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Study of the valorisation of the solid by-products obtained in the co-pyrolysis of different wastes

Dissertação para obtenção do grau de doutor em Energia e Bioenergia

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Dedicated to Gabriel.

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The author,
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RESUMO

A presente tese teve como objectivo o estudo das propriedades físico-químicas e ecotoxicológicas, da descontaminação e do uso de carbonizados obtidos como subprodutos na co-pirólise de resíduos de plásticos, borracha de pneus usados e biomassa de pinho, no sentido de se avaliar os seus potenciais de toxicidade e de valorização.

Os carbonizados estudados foram obtidos em processos de pirólise descontínuos, a temperaturas relativamente baixas (400 ºC), numa atmosfera de N_2, com tempos de reacção curtos (15 min) e velocidades de aquecimento baixas (5 ºC/min).

Os resultados obtidos permitiram concluir que a extracção dos alcatrões de pirólise que permanecem depositados na superfície dos carbonizados é significativamente importante por duas razões: (i) a descontaminação dos carbonizados e (ii) a recuperação de uma fonte de compostos alifáticos e aromáticos. O tratamento de descontaminação aplicado aos carbonizados e que foi direccionado para a fracção orgânica permitiu efectuar a remoção dos hidrocarbonetos aromáticos que mais contribuíam para a sua ecotoxicidade.

A introdução da borracha de pneus na mistura a pirolisar levou à produção de carbonizados que, após o tratamento orgânico, ainda apresentavam propriedades ecotóxicas e perigosas para ambiente, devido à presença de Zinco em concentrações significativas nas suas matrizes.

A caracterização textural dos carbonizados demonstrou que estes eram predominantemente macroporosos; no entanto, a introdução da borracha de pneu na mistura a pirolisar levou a um aumento de mesoporos e da área superficial nos carbonizados.

Os carbonizados foram utilizados na remoção de Pb^{2+} de meios aquosos, no sentido de se conhecer as suas propriedades de adsorção para metais pesados. O carbonizado com melhor desempenho no estudo da remoção de Pb^{2+} foi obtido a partir da mistura de 50% borracha de pneus + 50% plásticos. O mecanismo principal de adsorção neste carbonizado foi a troca catiónica, tendo o Zn^{2+} participado activamente no processo.

Palavras-chave: co-pirólise; carbonizados; descontaminação; lixiviação; ecotoxicidade; adsorção

ABSTRACT

The main aim of the present thesis was to study the physico-chemical and ecotoxicological properties, decontamination, and use of chars obtained as by-products in the co-pyrolysis of feedstock mixtures composed by plastic wastes, used tire rubber and pine biomass in order to assess their toxicity and potential valorisation.

The char samples studied were obtained in batch pyrolysis, at relatively low temperatures (around 400ºC), N_2 atmosphere, short reaction times (15 min), and low heating rates (around 5 ºC/min).

The results indicated that the extraction of the pyrolysis tars that remain deposited on the surface of chars is rather important for two main reasons: (i) the decontamination of the chars, and (ii) the recovery of an important feedstock of aliphatic and aromatic chemicals. The decontamination treatment applied to the crude chars that was directed to the organic fraction allowed the removal of aromatics hydrocarbons which were the main contributors to the ecotoxicity of chars.

The introduction of tire rubber in the pyrolysis feedstock produced chars that after the organic treatment still have hazardous and ecotoxic properties due to the presence of zinc with high concentrations in their matrices.

The textural characterisation showed that chars are predominantly of macroporous nature; however, the introduction of tire rubber in the pyrolysis feedstock enhanced the mesoporosity and surface area of the resulting chars.

An application of the chars to the removal of Pb^{2+} from aqueous medium provided some insight about their sorption properties for heavy metals. The highest Pb^{2+} removal was attained by the char resulting from a mixture of 50% tire rubber with 50 % plastics. In this char, cation-exchange played the major role on Pb^{2+} sorption with Zn^{2+} participating actively in the sorption process.

Keywords: co-pyrolysis; chars; decontamination; leaching; ecotoxicity; adsorption

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LIST OF ABBREVIATIONS, ACRONYMS AND SYMBOLS

ATT	Advanced Thermal Treatment
EU	European Union
FCT	Fundação para a Ciência e Tecnologia
MCES	Ministério da Ciência e Ensino Superior
MEC	Ministério da Educação e Ciência
PE	Polyethylene
PP	Polypropylene
PS	Polystyrene
ELT	End-of-Life Tires
SBR	Styrene–Butadiene Rubber
AEBIOM	European Association of Biomass
PAHs	Polycyclic Aromatic Hydrocarbons
TCLP	Toxicity Characteristic Leaching Procedure
USEPA	United States Environmental Protection Agency
EPA	Environmental Protection Agency
EC	European Regulation
CEMEW	Criteria and Evaluation Methods of the Ecotoxicity of Waste
UTCAE	Unidade de Tecnologias de Conversão e Armazenamento de Energia
LNEG	Laboratório Nacional de Energia e Geologia
AAS	Atomic Absorption Spectrometry
XRF	X-Ray Fluorescence
DCM	Dichloromethane
BTEX	Benzene, Toluene, Ethylbenzene and Xylenes
MSW	Municipal Solid Wastes
HS	Headspace Static
GC	Gas Chromatography
FID	Flame Ionization Detector
MS	Mass Spectrometry
LOD	Limits of Detection
LOQ	Limits of Quantification
R.S.D.	Relative Standard Deviation
DLLME	Dispersive Liquid-Liquid Microextraction
PCBs	Polychlorinated Biphenyls
BDF	Bioassay-Directed Fractionation
DMSO	Dimethylsulfoxide
MSTFA	*N*-methyl-*N*-trimethylsilyltrifluoroacetamide
EDTA	EthyleneDiamine Tetraacetic Acid
TOC	Total Organic Carbon
IC	Inorganic Carbon

BET	Brunauer–Emmett–Teller
BJH	Barrett, Joyner, and Halenda
IUPAC	International Union of Pure and Applied Chemistry
PCDDs	Polychlorinated Dibenzodioxins
PCDFs	Polychlorinated Dibenzofurans

CHAPTER 1

1. PURPOSE OF THE INVESTIGATION

- *Background of the study*
- *Motivation and objectives of the thesis*
- *Thesis outline*

1.1 BACKGROUND OF THE STUDY

Advanced Thermal Treatment (ATT) technologies, primarily pyrolysis and gasification based processes, are emerging and growing in importance in the field of “sustainable waste treatment options”, as well as in the field of “waste to energy”. This is because of their potential to convert wastes into added-value products for energetic and non-energetic applications.

The European Waste Framework Directive[1] established the waste management hierarchy (Figure 1) that should be adopted and applied by the member states of the European Union (EU) in order to deliver the best overall environmental, human health, economic and social impacts. This waste management hierarchy is generally followed all over the world.

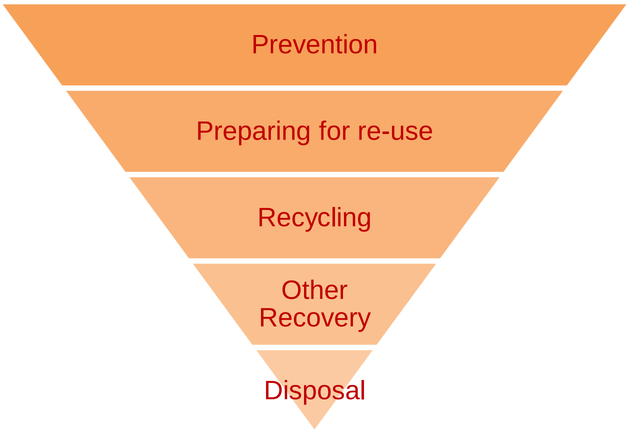

Figure 1. Waste management hierarchy in the Waste Framework Directive[1].

According to the European Waste Directive, thermal treatment processes such as Pyrolysis and Gasification are considered recovery operations. Incineration is only considered as such whenever energy recovery and generation are performed. Gasification, and particularly Pyrolysis, can also be included in the recycling category as organic waste materials can be reprocessed into new products for several applications through these processes.

This thesis is focused on the Pyrolysis process: the thermal degradation of a substance in the absence of oxygen supply. Organic waste materials can be converted by pyrolysis into the following products: char and synthesis gas (syngas). The syngas is a mixture of gases such as carbon monoxide (CO), hydrogen (H_2), methane (CH_4), some carbon dioxide (CO_2) and different hydrocarbons (C_nH_m), and a fraction of it can be condensed to produce oils, waxes and tars that can be used as fuels and/or as a basic chemical feedstock in refining industries[2-4]. The char is a carbonaceous solid material that retains the mineral matter initially present in the raw wastes and may contain significant amounts of the condensed pyrolysis products dispersed by its structure. Given their high carbon content, calorific values and reactivity, combustion applications for energy recovery has been the most frequent and recommended destination for these pyrolytic solids, as well as gasifier feedstock for syngas production[2,5-9]. Also, landfill deposition of pyrolysis carbonaceous residue has been suggested given their possible low economic value (due to the presence of metallic and organic contaminants), and significant immobilization of the contaminants on matrix of chars[10-13]. However, the pyrolysis char can be further processed for several other applications, namely, adsorption[14-17], catalysis[18-20], soil amendment[21-22] and metallurgical processes[23-24], among others[25].

