusted above 550 °C is considered to be mainly composed of inorganic matter and was designated by ashes.

2.4. Determination of the content in heavy metals in raw wastes and chars

A microwave acid digestion based in the EPA 3052 method [29] was used to digest the plastics, pine biomass and tire wastes.

The chars were submitted to a previous digestion made with hydrogen peroxide 30% (v/v) in a heated bath at a temperature of 95 °C followed by *aqua regia* (HCl:HNO$_3$, 3:1, v/v) at the same temperature. Finally, a microwave acidic digestion with *aqua regia* in closed PTFE vessels was used to complete the solubilization of the inorganic components of the samples.

A broad group of heavy metals were quantified in the digested samples using a Thermo Elemental Solaar atomic absorption spectrometry equipment.

2.5. Bioassays

All the crude extract solutions obtained with the different organic solvents were analysed for ecotoxicity with the standardized Microtox® bioassay based on the luminescence inhibition of the bacterium *Vibrio fischeri* when exposed to toxicants (Azur Environmental Microtox® System [30]). The Microtox® toxicity test adequate for organic extracts was followed in this work according the manufacturer's protocol. The extract solutions were first solvent-exchanged to the organic solvent dimethylsulfoxide (DMSO) and appropriately diluted in the osmotically adjusted 2% NaCl solution (Microtox® diluent solution) in order to achieve ≤1% DMSO at all concentrations, the maximum DMSO concentration that can be applied to Microtox® without any toxic effect [30]. Blank tests with DMSO were performed to confirm the non-toxicity of the solvent system. The luminescence inhibition of *V. fischeri* was evaluated for the exposure periods of 5, 15, and 30 min. The EC$_{50}$ values (effective concentration of toxicant resulting in a 50% decrease in bioluminescence) of the DMSO crude extracts were expressed as mass per liter of diluent.

2.6. Fractionation of the most toxic crude extract – bioassay testing and chemical analysis

The crude extract that presented the highest toxicity was fractionated into aliphatic, aromatic and polar fractions according to
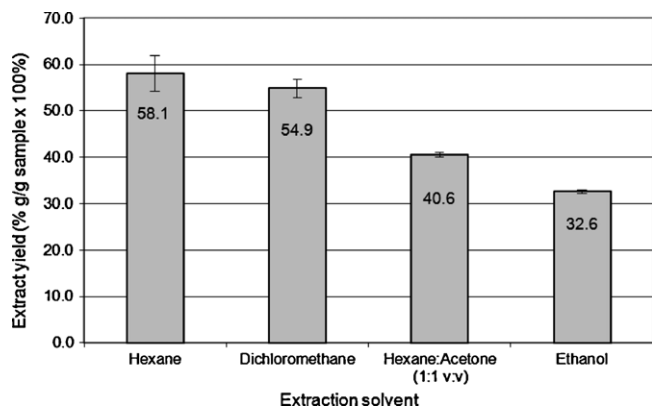
Fig. 1. Extract yields of the pyrolysis char obtained with the different extraction solvents. The mean and standard deviation of duplicates are shown.

the EPA 3611B method [18]. Although this EPA method is applicable to petroleum wastes it can be adapted to this work taking into account the physical and chemical similarities between petroleum wastes and our crude solvent extracts. The extract was fractionated on a glass column packed with alumina and the aliphatic, aromatic and polar fractions were eluted with hexane, dichloromethane and methanol, respectively.

The fractionated extracts (aliphatic, aromatic and polar) were analysed by the Microtox® assay following the same protocol used in the crude extracts.

The aliphatic and aromatic fractions were analysed for chemical composition using a Thermo Scientific Focus Gas Chromatograph equipped with an auto-sampler, a split-splitless injector, a TR-5MS (Thermo Scientific) capillary column (30 m × 0.25 mm I.D. × 0.25 μm film) and a Thermo Scientific Polaris Q mass spectrometer detector.

The carrier gas was helium at 1 mL/min; 1 μL of the samples were injected at 270 °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 270 °C and 250 °C, respectively; the oven temperature program was as follows: initial temperature of 35 °C (hold 1 min), up to 290 °C at a temperature rate of 3 °C/min (hold 15 min). The MS system was operated in the full scan mode with a mass range from m/z 50 to 650.

