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Characterization of Chars Produced in the Co-pyrolysis of Different Waste: Decontamination and Leaching Studies

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The aim of this work was the study of chars obtained in the co-pyrolysis of plastics, biomass and tyre wastes. The chars were extracted with several organic solvents in order to assess the more efficient in reducing the organic load of the chars and, therefore, their toxicity. 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. Leaching tests were carried out to evaluate the mobility of persistent contaminants. The results indicate that the more efficient extraction solvent was hexane. Zinc was the heavy metal present in higher amounts in the leachates.

1. Introduction

Plastics, biomass and tyre wastes are three types of residues that presently pose difficulties when addressing their final destination. Pyrolysis of these wastes is a valuable option since allow their energetic and chemical valorization. One of the by-products of the pyrolysis process is a carbon-rich solid residue (char) that can be used as carbon black or, alternatively, upgraded to activated carbon (González et al., 2009). These chars contain a broad range of toxic substances including heavy metals and organic compounds distributed by a porous structure (Mui et al., 2010). 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 tyres wastes. The composition of these chars is not yet well studied and only recently an attempt was made by Bernardo et al. (2010) to provide some information about the composition and risk assessment of these materials.

2. Experimental part

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. Pyrolysis experiments were conducted in a 1L autoclave, during 15 min at a temperature of

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420 ºC with an initial pressure of 0.41 MPa. More information about the pyrolysis installation and experiments can be found in previous papers (Paradela et al., 2007; Bernardo et al., 2010).

2.2 Chars extraction: solvents selection

The pyrolysis chars were submitted to a Soxhlet extraction according to the EPA 3540C Method (US EPA, 1996a). Several organic solvents were used: hexane, dichloromethane, a mixture of 1:1 (v/v) of hexane: acetone and ethanol. The solvents were removed from the extract solutions using a vacuum rotary evaporator. All extracts were equilibrated to room temperature and weighed to determine the extraction yields.

2.3 Toxicity bioassays

All the extract solutions were analysed for ecotoxicity with the standardized Microtox® bioassay based on the luminescence inhibition of the bacterium *Vibrio fischeri* when exposed to toxicants. A toxicity protocol adequate for organic extracts was followed in this work according the manufacturer (Microtox, 1992). The extract solutions were solvent-exchanged to dimethylsulfoxide (DMSO). The EC_{50} values (effective concentration of toxicant resulting in a 50 % decrease in bioluminescence) of the DMSO extracts were expressed as mass per liter of diluent.

2.4 Fractionation of the most toxic crude extract - chemical and bioassay analysis

The extract that presented the highest toxicity was fractionated into aliphatic, aromatic and polar fractions, according to the EPA 3611B Method (US EPA, 1996b). The aliphatic and aromatic fractions were analysed using gas chromatography with mass spectrometry. The polar fraction was not analysed and will be object of study in a future work. The fractionated extracts (aliphatic, aromatic and polar) were analyzed by the Microtox® assay following the same protocol used in the crude extracts.

2.5 Determination of the content in heavy metals in the chars

The raw and extracted chars were submitted to a digestion made with hydrogen peroxide 30 % (v/v) in a heated bath at 95 ºC and then with *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 dissolution of the metals from the samples. A broad group of heavy metals were quantified in the digested samples using atomic absorption spectrometry (AAS).

2.6 Leaching tests and leachate analysis

The extracted char was submitted to the leaching standard ISO/TS 21268-2 (ISO/TS 21268-2, 2007). The leachate was analyzed for the content of heavy metals using AAS.

3. Results and discussion

3.1 Extract yields for the different extraction solvents

The effects of organic solvents on the extraction yield were studied and the results are presented in Table 1. The most effective extractants 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 decreases with the solvent polarity, with ethanol being the solvent with the worst removal efficiency (32.6 %). 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.

Table 1: Extract yields obtained with the different extraction solvents.

Extraction solvent	Extract yield (% g/g sample)
Hexane	58.1
Dichloromethane	54.9
Hexane:acetone (1:1 v/v)	40.6
Ethanol	32.6

3.2 Toxicity of solvent extracts

The toxicities of the solvent extracts obtained in the different extractions are presented in Figure 1.

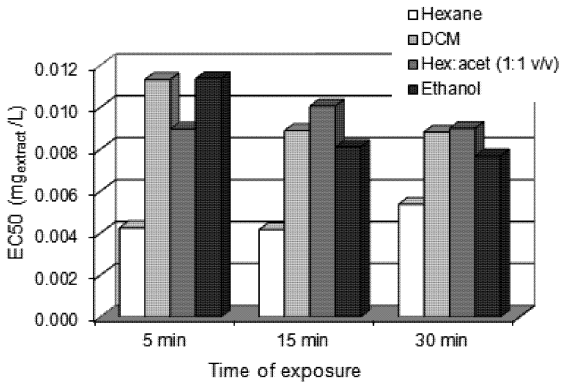

Figure 1: Toxicity data of solvent extract solutions (Hexane – hexane extract; DCM – dichloromethane extract; Hex:Acet (1:1 v/v) – extract obtained with the mixture 1:1 (v/v) of hexane and acetone; Ethanol – ethanol extract).

From the results obtained it is clear that all the solvent extracts presented severe toxic effects to *Vibrio fischeri* with EC_{50} values varying from 0.0042 to 0.0114 mg/L extract, being the hexane extract the most toxic. Hexane was the solvent that allowed to achieve the highest extraction yield in the pyrolysis chars 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 the higher toxicity.

3.3 Characterization of the hexane extract

The hexane extract was subsequently chosen to be chemically fractionated since it was the extract that presented the highest toxicity level and it is interesting to study the chemical composition of the fractions as well as their individual contribution to the global toxicity of the extract.