Polymers are considered a suitable pyrolysis feedstock, since through pyrolysis the high-molecular polymeric chains can be cracked into smaller chains of lighter hydrocarbons similar to petro-based refinery cracking products. Therefore, synthetic polymers, such as plastics and rubber, and natural polymers, such as lignocellulosic biomass, are the preferential feedstock materials.

Over the last years, the pyrolysis of waste and biomass has received a lot of attention from the scientific community, and commercial applications are increasingly being implemented[2-4,26-27]. The main focus of pyrolysis studies and applications has been the gaseous and condensed fractions in the context of energy demand and replacing of fossil fuels.

In the framework of the Waste Management Hierarchy and international greenhouse gas emission reduction commitments (Kyoto Protocol)[28], it is expected that waste treatment by pyrolysis based processes should grow in importance and application. It is anticipated therefore that large amounts of pyrolysis chars will be available as by-products or as main products in the near future. To minimize the associated costs and increase the sustainability of this thermochemical process, the resulting solid chars have to be properly studied and valorised as it is extensively being done for the gaseous and liquid products.

With this background, the main goal outlined for this thesis was the study of the properties, composition, decontamination, reuse, and risk assessment of chars obtained as by-products in the co-pyrolysis of plastic wastes, tire rubber and pine biomass, in order to exploit the potential value of these pyrolysis products.

In the beginning of this doctoral project, a deep literature review and a study of the state-of-the-art concerning this matter was performed which lead to the conclusion that there is a significant lack of information about the potential environmental impact associated with the use, application or disposal of pyrolysis solid products. This thesis aimed to fulfil that scientific gap providing an in-depth knowledge of pyrolysis chars and an evaluation of their possible routes of valorisation focused on applications as adsorbents.

1.2 MOTIVATION AND OBJECTIVES OF THE THESIS

In 2007, the PhD candidate was granted with a research fellowship under the project POCTI/ENR163388/2004 entitled “Valorization of used tires, plastics and biomass wastes by pyrolysis to produce valuable end products”. Both the project and the research fellowship grant were funded by Fundação para a Ciência e Tecnologia (FCT), of the former Ministério da Ciência e Ensino Superior (MCES), currently Ministério da Educação e Ciência (MEC). The fellowship started in June 1 and lasted for 6 months with the main objective to perform the chemical and ecotoxicological characterisation of the solid by-products resulting from the pyrolysis of biomass, plastics and tire rubber wastes. Under this project and before the beginning of the experimental work, a literature review about the theme with special focus on the potential toxicity of pyrolysis solid products, their safe disposal and valorisation was performed. A lack of information and knowledge concerning the application of leaching tests to these materials for the assessment of their environmental hazardousness was encountered.

Some of the results obtained in the project were object of publication in 2 scientific papers in international peer-reviewed journals[29-30] and one conference proceeding[31]. This constituted the beginning of the doctoral thesis. Given the acceptability by the scientific community of the work presented in those papers, it was considered that an extension and upgrade of the experimental research should be conducted. This decision led to an application for a doctoral grant submitted to FCT-MCES in 2008.

The doctoral grant with the reference SFRH/BD/43354/2008 was granted and the doctoral project started in April 2009 with the title of the present doctoral thesis “Study of the valorisation of the solid by-products obtained in the co-pyrolysis of different wastes”. The grant and the doctoral project finished both in July 31, 2013.

The main objective of the present thesis is the characterisation and decontamination of the solid by-products, named as “chars”, obtained in the co-pyrolysis of different mixtures composed by pine biomass, used tires and plastic wastes in order to assess their potential toxicity and valorisation for environmental applications.
To achieve this main goal, the following specific objectives were defined:

- Characterisation of the raw feedstock materials: plastic wastes (mixture of polyethylene, polypropylene and polystyrene), used tires and pine biomass;
- Chemical and ecotoxicological characterisations of the crude pyrolysis chars and their eluates;
- Application of decontamination treatments to the crude chars;
- Chemical and ecotoxicological characterisation of the decontaminated chars and their eluates;
- Study of the potential of chars to be used as adsorbents;
- Efficiency of chars for the removal of a specific contaminant (lately defined as Pb^{2+}) from aqueous medium.

1.3 THESIS OUTLINE

The present thesis includes the following chapters in addition to Chapter 1:

Chapter 2 – Introduction

This chapter presents an overview of the concepts and waste materials focused in the thesis:

- Why pyrolysis? Comparison with other waste thermal treatment processes.
- The choice of plastic wastes, used tires and pine biomass as raw materials for pyrolysis.
- Literature review focused on pyrolysis solid by-products, the chars.
- Environmental risk assessment of pyrolysis chars:
    - The importance of employing leaching tests.
    - The concept of ecotoxicity applied to chars.
- Originality and scientific innovations introduced by the thesis.

Chapter 3 – Chemical and ecotoxicological characterisation of chars obtained in the co-pyrolysis

This chapter aims to present the characterisation performed on the pyrolysis raw feedstock materials and provide the first insight and scientific knowledge into the subject of environmental hazard assessment of pyrolysis chars through the application of leaching tests and by combining chemical and ecotoxicological analyses.

Subchapter 3.1 – Characterisation of the raw feedstock materials: plastic wastes (mixture of polyethylene, polypropylene and polystyrene), used tires and pine biomass

This subchapter presents the results of the characterisation performed on the raw materials submitted to the pyrolysis experiments.

The results presented in this section were published, completely or partially, in the following papers:

- Bernardo, M.S., Lapa, N., Barbosa, R., Gonçalves, M., Mendes, B., Pinto, F., Gulyurtlu, I., Chemical and ecotoxicological characterisation of solid residues produced during the co-pyrolysis of plastics and pine biomass, *Journal of Hazardous Materials*, 166 (2009) 309–317. (doi: 10.1016/j.jhazmat.2008.11.031; IF: 4.173)

- Bernardo, M., Lapa, N., Gonçalves, M., Barbosa, R., Mendes, B., Pinto, F., Gulyurtlu, I., Toxicity of char residues produced in the co-pyrolysis of different wastes, *Waste Management*, 30 (2010) 628–635. (doi: 10.1016/j.wasman.2009.10.015; IF: 2.428)

- Bernardo, M., Gonçalves, M., Lapa, N., Barbosa, R., Mendes, B., Pinto, F., Characterisation of chars produced in the co-pyrolysis of different wastes: decontamination study, *Journal of Hazardous Materials*, 207–208 (2012) 28–35. (doi: 10.1016/j.jhazmat.2011.07.115; IF: 4.173)

- Bernardo, M., Mendes, S., Lapa, N., Gonçalves, M., Mendes, B., Pinto, F., Lopes, H., Leaching behaviour and ecotoxicity evaluation of chars from the pyrolysis of forestry biomass and polymeric materials, submitted to *Ecotoxicology and Environmental Safety*, 2013.

Subchapter 3.2 - Chars obtained in the co-pyrolysis of plastics and pine biomass

The main core of this section is based on the following 2 scientific papers and 1 oral communication that resulted from the work developed under the FCT project with the reference POCTI/ENR163388/2004:

- Bernardo, M.S., Lapa, N., Barbosa, R., Gonçalves, M., Mendes, B., Pinto, F., Gulyurtlu, I., Chemical and ecotoxicological characterisation of solid residues produced during the co-pyrolysis of plastics and pine biomass, *Journal of Hazardous Materials*, 166 (2009) 309–317. (doi: 10.1016/j.jhazmat.2008.11.031; IF: 4.173)

- Bernardo, M.S., Gonçalves, M., Lapa, N., Barbosa, R., Mendes, B., Pinto, F., Gulyurtlu, I., Determination of aromatic compounds in eluates of pyrolysis solid residues using HS-GC–MS and DLLME–GC–MS, *Talanta*, 80 (2009) 104–108. (doi: 10.1016/j.talanta.2009.06.037; IF: 3.794)

- Bernardo, M., Lapa, N., Gonçalves, M., Barbosa, R., Mendes, B., Pinto, F., Gulyurtlu, I, Evaluation of the environmental hazard of char residues produced in the co-pyrolysis of different wastes: chemical and ecotoxicological characterisation, *Book of Proceedings of the XII International Waste Management and Landfill Symposium*, Sardinia, Italy, 5-9 October 2009.

The studied chars in this subchapter were obtained in the co-pyrolysis of two materials: a mixture of plastic wastes and lignocellulosic biomass residues which are forestry pine.

Subchapter 3.3 - Chars obtained in the co-pyrolysis of plastics, used tires and pine biomass

The main core of this chapter is based on 2 published papers and 1 oral communication:

- Bernardo, M., Lapa, N., Gonçalves, M., Barbosa, R., Mendes, B., Pinto, F., Gulyurtlu, I., Toxicity of char residues produced in the co-pyrolysis of different wastes, *Waste Management*, 30 (2010) 628–635. (doi: 10.1016/j.wasman.2009.10.015; IF: 2.428)

- Bernardo, M., Gonçalves, M., Lapa, N., Mendes, B., Determination of alkylphenols in eluates from pyrolysis solid residues using dispersive liquid–liquid microextraction, *Chemosphere*, 79 (2010) 1026–1032. (doi: 10.1016/j.chemosphere.2010.03.062; IF: 3.206)

- Bernardo, M., Lapa, N., Gonçalves, M., Barbosa, R., Mendes, B., Pinto, F., Evaluation of the toxicity of char residues produced in the co-pyrolysis of different wastes, *CD of Proceedings of the ISWA/APESB 2009 World Congress – Turning Waste into Ideas*, Lisbon, Portugal, 12-15 October 2009.