Blank GC–MS analyses between extract fractions were performed.

In the aliphatic fraction, the main components were identified by comparison of their retention times and mass spectra with authentic standards (a hydrocarbon mixture from C10 to C30) and also by tentatively identification by the comparison of their mass spectra with references from the Wiley and NIST spectra libraries.

In the aromatic fraction the main components were tentatively identified by comparison of their mass spectra with references from the Wiley and NIST spectra libraries.

The polar fraction was not analysed and will be object of further study in future work.

3. Results and discussion

3.1. Extract yield for different extraction solvents

3.1.1. Single extraction

The effects of organic solvents on the extraction yield were studied and the results are presented in Fig. 1.

The most effective extractants for single extractions were hexane and dichloromethane with extract yields of 58.1% and 54.9%, respectively, which shows that most of the pyrolysis chars organic components are non-polar or with low polarity. The extract yields

Table 1
Sequential extraction experiment and extract yields of the pyrolysis char obtained in each extraction step.

Extraction step	Extraction solvent	Extract yield ± S.D.[a] ($n=2$) (% g/g sample)
1	Hexane	58.1 ± 3.9
2	Hexane:acetone (1:1, v/v)	17.2 ± 4.6
3	Ethanol	1.9 ± 1.8

[a] Standard deviation.

decreased with the solvent polarity, being ethanol the solvent with the worst removal efficiency (32.6%). Also, the colour of this extract was much lighter than the other extracts. Solvent polarity plays an important role in decreasing the solubility of organic contaminants from the pyrolysis chars. Nevertheless, even with the increasing polarity of the solvents, the extracts yields were considerable high, reflecting the complexity and diversity of char's composition with a wide range of organic compounds with different polarities and solubilities.

3.1.2. Sequential extraction

In order to achieve a more efficient removal of the different organic contaminants that might be present, a sequential extraction with different solvents of growing polarity was performed. The combination of organic solvents selected for the sequential extraction and the extract yields obtained in each extraction step is listed in Table 1.

In the first step of extraction, hexane was chosen to extract most of the organic non polar contaminants, since it was the less polar organic solvent that, individually, had the highest extract yield. In the second extraction step, with the mixture 1:1 (v/v) of hexane and acetone, a significant removal of organic compounds was still observed with an extract yield of 17.2%. Probably, the more polar components were extracted in this step. The last extraction step with ethanol removed a small amount of organic contaminants, with an extract yield not very significant (1.9%).

The global extract yield of the sequential extraction was around 65.9%, a value superior to the extraction yield of hexane (58.1%). This result indicates that a combination of extraction solvents, namely, an extraction with hexane followed by an extraction with solvents of higher polarity, could be used to remove more efficiently different classes of organic contaminants. The initial extraction with hexane removes a substantial fraction of the non-polar contaminants leaving the char and the more polar contaminants available for extraction by the solvents of medium to high polarity like acetone or ethanol.

3.2. Characterization of the solid chars after extraction

3.2.1. Organic matter content in the raw and extracted chars

The relative mass composition of the raw and extracted chars based on the volatility of their components (volatile, semi-volatile, fixed carbon and ashes) is presented in Fig. 2.

The extractions with the different organic solvents removed mainly the light organic contaminants from the raw char and, consequently, the heavier components, in particular the fixed carbon corresponds to higher relative mass fractions in the extracted chars.

Hexane was the organic solvent that was less efficient in reducing the volatile fraction from the char, but it was the more efficient one in removing the semi-volatile mass fraction. The char treated with hexane presented the higher content in fixed carbon due to a concentration effect resulting from the removal of semi-volatile compounds and, therefore, it may be the char with higher heating value. According Hwang et al. [31] as high the amount of fixed carbon in chars, higher heating values could be obtained and the char can be considered useful as fuel.
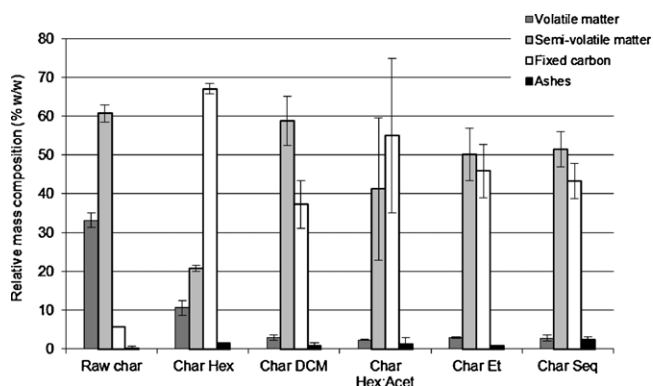
Fig. 2. Relative mass composition (% m/m relatively to the initial weight) of the raw and extracted chars (raw char, char non extracted; Char Hex, char extracted with hexane; Char DCM, char extracted with dichloromethane; Char Hex:Acet, char extracted with the mixture 1:1 (v/v) of hexane and acetone; Char Et, char extracted with ethanol; Char Seq, char sequentially extracted). Duplicate samples.