3.3.1 Hexane extract - Ecotoxicity of the aliphatic, aromatic and polar fractions

The results concerning the ecotoxicity data of the aliphatic, aromatic and polar fractions of the hexane extract are presented in Figure 2. 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.

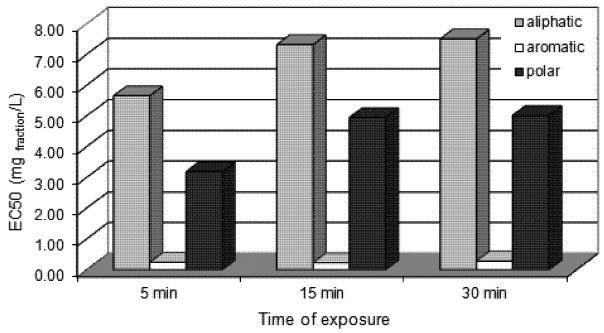

Figure 2: Toxicity data for the aliphatic, aromatic and polar fractions of the hexane extract.

3.3.2 Hexane extract - Composition of the aliphatic and aromatic fractions

Figure 3 shows the GC chromatogram for the aliphatic fraction. The aliphatic fraction shows a qualitative profile of *n*-alkanes from decane (C10) to triacontane (C30). It can be observed a group of lighter compounds, with retention times of 10 to 20 minutes, that corresponds mostly to branched and cyclic aliphatic hydrocarbons.

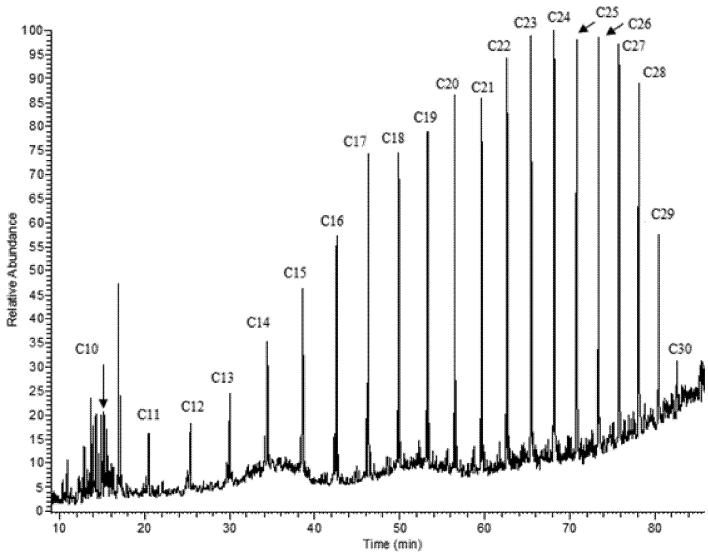

Figure 3: GC-MS chromatogram of the aliphatic fraction of the hexane extract.

Concerning the aromatic fraction, the GC chromatogram showed 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 in the aliphatic fractionation step and only the second fractionation step allowed to elute the remain aliphatic hydrocarbons. 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.

3.4 Inorganic characterization of the chars and leachates

Table 2 shows the content of heavy metals in the chars and leachate. For the leachate, the result is presented in leached substance mass per mass unit of char.

Table :. Heavy metal content in the raw char, char extracted with hexane and in leachate.

(mg/kg)	Raw char	Extracted char	ISO/TS 21268-2 leachate
Cd	<0.6	<0.6	<0.04
Pb	23.6±6.6	73.3±2.8	<0.07
Zn	3615±539	12 142±221	593±4
Cu	1.9±1.5	3.8±0.6	<1.0
Cr	<4.5	<4.5	<0.1
Ni	<1.8	<1.8	<0.1
Mo	<33.5	<33.5	<0.5
Ba	<11.3	<11.3	1.6±0.2
Hg	0.17±0.09	0.09±0.02	<0.01
As	0.09±0.04	0.21±0.07	<0.004
Se	<0.08	0.10±0.02	<0.08
Sb	0.26±0.13	0.49±0.18	<0.06

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

The heavy metals Cadmium (Cd), Chromium (Cr), Nickel (Ni), Barium (Ba) and Molybdenum (Mo) were not detected in any of the chars. Zinc (Zn) and Lead (Pb) were the metals quantified with higher amounts in the raw char obtained from the co-pyrolysis of the three wastes. The concentrations of metals in the extracted char were higher than in the raw char. This could be attributed to a concentration effect associated with the extraction treatment with solvent in which occurs mass reduction. Moreover, in the raw char some metals might be strongly associated with the organically char matrix and were not completely solubilised in the acid digestion whereby they might be under estimated.

Concerning the leachate, Pb and Cupper (Cu) that appeared with relatively high amounts in the treated char were absent from the leachate. Also, Mercury (Hg), Arsenic (As), Antimonium (Sb) and Selenium (Se) detected in the char, were not leached. Barium, which was not detected in the extracted char, was leached with a minor amount.

As expected from its concentration in the char, Zn is also the heavy metal present in the highest concentration in the leachate. Given the high concentration of Zn in the

extracted char, this metal can be a problem concerning their safe reutilization and/or final disposal. Strategies for removing Zn have to be evaluated in future works.

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, used tyres and biomass waste is hexane. The compounds removed from the char during the decontamination process are mainly aliphatic hydrocarbons and aromatic hydrocarbons, chemicals 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 have high amounts of Zn which can be a problem concerning their safe reutilization and/or final disposal. The introduction of tyres in the waste mixture (the source of Zn) must be controlled in order to obtain less toxic chars. Other decontamination treatments of Zn must be evaluated and combined with organic solvent extraction.

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