A different waste - used tires - was introduced in the pyrolysis feedstock mixture which leads to the production of chars that may present significantly different composition and leaching behaviour from the chars of blend only with plastics and pine biomass, influencing their ecotoxicity.

Therefore, the strategy used in the previous subchapter was extended and applied to the characterisation of the chars obtained in these pyrolysis experiments. Also, a focus on the importance of using decontamination treatments to reduce the organic contaminants that contribute to the potential toxicity of the chars was introduced here.

Chapter 4 – Decontamination study of chars obtained in the co-pyrolysis of plastics, used tires and pine biomass

The main core of this chapter is based on 1 published paper and 2 oral communications:

- Bernardo, M., Gonçalves, M., Lapa, N., Barbosa, R., Mendes, B., Pinto, F., Characterisation of chars produced in the co-pyrolysis of different wastes: decontamination study, *Journal of Hazardous Materials*, 207–208 (2012) 28–35. (doi: 10.1016/j.jhazmat.2011.07.115; IF: 4.173)

- Bernardo, M., Lapa, N., Gonçalves, M., Barbosa, R., Mendes, B., Pinto, F., Characterisation of chars produced in the co-pyrolysis of different wastes: decontamination study, *Book of Proceedings of The Second International Conference Hazardous and Industrial Waste Management*, Crete, Greece, 5-8 October 2010.

- Bernardo M., Lapa N., Gonçalves M., Mendes B. and Pinto F., Characterisation of chars produced in the co-pyrolysis of different wastes: decontamination and leaching studies, *Chemical Engineering Transactions*, 25 (2011) 521-526. (doi: 10.3303/CET1125087)

From the previous chapter, particularly subchapter 3.3, regarding the characterisation of chars produced in the co-pyrolysis of plastics, used tires and pine biomass, a main conclusion arose: submitting the pyrolysis chars to an appropriate treatment that reduce their content in organic compounds leads to a significant reduction in their ecotoxic properties. Therefore, this chapter presents a study of the decontamination of the same pyrolysis chars focused on their organic fraction originated mainly from the condensed pyrolysis oils that remained trapped on the matrix of char.

Several organic solvents with different polarities were used to extract the toxic organic compounds present in the chars. The efficiency of each solvent was evaluated by applying a bioassay-directed fractionation: a technique that consists in performing a bioassay in the different solvent extracts obtained as well as in each of the organic fractions obtained in a chemical fractionation of the extracts. The main aim of this procedure was to evaluate which solvents removed the organic compounds more efficiently.

Chapter 5 – Leaching behaviour and ecotoxicity evaluation of the decontaminated pyrolysis chars

The main core of this chapter is based on 1 published paper, 1 submitted paper and 3 oral communications:

- Bernardo, M., Lapa, N., Gonçalves, M., Mendes, B., Pinto, F., Fonseca, I., Lopes, H., Physico-chemical properties of chars obtained in the co-pyrolysis of waste mixtures, *Journal of Hazardous Materials*, 219–220 (2012) 196 – 202. (doi: 10.1016/j.jhazmat.2012.03.077; IF: 4.173)

- Bernardo, M., Mendes, S., Lapa, N., Gonçalves, M., Mendes, B., Pinto, F., Lopes, H., Leaching behaviour and ecotoxicity evaluation of chars from the pyrolysis of forestry biomass and polymeric materials, submitted to *Ecotoxicology and Environmental Safety*, 2013.

- Bernardo, M., Lapa, N., Gonçalves, M., Mendes, B., Pinto, F., Physico-chemical properties and adsorption characteristics of chars produced in the co-pyrolysis of biomass, plastic and Tire wastes, *Proceedings of the 1st International Conference: WASTES: Solutions, Treatments and Opportunities*, Guimarães, Portugal, 12-14 September 2011.

- Bernardo, M., Lapa, N., Gonçalves, M., Mendes, B., Pinto, F., Study of the organic extraction and acidic leaching of chars obtained in the pyrolysis of plastics, tire rubber and forestry biomass wastes, *Procedia Engineering*, 42 (2012) 1909–1916. (doi: 10.1016/j.proeng.2012.07.567)

- Bernardo, M., Lapa, N., Gonçalves, M., Mendes, B., Pinto, F., Fonseca, I., Lopes, H., Characterisation and potential applications of chars from the pyrolysis of polymeric residues, *Proceedings of The 4th International Conference on Engineering for Waste and Biomass Valorisation*, Porto, Portugal, 10-13 September 2012.

Three chars obtained from the pyrolysis of three different waste mixtures composed by plastic wastes, used tires and pine biomass were studied in this chapter, after being submitted to an appropriate decontamination treatment according to the results obtained in chapter 4.

Anticipating possible applications of these treated chars to environmental matrices, particularly aqueous media, the leaching behaviour and potential environmental impact associated with the use or valorisation of these materials was assessed in this chapter by using the integrated strategy previously developed of combining chemical analyses with ecotoxicological tests. Metallic contaminants and their contribution to the ecotoxicity levels of the chars are in focus in this chapter.

Chapter 6 - Study on the potential of chars to be valorised as adsorbents: removal of Pb^{2+} from aqueous medium

The main core of this chapter is based on 1 published paper and 1 oral communication:

- Bernardo, M., Mendes, S., Lapa, N., Gonçalves, M., Mendes, B., Pinto, F., Lopes, H., Fonseca, I., Removal of lead (Pb^{2+}) from aqueous medium by using chars from co-pyrolysis, *Journal of Colloid and Interface Science*, 409 (2013) 158–165. (doi: 10.1016/j.jcis.2013.07.050; IF: 3.172)

- Bernardo, M., Mendes, S., Lapa, N., Gonçalves, M., Mendes, B., Pinto, F., Fonseca, I., Sorption of Lead (Pb2+) from aqueous solutions using chars obtained in the pyrolysis of forestry pine, rubber tires and plastics, *Book of Congress of VIII Jornadas Técnicas Internacionais de Resíduos - Waste Management for Resources Sustainability*, Lisbon, Portugal, 16-18 July 2013.

The sorption properties of the three chars studied in the chapter 5 are evaluated in the present chapter and a particular application for the removal of a toxic heavy metal from aqueous solutions is studied. The removal efficiency for lead (Pb^{2+}) is determined and the influence of several experimental parameters on the sorption is studied. The mechanisms associated to the sorption process are investigated.

Chapter 7 – Conclusions and future work

This final chapter presents an overview of the main conclusions that arise from the work developed in the thesis as well as suggestions for future research.

CHAPTER 2

2. INTRODUCTION

- *Why pyrolysis? Comparison with other waste thermal treatment processes.*
- *The choice of plastic wastes, used tires and pine biomass as raw materials for pyrolysis.*
- *Literature review focused on pyrolysis solid by-products; the chars.*
- *Environmental risk assessment of pyrolysis chars:*
    - *The importance of employing leaching tests.*
    - *The concept of ecotoxicity applied to chars.*
- *Originality and scientific innovations introduced by the present thesis.*

2.1 ADVANCED THERMAL TREATMENT OF WASTES

The most common processes for treatment and disposal of waste are landfill and mass burning (incineration)[32]. They are applied worldwide but both methods are wasteful of resources and have significant negative environmental impacts.

Nevertheless, most of industrialized/developed countries are adopting environmental policies of sustainable waste management options focused on material and energy recovery.

Thermal treatment technologies (waste treatment technologies that involve high temperatures in the processing of the waste feedstock) offer the possibility of resource and energy recovery with the advantage of waste reduction in volume and weight.

Thermal treatment options can be divided and classified on the basis of how much air or oxygen is consumed in the process[33]:

- Incineration: combustion of waste in an excess of oxygen, resulting in fully oxidized products;
- Gasification: occurs with a limited amount of air or oxygen or even with steam, leading to an incomplete combustion or oxidation. When air or oxygen is used only a fraction of the material burns thereby generating sufficient heat to decompose thermally the rest of the material;
- Pyrolysis: thermal processing in the absence of air or oxygen; therefore, no combustion or oxidation takes place, but thermal degradation of the material is effected by adding heat directly or indirectly.

Incineration can reduce the volume of wastes by 90% and its weight by 75% converting them to carbon dioxide, water vapour and ash. It is particularly appropriate and efficient for medical waste and high-hazard materials as it provides sterilization due to the high temperatures used in the process (over 850ºC). Incineration offers the possibility of a high recover of the thermal energy released in the process as heat (hot water/steam) or electric power or combinations of these. However, incineration of wastes suffers from several concerns which the most important is the generation of a large amount of gaseous emissions which requires an extensive flue gas cleaning system, that produces fly ash and flue gas cleaning products.

Gasification and Pyrolysis are considered as waste Advanced Thermal Treatments (ATT) because the waste is thermally treated with the primary goal of obtaining secondary products (gas, liquid and/or solid) from which energy can be generate in addition to other uses. Moreover, ATT’s offer the advantages of less flue gas volumes to be treated and the formation of dioxins and furans are inhibited due the oxygen-deficient atmosphere in these processes, which considerably reduce the costs and complexity associated to air pollution control systems.