The relative mass composition profile of the chars extracted with dichloromethane, ethanol and the char sequentially extracted is very similar indicating that these solvents remove organic compounds with the same volatility characteristics.

The char treated with the mixture of hexane and acetone presents a profile more close to the char treated with only hexane. The small differences between these chars could be attributed to the presence of acetone, that allowed to extract more volatile contaminants.

3.2.2. Mineral composition of the raw wastes and chars

Table 2 shows the content of heavy metals in the raw wastes and in chars (extracted and not extracted).

A wide range of heavy metals was chosen to be quantified in the raw wastes and in the chars (extracted and not extracted) in order to give complete information about the metal content.

The heavy metals cadmium (Cd), chromium (Cr), nickel (Ni) and molybdenum (Mo) were not detected in any of the raw wastes or chars.

Alkali metals are present in high amounts in the raw wastes, in particular the content of calcium (Ca) were significant for all the three wastes.

Zinc (Zn) and lead (Pb) were detected in the wastes in significant concentrations. Plastic additives are, usually, the major source for metals contamination in plastic wastes. Zn was present with major amounts in tyres since zinc oxide is added as an activator during the vulcanizing process [32].

As expected from its concentrations in the raw wastes, Zn and Ca were the metals quantified with higher amounts in the raw char obtained from the co-pyrolysis of the three wastes.

Although mercury (Hg) was detected in plastics in significant quantities, its concentration in the raw char was not significant. The same was observed for barium (Ba), which was quantified with a significant amount in tire wastes but in the resulting pyrolysis char it was below the detection limit. Probably mercury suffered volatilization during pyrolysis and barium was dissolved in the liquid fraction.

In general, the concentrations of metals in the extracted chars were higher than in the raw char. This could be attributed to a concentration effect associated with the extraction treatment with solvents in which mass reduction occurs. Moreover, in the raw char some metals might be strongly associated with the organically char matrix and they are not easily solubilised with acids and/or they are matrix-encapsulated as fine mineral particles to which an acid solution is hardly accessible [33,34]. Therefore, the heavy metal content in the raw char may be under estimated. After the treatment with
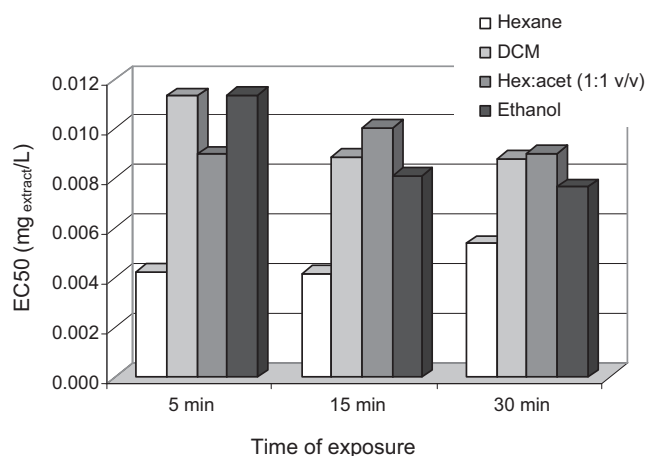

Fig. 3. Toxicity data of crude solvent extract solutions. Hexane, hexane crude extract; DCM, dichloromethane crude extract; Hex:Acet (1:1, v/v), crude extract obtained with the mixture 1:1 (v/v) of hexane and acetone; ethanol, ethanol crude extract.

the organic solvents, the carbon structure of the chars may have suffered some changes and the organically associated elements may be transformed to acid soluble species [35,36].