Figure 2 presents an overview of thermal treatment processes and their main differences.

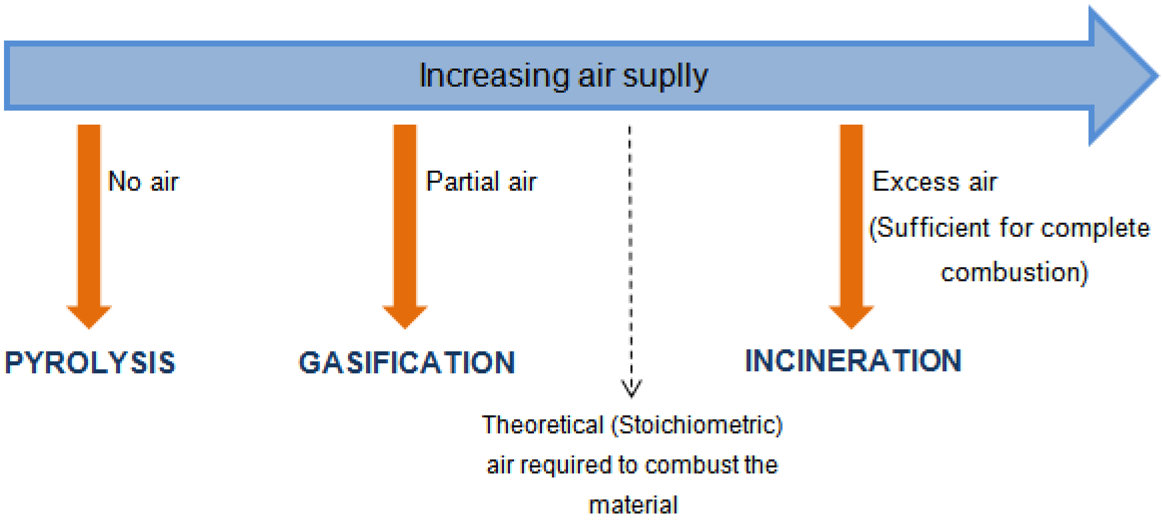

Figure 2. Thermal treatment processes and levels of air present (Adapted from [34]).

The main product of gasification is a synthesis gas (syngas) which essentially contains CO, H_2, CH_4, some CO_2 and different hydrocarbons (C_nH_m). Typically, the syngas generated from gasification with partial air or oxygen will have a heating value of 4-14 MJ/m^3. It can attain the range of 14-20 MJ/m^3 if gasification proceeded with steam[35]. Besides its use as fuel, syngas is widely used as intermediate gas for several chemical syntheses (example: the Fischer-Tropsch process).

Tars are also produced in the gasification of wastes and their deposition in the gasification installation can cause blockages and other operational problems. In addition, these tars may contain toxic and carcinogenic compounds. A secondary product of gasification which is produced in low amounts is a solid residue of non-combustible materials (ash) with a relatively low level of carbon. This residue is similar to pyrolysis char, although usually presents lower carbon content.

Pyrolysis is the ATT in focus in this thesis and will be described in the next section.

2.2 PYROLYSIS OF WASTES

Pyrolysis is an endothermic process (requires energy input) that induces the thermal decomposition of feed materials without the addition of any reactive gases, such as air or oxygen. The thermal energy used to drive the pyrolysis reaction is usually applied indirectly by thermal conduction through the walls of a reactor36 but other procedures to supply the energy needed by pyrolysis may also be used. During pyrolysis, the wastes are thermally decomposed typically at temperatures between 300 to 850ºC and moderated conditions of pressure, giving rise to volatile matter and a carbon-rich solid residue named as char. The volatile matter comprises condensable vapours (oils, waxes and/or tars), and non-condensable gases (also named as syngas). The syngas has a low to medium calorific value, around 10-20 MJ/m3, and has the same applications indicated for the syngas from gasification processes. The condensable pyrolytic product, mostly oils, considerably depends on the feedstock composition which will determinate its possible applications: as fuel oil substitute or as chemical refinery feedstock to recover valuable chemicals.

Figure 3 presents images of typical liquid and solid pyrolysis products.

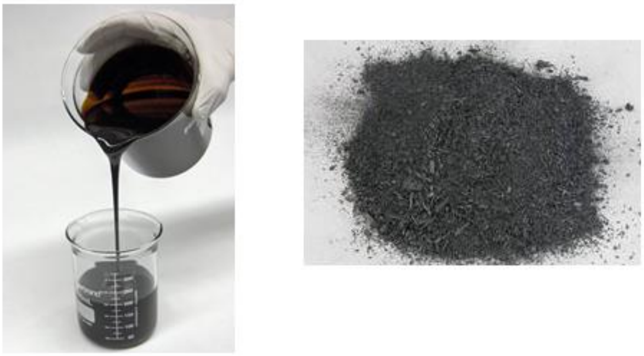

Figure 3. Typical pyrolysis oil and char (Images from[37-38]).

The heating rate, heat transfer rate, and residence time in the reactor influence the product distribution. Slow pyrolysis is characterised by low heating rates, relatively long solid and vapour residence times and sometimes by low temperatures[39]. Long residence times leads to secondary conversion of primary products, yielding more char, tar, as well as thermally stable products. That's why slow pyrolysis is also referred as carbonisation. High heating rates with short hot zone residence times and rapid quenching of the products (volatiles) favour the formation of liquid products, since the volatiles released in the pyrolysis process are condensed before further reaction breaks down the highest molecular weight species into gaseous products[39]. Figure 4 presents an overview of a waste pyrolysis process with the possible applications.

Pyrolysis, as any other waste thermal treatment process, is not free of drawbacks. The exhaust gases still have to be decontaminated and the pyrolytic oils/tars may have toxic and carcinogenic compounds depending on the pyrolysis feedstock.

Pyrolysis is a thermal treatment included in the European Waste Incineration Directive[40], therefore it must meet the operational requirements and emissions standards defined for incineration plants.

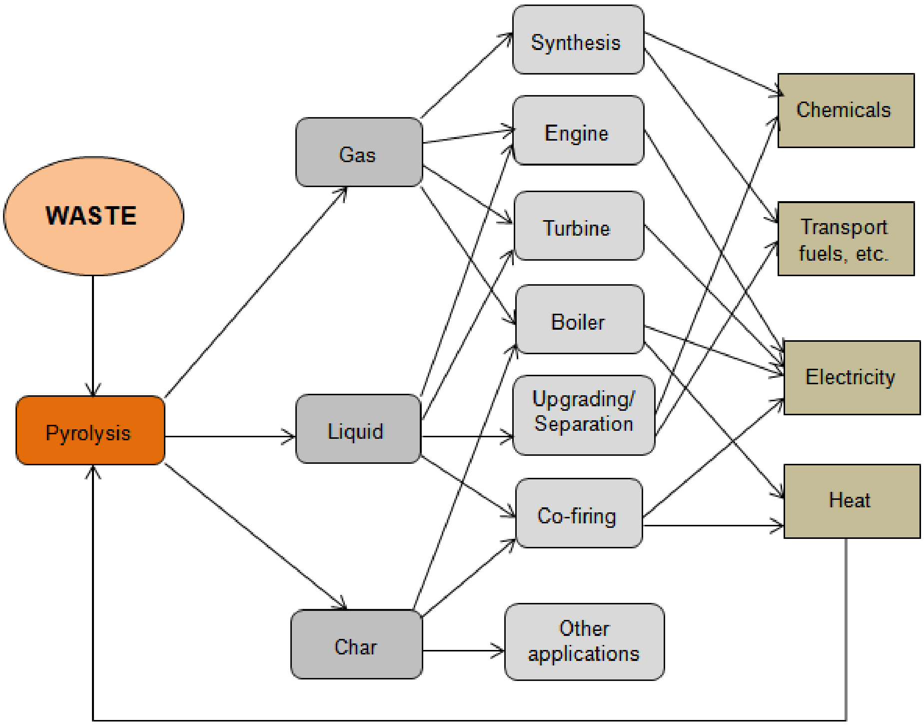

Figure 4. Overview of waste pyrolysis processes (Adapted from [27]).

2.3 PYROLYSIS OF PLASTICS, USED TIRES AND PINE BIOMASS

2.3.1 Plastics

Polymers, particularly plastics, have been a common feedstock used in pyrolysis processes. Through pyrolysis, the polymeric materials can be easily broken down to yield their individual components (monomers), and/or a mixture of hydrocarbon compounds similar to crude oil.

Polyethylene (PE), polypropylene (PP) and polystyrene (PS) have been the most studied polymers as pyrolysis feedstock[4,41-43]. The reason for this preference on these polymers is their chemical composition (mainly carbon and hydrogen and no heteroatoms), and because they are dominant on post-consumer plastic wastes[44-45].

Several commercial pyrolysis plants of plastic wastes have been implemented all over the world, and mainly in Europe and Japan, with the main aim of feedstock recycling/recovery[41-42,45].

2.3.2 Used tires

Several countries are adopting policy measures to divert end-of-life tires (ELT) from landfill disposal. An example is the European Landfill Directive[46], which has banned the landfilling of ELTs since July 2006. Given the fact that only in Europe around 3.3 million tonnes of used tires are generated annually[47], it becomes urgent to find alternative and sustainable management options to these wastes.