No significant differences were observed in the metal content of the different extracted chars. The small differences in the concentrations of metals might be because of the heterogeneities of the chars or, as said before, because of some changes that occur in the char matrix after the treatment with organic solvents that affected the metals availability.

Thus, in spite of the organic solvents reduce significantly the potential toxic organic matter, the chars still have huge amounts of some metals which can be a problem concerning their safe reutilization and/or final disposal. Zinc represents the major problem taking into account its higher concentration in the treated chars and although it was previously demonstrated that Zn mobility/leachability [8] is suppressed in the extracted pyrolysis chars, its release has to be monitored. This will be object of study in a future work.

3.3. Ecotoxicity of crude solvent extracts

3.3.1. Single extraction

The toxicities of the crude solvent extracts obtained in the single solvent extractions are presented in Fig. 3. From the results obtained is clear that all the crude solvent extracts present severe toxic effects to *V. fischeri* with EC_{50} values varying from 0.0042 to 0.0114 mg extract/L being the hexane crude extract the most toxic. Hexane was the solvent that allowed to achieve the highest extraction yield in the pyrolysis chars (58.1%) and the higher amount of extract obtained can explain the highest toxicity. Also, the classes of compounds that were extracted with this solvent as well as some synergistic effects between them can be responsible for higher toxicity.

Although the extraction yield with dichloromethane was also high (54.9%), the toxicity of the extract obtained was lower than the toxicity of the hexane extract. The toxicity of the dichloromethane extract is very similar to the toxicity of the crude extracts obtained in the extractions with the more polar solvents, in spite of the lower extractions yields obtained with these solvents. Hexane extracted mostly non-polar compounds rather than polar compounds and they may be the major cause of toxicity to *V. fischeri*. Dichloromethane, the mixture of hexane and acetone and ethanol probably extracted the same classes of compounds, as it was

Table 2
Inorganic characterization of the raw wastes and chars.[a]

Metals (mg/kg)	Plastics	Pine biomass	Tyres	Raw char	Char hex	Char DCM	Char hex:acet	Char et	Char seq
Cd	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
Pb	4.8 ± 1.0	4.3 ± 0.004	14.5 ± 1.0	23.6 ± 6.6	73.3 ± 2.8	61.5 ± 0.3	61.6 ± 2.0	55.1 ± 5.9	76.6 ± 5.9
Zn	9.2 ± 1.0	22.9 ± 1.3	31 193 ± 441	3 615 ± 539	12 142 ± 221	9 868 ± 352	8 388 ± 1267	6 686 ± 612	9 128 ± 183
Cu	<1.0	19.1 ± 1.6	<1.0	1.9 ± 1.5	3.8 ± 0.6	4.0 ± 2.6	<1.0	3.4 ± 0.5	4.5 ± 2.5
Cr	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5	<4.5
Ni	<1.8	<1.8	<1.8	<1.8	<1.8	<1.8	<1.8	<1.8	<1.8
Mo	<33.5	<33.5	<33.5	<33.5	<33.5	<33.5	<33.5	<33.5	<33.5
Ba	<11.3	<11.3	21.7 ± 3.1	<11.3	<11.3	<11.3	<11.3	<11.3	<11.3
Hg	5.4 ± 1.0	0.13 ± 0.04	0.10 ± 0.02	0.17 ± 0.09	0.09 ± 0.02	0.22 ± 0.01	0.27 ± 0.10	0.24 ± 0.02	0.25 ± 0.05
As	<0.1	<0.1	1.00 ± 0.03	0.09 ± 0.04	0.21 ± 0.07	0.12 ± 0.03	0.30 ± 0.08	0.24 ± 0.05	0.29 ± 0.01
Sb	0.28 ± 0.01	0.18 ± 0.01	1.20 ± 0.18	0.26 ± 0.13	0.49 ± 0.18	0.69 ± 0.13	0.70 ± 0.17	0.66 ± 0.23	0.76 ± 0.34
K	<2.6	1050 ± 173	738 ± 16	195 ± 45	646 ± 66	551 ± 64	425 ± 3	309 ± 98	407 ± 61
Mn	<1.6	11.3 ± 0.1	2.7 ± 1.0	4.1 ± 0.9	6.9 ± 3.2	7.2 ± 2.9	9.2 ± 1.5	6.8 ± 0.9	11.5 ± 0.3
Fe	<15.8	<15.8	97.7 ± 18.6	28.6 ± 5.0	142 ± 38	181 ± 56	44.8 ± 21.3	68.5 ± 15.0	174 ± 15
Na	63.9 ± 8.3	146 ± 16	167 ± 31	69.7 ± 29.2	143 ± 30	230 ± 24	276 ± 108	127 ± 35	256 ± 40
Ca	852 ± 140	859 ± 283	2402 ± 91	2508 ± 403	2668 ± 98	673 ± 87	487 ± 26	1281 ± 61	3723 ± 412
Al	<1.5	<1.5	150 ± 35	55 ± 4	120 ± 12	111 ± 34	63.6 ± 15.4	81.4 ± 36.1	180 ± 67
Mg	19.1 ± 0.7	212 ± 6	333 ± 19	112 ± 78	706 ± 88	304 ± 15	269 ± 68	219 ± 71	341 ± 91