A major route for ELT valorisation has been their use as a supplemental fuel in power plants and cement kilns by co-incineration with other waste as well as material recycling[47].

Pyrolysis has been quite suggested as a thermal treatment option of ELT against incineration, due to the main reasons already stated in section 2.1.

Major compounds of tires are styrene–butadiene rubber (SBR), synthetic and natural polyisoprene rubber. So, given its polymeric character, rubber from tires has been considered a suitable pyrolysis feedstock for depolymerisation and to obtain hydrocarbon oil rich in aromatics.

Several studies have been carried out dealing with the pyrolysis of tires and some industrial applications are already implemented[3,39,48].

2.3.3 Pine biomass

In recent years, several countries around the world are adopting policies that require, or strongly encourage, a significant increase in the production and use of biofuels[49]. Pyrolysis of biomass to obtain bio-oil is becoming increasingly important and has received a lot of attention from the scientific community in this context[2,27,50].

The use of pine biomass (*Pinus pinaster*) as pyrolysis feedstock in this thesis is justifiable given the fact that it is an abundant species in the Mediterranean forests and the dominant one in the Portuguese forests[51]. Moreover, according to the European Association of Biomass (AEBIOM), the maximum of EU potential of forest residues is 251 million m^3, of which the harvestable potential is 140 million m^3. Only less than 5% of the harvestable potential is currently utilised indicating that forest residues are an underexploited source of bioenergy[52]. In this framework, it is reasonable to assume that one of the major sources of forest residues is pine biomass.

The pyrolysis of pine biomass has been already studied with the main aim to obtain bio-oil[53-57], and the results showed that those pyrolysis liquids were highly complex mixtures of oxygenated, aliphatic and aromatic compounds as it is typical in bio-oils from biomass pyrolysis. The pyrolytic oil obtained can be used as feedstock for synthesis of fine chemicals, adhesives, fertilizers, etc., but if an alternative to traditional fuels is considered, the bio-oil has to be subjected to upgrading processes such as hydrogenation or hydrodeoxygenation, given its high viscosity, thermal instability, low heating value and corrosiveness promoted by the high oxygen content and unsaturated compounds[58-59].

2.3.4 Co-pyrolysis of plastics, used tires and pine biomass

To overcome the negative characteristics of the bio-oils from pine biomass to be used as fuels, the approach of co-processing the pine biomass with polymers such as plastics (especially polyolefins) by pyrolysis has been undertaken[60-68]. The primary goal has been the improving of hydrogenation and/or hydrodeoxygenation reactions during thermal decomposition of the woody biomass, due to H-transfer provided by the plastics, leading to an increase of liquid quantity and quality.

Also the co-pyrolysis of wood sawdust and used tires was studied[69] with the same objective of reducing the oxygen content in the resulting pyrolysis oil and at the same time to supress the formation of the undesired Polycyclic Aromatic Hydrocarbons (PAH's) that usually appear in the oil produced during the pyrolysis of tires when used as the only feedstock.

Miranda[70] studied the co-pyrolysis of used tires and plastic wastes in order to promote the synergisms between these two materials that could improve liquid yields and its fuel properties.

Concerning the pyrolysis of ternary mixtures composed by the raw materials (plastics, rubber of tires and wood biomass), there is little information available and only the work from Paradela[71] studied the synergetic effects and the advantages of the ternary co-pyrolysis in the fuel properties of the gases and liquid products.

Processing different materials has also the advantage of guaranteeing the feedstock supply security in an industrial unit.

2.4 PYROLYSIS CHARS

As already referred in section 2.1.1, the wastes are thermally decomposed giving rise to volatile matter and a carbon-rich solid residue named as char.

A relatively long vapour residence time and a low heating rate as observed in slow pyrolysis are the key parameters that favour char production.

The process by which the pyrolysis chars are formed is designated by carbonization consisting in complex reactions that take place concurrently. Some of these reactions are dehydrogenation, condensation, hydrogen transfer, isomerization, among others[72].

Chars contain both primary char (resulting from primary pyrolytic reactions) and a secondary char that is a coke derived from the decomposition or secondary cracking of the organic vapours (tars) onto the carbonaceous solid[73]. Therefore, the pores developed in the primary char due to volatiles release will become blocked due to the deposit of the coke resulting from the secondary cracking of those volatiles. For this reason, usually chars from pyrolysis present low surface areas and an incipient porosity.

2.4.1 Lignocellulosic chars

Hemicellulose, cellulose and lignin are the three main components of biomass and they cover around 20–40%, 40–60%, and 10–25 wt%, respectively, of lignocellulosic biomass[74]. Generally, biomass thermal decomposition can be divided into four individual stages: moisture evaporation (100ºC), hemicellulose decomposition (220–315°C), cellulose decomposition (315–400°C), and lignin decomposition (160-900°C) being suggested that the pyrolysis of any biomass can be considered as the superposition of the individual components decomposition[74].

Lignin is the main source of char since its individual decomposition gives origin to around 40-50 wt% of char yield. Hemicelluloses decomposition yields around 20-30 wt% of char, while cellulose thermal decomposition yields only about 10 wt%[74-75]. The differences in the chemical structures of the three components of lignocellulosic biomass can explain the different char yields. Lignin has the most complex structure with highly cross-linked polyphenolic polymers without any ordered repeating units, unlike cellulose that has a simplest structure consisting in a long polymer without branches.

Cellulose polymer carbonizes through dehydration, cross-linking reactions and the unzipping of the polymer chain leading to the formation of the monomer unit levoglucosan. The char is originated from the decomposition of the dehydrated product (dehydrocellulose) and from secondary reactions of levoglucosan like repolymerization that yield polynuclear aromatic structures and graphite carbon structures[76-77].

Hemicellulose is the other polysaccharides of biomass and exhibits a similar decomposition pathway to cellulose, with depolymerization and dehydration reactions, but the primary products (also anhydrosugars) are different and more complex, yielding more char through condensation/repolymerization[77-78].

The mechanisms of lignin decomposition are not well known due to its extremely complex structure. It is known that the primary products are aromatics and oligomers (polymer units with 10 or fewer monomer units) being very reactive and susceptible to secondary reactions lead to high char formation[79-80].

The pyrolysis of lignocellulosic biomass, at mild temperatures, generally produces chars characterized by low surface areas and micro-macroporous structures[16,81-82].

2.4.2 Chars from plastics

PE, PP and PS, the plastics in focus in the present thesis, are carbonaceous thermoplastics that under pyrolysis decompose by a mechanism involving the breaking of bonds in the main polymer chain. These chain scissions may occur at the chain end or at random locations in the chain. End chain scissions result in the production of monomer, and the process is often known as unzipping. Random-chain scissions generally result in the generation of monomers and oligomers as well as a variety of other chemical species. Cross-linking is another reaction involving the main chain. It generally occurs after some stripping of substituents and involves the creation of bonds between two adjacent polymer chains. Cross-linking as well as cyclization reactions are important in the formation of chars[83].

However, the production of chars from thermoplastics pyrolysis is usually quite low, mainly resulting from secondary tar cracking reactions and for this reason it is mainly designated as coke[41,84].

PS is an exception since under certain conditions may yield significant char/coke due to the formation of non-volatile polyaromatic residues resulting from secondary reactions of instable aromatic intermediate products[41,85-86].

2.4.3 Tire rubber derived chars

The pyrolysis of tires rubber usually leads to a significant char yield of around 30-50%[39,48,87]. The main source of the carbonaceous char is the original carbon black used as filler in tire rubber production, since the main rubber components only produce about 4% of char. The char originated from the rubber components (styrene–butadiene rubber, natural rubber and polybutadiene rubber) is mainly a coke from secondary reactions. The char may also contain condensed organic vapours adsorbed onto its surface and several inorganics used in the tire rubber manufacture such as Zn, Ca and Si[39,48,87].

The textural properties of tire rubber derived chars resemble the textural characteristics of the carbon black from the original tire rubber material that remains in the chars after pyrolysis. Carbon black is typically a mesoporous material with a low surface area and these characteristics are transferred to the resulting char[88-90].

2.4.4 Chars from the co-pyrolysis of plastics, used tires and pine biomass

Chars from pyrolysis of pine biomass mixed with plastics such as PE, PP and PS have their carbonaceous structure mainly originated from the thermal decomposition of the lignocellulosic material, being observed an increase in the char yields with the increasing of biomass proportion in the feedstock mixture[60-64,66-68]. This suggests that interactions between the raw materials for char formation are not quite relevant.

However, some authors suggest that the degradation products from biomass have some type of interaction with the decomposition products of plastics, because char yields from co-pyrolysis process were lower than theoretical values considering the pyrolysis of the materials alone, leading to an increase in the liquid yields. The explanation for this observation was the H-donor effect of the plastics; it seems that the hydrogen may partly inhibit the recondensation reactions that lead to the formation of char[60,64,66,91].

Pine biomass starts to decompose at a lower temperature (~200ºC) than plastics (~400-500ºC), but the slow charring reaction of wood is still continuing in the temperature range of plastic decomposition. Therefore, it is expected that interactions between the volatiles released from the plastics and from the char might occur. These interactions may be reflected in lower char formation, as already referred, but on the other hand, there is also the possibility that those interactions favour secondary reactions yielding to the production of more char[65].

Concerning the co-pyrolysis of biomass with tire rubber, interactions among the pyrolysis vapours were observed by Cao et al.[69], which was reflected in an increase of liquid yield with the increase of tire rubber in the feedstock, justified by the H-donor effect of tire rubber; the char yield increased by comparison with the char yield of biomass alone and decreased by comparison with the pyrolysis of tire alone. The alkali metals present in the biomass may catalyse the reactivity of the tire rubber derived char leading to a decrease of char yield[92].

Miranda[70] showed that chars from the co-pyrolysis of tire rubber and plastics increased with the increasing of tire mass in the feedstock. Given the similar degradation temperature range of the raw materials, it is expected that the volatiles from the tire rubber and from the plastics will interact affecting the production of coke that appear deposited in the carbon black from the tires.

The pyrolysis of mixtures composed by the three materials, plastics, tire rubber and wood biomass was studied by Paradela[71]. The obtained chars were a mixture of chars from the individual pyrolysis of pine biomass and the individual pyrolysis of tires. Also the experimental char yields from the co-pyrolysis of the three raw materials were similar to the theoretical yields of the pyrolysis of the individual materials which indicate a lack of interactions.

2.4.5 Valorisation and applications of pyrolysis chars

Traditionally, combustion with energy recovery has been the most frequent and recommended destination for the pyrolysis chars, as well as gasification for syngas production[2,5-9]. The reason is the high carbon content, calorific value and reactivity of chars.

Metallurgical applications as reducing agents have been tested[23-24,93-94], however the chars must present high fixed carbon content (around 90%), low ash content and low volatiles (<10%). These requirements are only possible if the pyrolysis process proceed at high temperature and with non-contaminated raw materials.

Also, applications as catalysts or as catalyst supports were suggested[18-20,95-96] given the fact that some chars may possess a composition rich in Si, Na, Ca, K, P and S, which are elements with proven catalytic activity, and because chars may have relatively porous structures able to support catalysts.

More recently, the use of chars in soil amendment practices[21-22,97] and as adsorbents[98-105] have gained an increasing interest.

Soil amendment applications have been focused mainly in biochars with the intention to improve soil properties, for sequestering heavy metals, releasing essential nutrients, retaining water and sequestering carbon in soils.

Adsorption applications have been mainly carried out by using biomass derived chars. The adsorption properties of pine biomass chars for heavy metals and organic compounds were already object of attention with successful results[102,106-114].

Applications of tire derived chars as adsorbents of organic compounds[88-89,101,115-119] have been widely studied, particularly for bulky molecules given the large pores of these chars; studies on the removal of inorganics such as metallic elements by tire chars have recently risen[14,118,120-122], but the mechanisms involved are still not well understood.

Chars from plastics, particularly thermoplastics such as PE, PP and PS, have not been contemplated in adsorption studies given their characteristics more close to “coke” than to porous chars.

To the author’s knowledge, there are no studies devoted to the application of chars resulting from co-pyrolysis of the raw materials in focus in this thesis as adsorbents. The main application suggested for chars resulting from the co-pyrolysis of blends of plastics, tires and pine biomass was energy recovery through combustion[63,66].

2.5 ENVIRONMENTAL RISK ASSESSMENT OF PYROLYSIS CHARS

The valorisation of the pyrolysis chars through the application routes exposed in the previous section requires the knowledge of their composition, properties and risk assessment, mainly due to environmental and economic reasons. Specially, the increasing interest in these materials during the recent past years for environmental applications, particularly those related to soil and water, demands studies about the potential environmental impact associated with their use in order to avoid problems of secondary environmental pollution, due to the potential release or leaching of some toxic elements into the environment. Chars are essentially carbon materials that retain the mineral matter initially present in the raw wastes and may contain significant amounts of the pyrolytic tars. Therefore, the release of toxic compounds is a possibility that might restrict their applications

2.5.1 The importance of performing leaching tests in the characterisation of materials

The application of standard leaching tests is a common practice to characterize and assess the constituents that can be released from materials exposed to water and that can present potential risk to the environment. Assessing the environmental performance based on the total concentration of elements present in a material provides highly overestimated predictions of the risk level which would limit application opportunities. It is for this reason that the prediction of contaminants mobility through leaching tests is so important in the characterisation, environmental risk analysis and for the end-use evaluation of a given material[123-124].

There is a wide range of standardized leaching tests[123-125] with variable parameters and conditions, designed to characterize and define the use, treatment or disposal of contaminated soils, sediments, sludge, wastes and construction materials. Most of these tests are primarily designed to measure the mobility of inorganic compounds and until recently only the Toxicity Characteristic Leaching Procedure (TCLP) from the United States Environmental Protection Agency (USEPA)[126] contemplated the mobility of both organic and inorganic analytes from wastes. However, some limitations of the TCLP were already addressed[127-129].

However, for some contaminated or organic-rich materials, there is the potential leaching of organic contaminants. Thus, it is important to implement leaching tests to evaluate the release of organic compounds in the materials risk assessment.

Several efforts have been made in the last years with publications reporting methods for testing the leaching of organic compounds[130-138] with the premise that the existing standard procedures for inorganic contaminants are suitable to test the leaching of organic pollutants. However, in certain cases, slight modifications of the existing standards were performed to take into account the specific physico-chemical properties of the organics such as hydrophobicity.

Also recommendations for leaching procedures adequate to organic compounds were made[139-141] and recently, an ISO/TS leaching standard (ISO/TS 21268[142]), dealing with the release of non-volatile organic compounds in soils and soil materials has been published. Nevertheless, there is still a lack of consensus on the standardization and application of tests feasible to describe the leaching of organic compounds.

2.5.1.1 Leaching behaviour of chars

In the beginning of this doctoral project, a brief review of the literature revealed a lack of information about the leaching behaviour of chars resulting from thermochemical processes. Only very few works devoted to the study of the leaching of heavy metals from pyrolysis chars from the standpoint of landfilling were found[10-12]. Also one study dealing with the leachability of inorganic elements from tire derived chars for water treatment applications was identified[143]

In the meantime and following the first publications resulting from the present thesis, a few studies dealing with this subject were published. Agrafioti et al.[144] studied the feasibility of applying sewage sludge biochar to soils and as adsorbent in aqueous solutions, having examined the potential release of heavy metals from that biochar by performing standard leaching tests. Galhetas et al.[145] performed the evaluation of environmental toxicity of gasification chars from coal and pine biomass through the application of different standard leaching tests focused on heavy metal leachability. Griffith et al.[146] characterized the char produced in the gasification of Kentucky bluegrass biomass with respect to its leaching behaviour under standard conditions for polycyclic aromatic hydrocarbons and some heavy metals in order to determine its suitability for agricultural application as soil amendment. Fuente-Cuesta et al.[147] studied the leaching of major and trace metallic elements from paper-plastic gasification char, over a wide range of pH values, considering its application as adsorbent.

A common conclusion among the referred studies is that heavy metals are immobile and stable in char matrices and that the thermochemical process is able to reduce their potential release. Possible explanations were the pH values of carbonaceous chars that typically are in a neutral range, but also the textural properties of the chars, such as pore structure and surface area that can restrain heavy metal leaching.

The study of the leachability of organic compounds from chars has been neglected and only the work of Griffith et al.[146] was also devoted to the release of toxic organic compounds, such as PAH, dioxins and furans from the char materials.

Several potential toxic organic compounds may be present in chars as a result of tars deposition in their surface and may include classes of compounds such as aromatic and polyaromatic hydrocarbons, aliphatic hydrocarbons, oxygen-containing hydrocarbons, polychlorinated biphenyls and dioxins, among others[148], depending of the raw materials subjected to pyrolysis. Some of these compounds have particularly high environmental mobility, which makes even more important the evaluation of the leaching properties of organic compounds from char materials.

2.5.2 The concept of ecotoxicity

According to the European Hazardous Waste Directive[149] and the European Waste Framework Directive[1], substances, preparations and wastes that present or may present immediate or delayed risks for one or more sectors of the environment are considered to have ecotoxic properties.

According to the USEPA[150], the ecotoxicity tests are performed to evaluate the ability of a chemical or physical agent to have an adverse effect on the environment and the organisms living in it, such as fish, wildlife, insects, plants and microorganisms.

Ecotoxicity can be estimated using two approaches: a chemical specific approach and a toxicity based approach. In the first case, the chemical analyses are compared to quality criteria or threshold values to estimate the ecotoxicity; in the second case, ecotoxicity is measured directly using biological indicators.

Combining chemical analyses with ecotoxicological tests, as an integrated strategy to characterize the environmental impact assessment of a given sample, has the advantage of providing a more complete set of information about its global toxic effect. The determination of pollutants in complex mixtures of unknown composition is an extremely difficult task and does not allow a proper prediction of the ecotoxicological effects; therefore, the bioassays integrate the effects of all contaminants including additive, synergistic and antagonistic effects[151]. The assessment of the ecotoxic properties of a sample with bioassays should include test organisms representing different environmental compartments. The most common and standardized bioassays include tests on aquatic organisms such as daphnia, algae, bacteria and fish, and tests performed on terrestrial organisms such as earthworms and plants, among others[151-155]. The evaluation of the ecotoxicity of a sample can be made by applying the biological tests to the raw materials or to their aqueous extracts. Assays on the aqueous eluate of the sample are the most commonly employed method for ecotoxicity assessment, particularly for materials potentially exposed to water. The analogy is the same as for leaching tests applied to the characterisation of materials: assessing the ecotoxicity on the aqueous soluble fraction of the material provides a more accurate risk to the environment instead of considering the all sample composition which would provide an overestimated prediction of the ecotoxic risk.