[a] The mean and standard deviation of duplicates are shown. Raw char, char non extracted; char DCM, char extracted with dichloromethane; char hex, char extracted with hexane; char hex:acet, char extracted with the mixture 1:1 (v/v) of hexane and acetone; char et, char extracted with ethanol; char seq, char sequentially extracted.

already seen in Section 3.2.1, and those compounds with higher polarity have low inhibitory effects on the bacterium.

The toxicity of crude extracts obtained with dichloromethane and ethanol was observed to decrease with time whereas the toxicity of the hexane extract increased with time and for the extract obtained with the mixture of hexane:acetone no direct relation with time was observed.

3.3.2. Sequential extraction

The toxicities of each crude extract obtained in each of the extraction steps in the sequential extraction are presented in Fig. 4.

As expected, the toxicity decreases in each extraction step accordingly with the sucessive lower extraction yields obtained. The 1st extraction step with hexane allowed to remove the most toxic contaminants. The subsequently extraction steps with the more polar solvents allowed to eliminate the residual polar contaminants that remained in the pyrolysis char that, according to the results, are less toxic to *V. fischeri*. These result suggests that could be useful to perform the sequential extraction for a better decontamination of the raw pyrolysis char.

3.4. Characterization of the hexane crude extract

The hexane crude extract was subsequently chosen to be fractionated into aliphatic, aromatic and polar fractions in the alumina column by elution of solvents with increasing polarity (hexane, dichloromethane and methanol) since it was the extract that presented the highest toxicity level and because it is interesting to study the chemical composition of the fractions as well as their individual contribution to the global toxicity of the crude extract.

3.4.1. Fractionation of the hexane extract – ecotoxicity of the aliphatic, aromatic and polar fractions

The results concerning the toxicity data of the aliphatic, aromatic and polar fractions of the hexane crude extract are presented in Fig. 5. It can be observed that the most toxic fraction is the aromatic one (with EC_{50} values around 0.3 mg fraction/L), followed by the polar fraction and with the aliphatic fraction playing the minor role to the total toxicity of the crude extract.

In general, the toxicity of the fractions increases with time, in particular from 5 to 15 min and then stabilise. This is more evident to the aliphatic and polar fractions.