Until recently, there was a lack of representative methodologies to estimate the potential ecotoxicity of a given sample as well as specific threshold values.

The International Standard ISO 17616:2008[156] when it was published was the only guide on the choice and evaluation of the test batteries to be used to perform ecotoxicological characterisation, but only for samples such as soil and soil materials.

The European Regulation (EC) 1272/2008[157] introduced criteria for classifying and categorizing substances and mixtures as ‘hazardous to the aquatic environment’ based on biological tests commonly used in ecotoxicity assessment.

The European Regulation (EC) 440/2008[158] specifies and describes tests methods to be used in the ecotoxicity assessment of substances and preparations pursuant the REACH Regulation (Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals)[159].

The European Technical Report CEN/TR 16110[160], released in 2010, constituted a step forward on the ecotoxicity assessment, as this standard provides a guide on the battery of standardized biological tests that should be applied for testing the ecotoxicity of waste materials and also toxicity criteria are presented.

Therefore, the harmonization of a classification system with specific limit-values to assess the ecotoxicity of a sample is needed and has to be implemented in legislation.

To the author knowledge, the only attempt to establish a regulatory methodology for the evaluation of ecotoxicity integrating both chemical and biological characterisations and for defining limit-values was the Criteria and Evaluation Methods of the Ecotoxicity of Waste (CEMEW)[161], published by the French Ministry of Environment in 1998. However, this proposal was not officially integrated in the European legislation.

2.5.2.1 Ecotoxicity assessment of pyrolysis chars

The evaluation of the ecotoxicological properties of pyrolysis chars based on biological tests was not found in the scientific literature at the beginning of this doctoral project and only very recently Oleszczuk and co-workers[162] presented a study of the ecotoxicological assessment of biochars for soil amendment by using chemical and biological analyses.

Although there are no official standards or regulations concerning the application of biological tests to evaluate the ecotoxic properties of these materials, adaptations of the existing methodologies and tests may be performed and applied to chars in order to provide knowledge about their potential risks to the environment.

2.6 ORIGINALITY AND SCIENTIFIC INNOVATIONS INTRODUCED BY THE THESIS

The originality of this thesis lies on the fact that it wants to contribute with significant new scientific knowledge on the composition, properties and environmental hazard assessment of the carbonaceous solid products (chars), resulting from the thermochemical processing of three materials commonly found in waste streams: plastics, used tires and forest biomass. The integrated strategy of combining data from chemical, physical and ecotoxicological analyses to provide a more correct and realistic assessment of the environmental risks associated to the different end-uses of chars had not been investigated before.

The significance of this investigation is emphasized with the marked increase in recent years on the study of the use of chars in several fields (catalysts, adsorbents, soil amendment, energy,…) which imposes, in a near future, the development of official regulations and/or guides to evaluate the risks. This thesis wants to contribute with scientific insight for this evaluation.

The innovation of the work developed by this thesis may be enlightened by the following:

- Pyrolysis of ternary wastes blends;
- Some of the techniques and procedures used to characterize the char samples, particularly their organic chemical composition;
- Application of leaching tests to the chars to evaluate the potential release of contaminants to aquatic compartments;
- Combining chemical and ecotoxicity approaches to estimate the potential hazardous properties of chars with respect to the environment;
- Application of decontamination treatments to reduce the potential toxicity of the chars;
- Study the adsorption properties of the char samples to heavy metals contaminants present in waters, more specifically lead (Pb^{2+}), as well as the related mechanisms.

CHAPTER 3

3. CHEMICAL AND ECOTOXICOLOGICAL CHARACTERISATION OF CHARS OBTAINED IN THE CO-PYROLYSIS

This chapter aims to present the characterisation performed on the pyrolysis raw feedstock materials and provide the first insight and scientific knowledge into the subject of environmental hazard assessment of pyrolysis chars through the application of leaching tests and by combining chemical and ecotoxicological analyses.

3.1 CHARACTERISATION OF THE RAW FEEDSTOCK MATERIALS: PLASTIC WASTES (MIXTURE OF POLYETHYLENE, POLYPROPYLENE AND POLYSTYRENE), RUBBER OF USED TIRES AND PINE BIOMASS

Abstract: In this subchapter, the characterisation of raw materials used in this thesis, plastic wastes (blend of PE, PP and PS), rubber of used tires and pine biomass are shown. A thermal analysis was performed on the raw materials that allowed defining their composition in terms of the volatility of their components and also to evaluate their thermal decomposition profiles. The raw materials were also submitted to an elemental analysis and their mineral content was determined by microwave acidic digestion and elemental quantification through atomic absorption spectrometry.

Tire rubber presents the highest ash content with a high level of metallic elements in its composition, particularly Zinc. This feedstock also was the raw material that presented the highest decomposition temperature, due to its composition on synthetic rubbers that degraded up to 750 ºC. The blend of plastics presented a significant level of metallic contamination probably due to the additives used during their manufacturing. Plastics were the raw materials with the highest fixed residue content in the thermal analysis. Pine biomass was the material with the highest oxygen content due to its lignocellulosic character structure. Pine presented alkali and alkaline-earth metals as the major elements.

The results presented in this section were published, partially or completely, in the following papers:

Bernardo, M.S., Lapa, N., Barbosa, R., Gonçalves, M., Mendes, B., Pinto, F., Gulyurtlu, I., Chemical and ecotoxicological characterisation of solid residues produced during the co-pyrolysis of plastics and pine biomass, Journal of Hazardous Materials, 166 (2009) 309–317. (doi: 10.1016/j.jhazmat.2008.11.031; IF: 4.173)

Bernardo, M., Lapa, N., Gonçalves, M., Barbosa, R., Mendes, B., Pinto, F., Gulyurtlu, I., Toxicity of char residues produced in the co-pyrolysis of different wastes, Waste Management, 30 (2010) 628–635. (doi: 10.1016/j.wasman.2009.10.015; IF: 2.428)

Bernardo, M., Gonçalves, M., Lapa, N., Barbosa, R., Mendes, B., Pinto, F., Characterisation of chars produced in the co-pyrolysis of different wastes: decontamination study, Journal of Hazardous Materials, 207–208 (2012) 28–35. (doi: 10.1016/j.jhazmat.2011.07.115; IF: 4.173)

Bernardo, M., Mendes, S., Lapa, N., Gonçalves, M., Mendes, B., Pinto, F., Lopes, H., Leaching behaviour and ecotoxicity evaluation of chars from the pyrolysis of forestry biomass and polymeric materials, submitted to Ecotoxicology and Environmental Safety, 2013.

3.1.1 Description of the raw materials

The plastics used in the pyrolysis experiments were a mixture of 56% (w/w) of PE, 27% (w/w) of PP and 17% (w/w) of PS from a recycling company in the form of pellets with a diameter around 2-5 mm. The composition of the mixture of plastics attempted to reflect the average composition found in the Portuguese Municipal Solid Wastes. Figure 5 presents a picture of the plastics used. The green particles are PS, black pellets are PP and PE corresponds to the grey/white pellets.

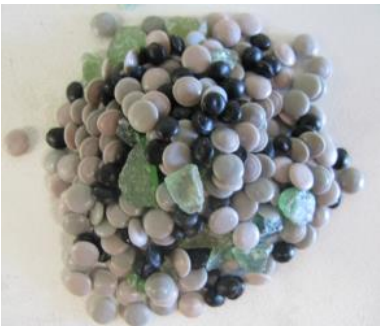

Figure 5. Plastic blend used in the pyrolysis experiments.

The rubber of used tires were in the form of strips with around 2 cm of length and 1-2 mm of diameter (Figure 6) and were provided by a recycling plant of scrap tires after the removal of metal and textile components.

Figure 6. Tire rubber used in the pyrolysis experiments.

Pinus pinaster or Maritime pine was the biomass used in the pyrolysis experiments. This biomass was in the form of shredded pieces (Figure 7) similar to the pieces of scrap tires and it was obtained from a saw mill.

Figure 7. Pine biomass used in the pyrolysis experiments.

3.1.2 Experimental part

3.1.2.1 Thermal analysis of raw materials

The plastic blend, pine residues and rubber of used tires were submitted to a thermal analysis that consisted in measuring the progressive weight loss associated with the combustion of samples in a CEM microwave furnace MAS 7000, under an air atmosphere, from room temperature up to 800 ºC with increments of 50 ºC. The feedstock materials remained 10 min in 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. The mass of sample used in the experiments was 0.5 g. This thermal analysis allow to define the composition of the materials in terms of the volatility of their components: volatile organic compounds were those volatilized up to 250 ºC[163-164]; the weight loss registered between 250 ºC and 350 ºC was attributed to semi-volatile compounds[164]; the weight decrease observed from 350 ºC to 600 ºC was assigned to the volatilization and combustion of heavy compounds and were denominated as fixed residue; the residue non-combusted above 600 ºC that presented a stable weight was considered as ashes[165].

3.1.2.2 Elemental analysis of raw materials

Elemental analysis was performed at Unidade de Tecnologias de Conversão e Armazenamento de Energia – Laboratório Nacional de Energia e Geologia (UTCAE-LNEG), with a LECO elemental analyser.