3.4.2. Fractionation of the hexane extract – composition of the aliphatic and aromatic fractions from the hexane extract

The chemical composition of the aliphatic and aromatic fractions from the hexane crude extract was analysed using GC–MS. Figs. 6 and 7 show the GC chromatograms for the aliphatic and aromatic fractions, respectively.
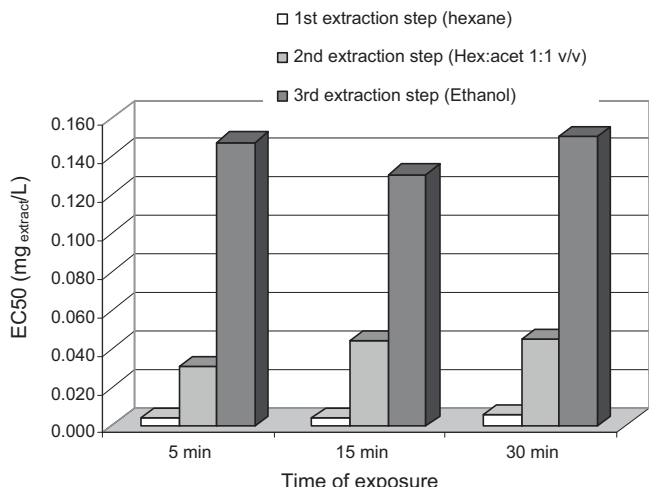
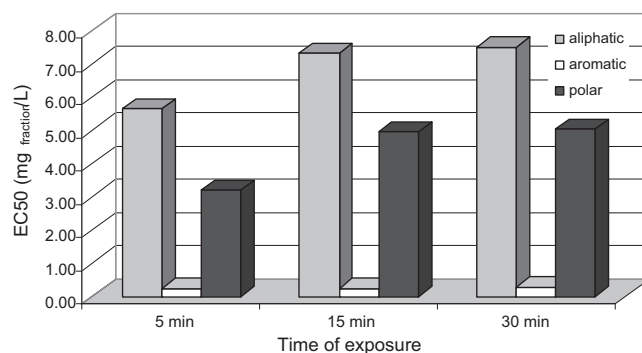**Fig. 4.** Toxicity data of crude extracts in the sequential extraction.

Fig. 5. Toxicity data for the aliphatic, aromatic and polar fractions of the hexane crude extract.
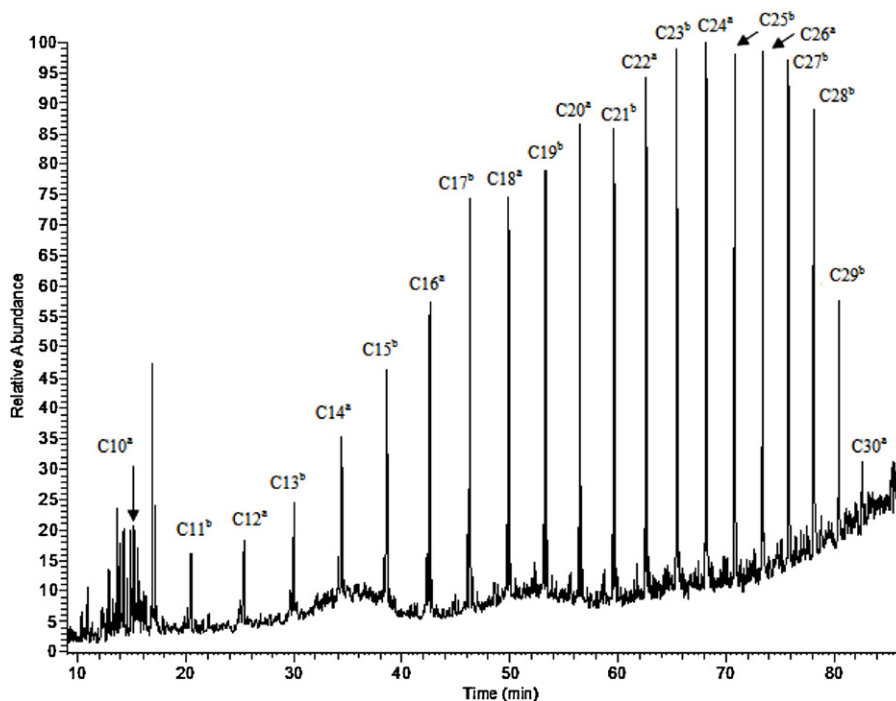
Fig. 6. GC–MS chromatogram of the aliphatic fraction of the hexane crude extract. [a]Compound identified by co-injection of standards; [b]compound tentatively identified by comparison with the spectra of NIST and Wiley libraries.

The aliphatic fraction shows a qualitative profile of n-alkanes from decane (C10) to triacontane (C30). Each n-alkane peak has coupled a smaller peak that corresponds to the homologous n-alkene. It can also be observed a group of lighter compounds, with retention times of 10–20 min, that corresponds mostly to branched and cyclic aliphatic hydrocarbons. It should be noted that some part of lighter hydrocarbons may have escaped by evaporation during the fractionation procedure.

Concerning the aromatic fraction, the GC chromatogram (Fig. 7) shows several peaks that corresponds mostly to aromatic compounds (54.1%) and aliphatic hydrocarbons (45.9%). Thus, there were several aliphatics of long chain that were not eluted by hexane in the first fractionation step and only the second fractionation step with dichloromethane allowed to elute the remaining aliphatic hydrocarbons.
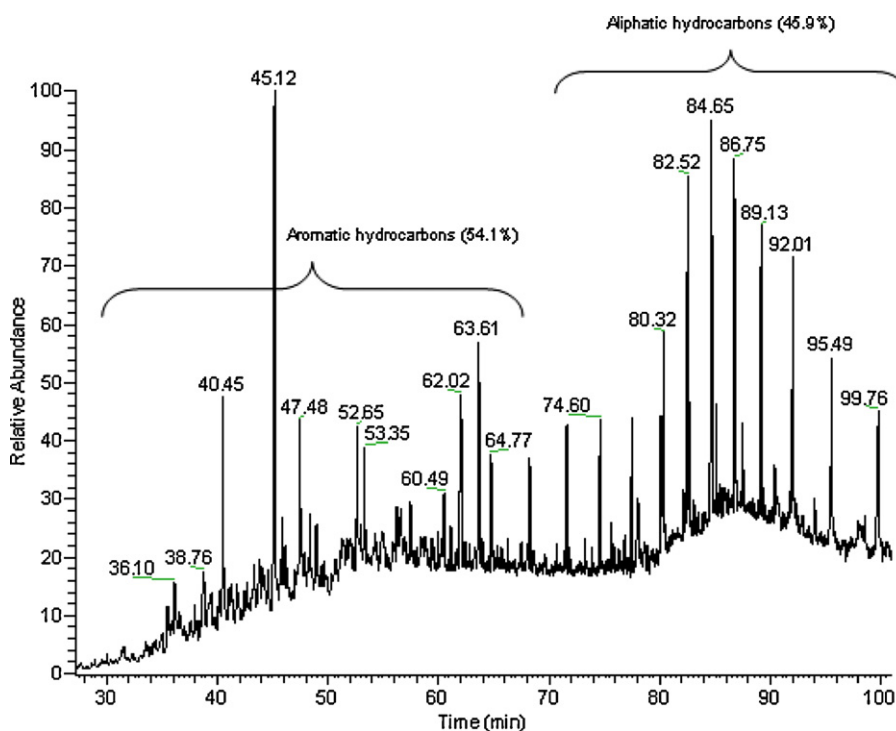

Fig. 7. GC–MS chromatogram of the aromatic fraction of the hexane crude extract.

Table 3
List of aromatic compounds identified in the aromatic fraction of the hexane crude extract.

Retention time (min)	Compound	Relative concentration $\pm$ S.D.[a] ($n = 2$) (%)
36.10	Dimethylnaphthalene	0.74 $\pm$ 0.24
38.76	Diphenylmethane	1.04 $\pm$ 0.15
40.16	Trimethylnaphthalene isomer	0.54 $\pm$ 0.06
40.45	Trimethylnaphthalene isomer	2.74 $\pm$ 0.00
41.02	Trimethylnaphthalene isomer	0.32 $\pm$ 0.01
41.24	Trimethylnaphthalene isomer	0.53 $\pm$ 0.01
43.79	Isopropylmethylnaphthalene	0.38 $\pm$ 0.01
45.12	Diphenylpropane	5.19 $\pm$ 0.25
45.84	Isopropyldimethylnaphthalene	1.09 $\pm$ 0.08
47.48	Tetramethylnaphthalene	2.01 $\pm$ 0.14
47.87	Dimethylbiphenyl	0.27 $\pm$ 0.05
48.31	Isopropylbiphenyl	1.17 $\pm$ 0.07
52.65	Phenyldodecane	1.68 $\pm$ 0.20
53.35	Diphenylhexane	1.00 $\pm$ 0.13
56.6	Phenylnaphthalene	0.54 $\pm$ 0.12
60.49	Propenylanthracene	1.00 $\pm$ 0.06
62.02	Terphenyl	2.45 $\pm$ 0.21
63.61	Tetramethylphenanthrene	2.22 $\pm$ 0.08

The compounds were tentatively identified by comparison with the spectra of NIST and Wiley libraries.

[a] The mean and standard deviation of duplicates are shown.

Table 3 shows the aromatic compounds identified at sufficient concentration to enable the acquisition of elucidative mass spectra. Several other minor peaks that corresponds to substitute benzenes can be observed in the chromatogram. The aromatic compounds identified in this fraction were mainly polyciclic aromatic hydrocarbons (PAHs) derivatives as well as phenyl derivatives. Among the PAHs, naphthalene derivatives were the predominants.

3.5. Comparison of chemical and toxicity results – overview and discussion

The solvent extract obtained in the extraction of the raw pyrolysis char with hexane presented the highest toxicity level to *V. fischeri.* This crude solvent extract was fractionated into different groups of compounds in order to assign their contribution to the overall toxicity. The aromatic fraction obtained in this fractionation procedure was the most toxic one and its GC analysis showed that is mainly composed by PAHs derivatives, phenyl derivatives and aliphatic hydrocarbons. Therefore, it is plausible to assume that the compounds dominating quantitatively this fraction contribute to the observed toxicity in the hexane crude extract.

However, some care has to be taken in establishing a causal link between these compounds and the sample toxicity. It cannot be excluded that the compounds present in the aliphatic and polar fractions may contribute significantly to the toxicity of the crude extract. The aliphatic fraction was composed by a broad range of *n*-alkanes that by themselves cannot induce a marked toxic effect, but together with other compounds, some synergies may arise and originate a combined toxicity. The same can be applied to the polar fraction.

The "petroleum like" profile of the aromatic fraction can explain the high toxicity exhibithed. It was previously demonstrated that organic extracts with a "petroleum like" hydrocarbon profile present more toxicity to *V. fischeri* than organic extracts where a aliphatic hydrocarbon profile prevails [24].

Low molecular PAHs and in particular their alkylated or substituted congeners that are present in high concentrations in the aromatic fraction of the crude extract as well as the phenyl derivatives present acute toxicity in the Microtox assay [37]. So it could be argued that the highest toxicity level of the aromatic fraction can be attributed to the presence of these compounds. Hartnik et al.

[19] showed that PAHs derivatives in particular the alkylated naphthalenes, that were also detected in hight amounts in the aromatic fraction, play a significant role in one of the most toxic fractions obtained from the extract of a creosote groundwater sample.

Several other compounds present in the aromatic fraction could not be identified by GC–MS because they are not included in the spectral databases used and on the other hand there is the possibility of others compounds may exist in concentrations below the detection limit of the analytical method but still be able to cause ecotoxicological effects.

It is difficult to make definite conclusions, but it is possible to establish correlations for the probable cause of toxicity in case of compounds with relatively high concentration and some tentative explanations have to include antagonistic/synergistic behaviours.

4. Conclusions

The results obtained in this study indicate that the more efficient extraction solvent to be used in the organic decontamination of chars obtained in the co-pyrolysis of plastics, tyres and biomass waste is hexane. Higher extraction efficiency concerning extraction yield and removal of toxic organic pollutants was achieved with this solvent.

A sequential extraction with solvents of increasing polarity can provide a better decontamination of the raw pyrolysis char than any individual extraction.

The compounds removed from the char during the decontamination process are mainly aliphatic hydrocarbons and aromatic hydrocarbons, therefore a material that may be upgraded to be used as a fuel and/or as raw material for the organic chemical industry. However, the char obtained after the organic decontamination still contains high amounts of metals which can be a problem concerning their safe reutilization and/or final disposal. The leachability of these metals has to be studied and strategies for removing them have to be evaluated.

The bioassay-directed fractionation applied in this work led to the conclusion that the toxicity of the raw pyrolysis char may be mostly attributed to aromatic compounds like PAHs derivatives and, probably, hexane was the organic solvent that has the higher selectivity and affinity towards these organic contaminants.

The polar fraction of the hexane crude extract are currently being analysed to be presented in a future work and with the primary pollutants present in this fraction identified, more conclusions may arise about the main compounds responsible by the high toxicity exhibithed by the hexane extract obtained.

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