3.1.2.3 Determination of the mineral content of raw materials

A microwave acid digestion based in the EPA 3052 method[166] was used to digest the plastics, pine biomass and rubber of used tires. Briefly, 0.25 g of each sample was digested with 0.9 mL of HNO_3 65% (v/v) in a Milestone ETHOS 1600 microwave heating system. The temperature of each sample achieved 180±5 ºC in 5.5 min, and remained at this temperature for 9.5 min. The digested samples were filtrated using Whatman filter paper grade 595 and a broad group of metals were quantified in the filtrates using a Thermo Elemental Solaar Atomic Absorption Spectrometry (AAS) equipment: Cadmium (Cd), Lead (Pb), Zinc (Zn), Copper (Cu), Nickel (Ni), Potassium (K), Manganese (Mn), Iron (Fe), Sodium (Na) and Magnesium (Mg), which were analysed using the air-acetylene flame technique; Barium (Ba), Molybdenum (Mo), Aluminium (Al), Chromium (Cr) and Calcium (Ca) were analysed using the acetylene-nitrous oxide flame technique; Mercury (Hg), Arsenic (As), Selenium (Se), Antimony (Sb), which were quantified using the hydride generation technique.

3.1.2.4 Qualitative chemical analysis of plastics

The qualitative chemical content of PE, PP and PS was determined by X-Ray Fluorescence (XRF) and the results were provided by UTCAE-LNEG.

3.1.3 Results and discussion

3.1.3.1 Thermal analysis of raw materials

Table 1 shows the relative mass composition of plastic blend, pine and rubber of used tires in terms of the volatility of their components determined by the thermal analysis performed on the materials.

Table 1. Relative mass composition (% w/w) of each material given by the thermal analysis.

	Rubber of used tires	Pine biomass	Plastic blend
Volatiles (% w/w)	0.46	14.0	0.14
Semi-volatiles (% w/w)	19.7	43.2	5.9
Fixed Residue (% w/w)	76.7	42.4	93.4
Ashes (% w/w)	3.14	0.39	0.60

Pine biomass presented the highest volatile content in which 6.33% is attributable to moisture.

Figure 8 shows the weight loss of each material as a function of the temperature. From Figure 8 it can be seen that pine starts to decompose immediately with the increasing temperature due to dehydration. The major weight loss occurred between 200ºC and 350ºC that corresponds to the decomposition of hemicellulose and cellulose. Hemicellulose is the less stable of the three main components of pine (decomposition temperature of 200-350ºC), and cellulose starts to decompose around 300ºC and finishes around 375ºC[74,167]. The inflexion observed in the curve of pine decomposition at 350ºC can be attributed to the maximum decomposition temperature of cellulose[167]. Also, the decomposition of lignin that starts around 200ºC contributes to the weight loss observed in the range of temperature for semi-volatile components. Above 375 ºC, the loss of weight observed up to 550ºC for pine is mainly attributed to lignin decomposition[167]. Therefore, the fixed residue content for pine (42.4%) is mainly composed by lignin. The ash content of pine biomass was quite low (0.39%).

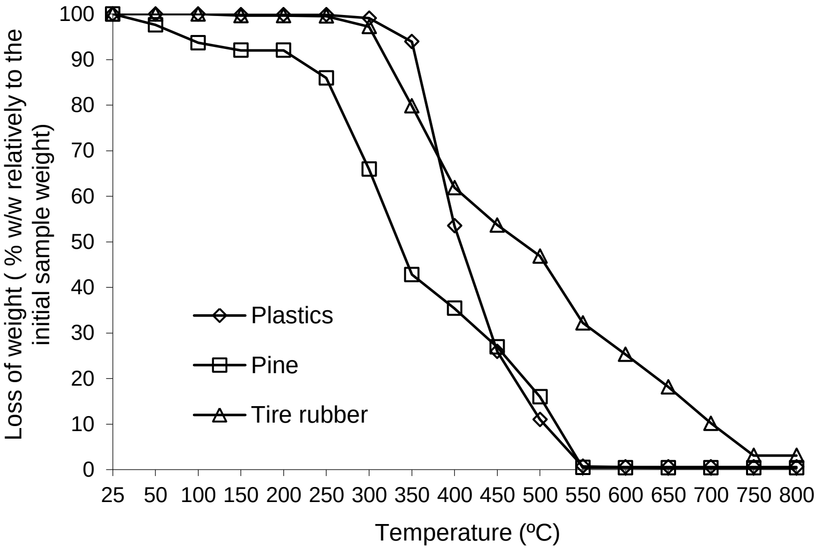

Figure 8. Loss of weight (% w/w relatively to the initial sample weight) of the raw feedstock materials by combustion in a microwave furnace up to 800 ºC.

Plastics and tire rubber did not presented a significant weight loss up to 250ºC, indicating that the volatile content is negligible. Tire rubber started to decompose significantly at 300 ºC, whereas plastics only started to lose weight significantly above 350 ºC. Therefore, the semi-volatile content for tire rubber is more significant than for plastics. However, the rate of mass loss for plastics is much higher than for tire rubber, as at 550 ºC all the plastics were degraded leading to high fixed carbon content, but at the same temperature there was still 32% of the initial mass of tire rubber. The decomposition of the plastic blend seemed to occur in a single step up to 450ºC. At this temperature a small irregularity was observed. PP, PE and PS start to decompose under oxidative conditions at temperatures in the range of 287-302 ºC, with maximum decomposition temperatures of 405-411 ºC for PP and PS, respectively and around 459-482 ºC for PE[168-169]. Therefore, the slight inflexion at 450ºC can be attributed to PE degradation.

Tire rubber presented two major different decomposition patterns: (i) a step up to 500ºC which is associated with the decomposition of the hydrocarbons, oils, plasticizers and additives and also to the degradation of natural rubber that makes part of tire rubber composition; (ii) around 500ºC and up to 750 ºC, the other components such as synthetics rubbers (styrene–butadiene, polybutadiene rubber,…) present the major thermal decomposition[170-171]. Tire rubber was the raw material that presented the highest ash content with around 3% of inorganic matter.

3.1.3.2 Elemental analysis of raw materials

Table 2 presents the results of the elemental analysis performed on the raw feedstock materials.

Table 2. Elemental analysis of raw materials.

	Tire rubber	Pine biomass	PE	PP	PS
C (% daf)	86.1	50.6	84.8	70.5	86.1
H (% daf)	7.2	6.4	14.5	11.6	7.4
S (% daf)	1.5	0.2	0.3	(<LQ)	(<LQ)
N (% daf)	0.2	0.2	0.3	0.5	6.1
Cl (% daf)	-	0.07	-	-	-
O (% daf)[a]	0.1	42.5	-	-	-

[a]Estimated by difference; daf – dry ash free; LQ – Limit of Quantification.

Tire rubber and plastics were mainly composed by carbon and hydrogen which were expected given their hydrocarbon character with very low heteroatoms content. However, tire rubber presents relatively significant sulphur content as the vulcanisation process of tire rubber is performed with sulphur[172]. The high nitrogen content of PS should also be underlined being most likely associated to an additive of this plastic. As expected, pine presented the highest oxygen content.

3.1.3.3 Mineral content of the raw materials

Table 3 shows the mineral composition of the raw materials determined by the microwave acidic digestion procedure.

Table 3. Mineral composition of raw materials.

Metals (mg/kg) wb	Plastics	Pine Biomass	Tire rubber
Zn	9.2±1.0	22.9±1.3	31193±441
Pb	4.8±1.0	4.3±0.0	14.5±1.0
Cu	<1.0	19.1±1.6	<1.0
Hg	5.4±1.0	0.13±0.04	0.10±0.02
As	<0.1	<0.1	1.00±0.03
Se	0.3±0.2	0.6±0.1	0.50±0.01
Sb	0.28±0.01	0.18±0.01	1.20±0.18
Ba	<11.3	<11.3	21.7±3.1
Cd	<0.6	<0.6	<0.6
Cr	<4.5	<4.5	<4.5
Ni	<1.8	<1.8	<1.8
Mo	<33.5	<33.5	<33.5
Ca	852±140	859±283	2402±91
K	<2.6	1050±173	738±16
Mg	19.1±0.7	212±6	333±19
Na	63.9±8.3	146±16	167±31
Al	<1.5	<1.5	150±35
Fe	<15.8	<15.8	97.7±18.6
Mn	<1.6	11.3±0.1	2.7±1.0

wb – wet basis; The mean and standard deviation of duplicates are shown

The heavy metals Cd, Cr, Ni and Mo were not detected in any one of the raw materials. Alkali metals were present in high amounts; in particular, the Ca content was significant for all the three materials; tires rubber presented the highest Ca content. Calcium is added as carbonate during tire manufacturing to act as filler[173].

Pb, Zn and Hg were detected for plastics in significantly high concentrations. Plastic additives are usually the major source for metals contamination in plastic wastes[174].

Zn was present in major amounts (around 31 g/kg wet basis) in tires rubber as zinc oxides, as well as magnesium oxides, are added as activators during the vulcanizing process[172]. This waste also presented detectable amounts of other elements that were not detected in plastics and biomass, such as Ba, As and Fe.

As expected, the major elements in pine biomass were alkali metals.

For comparison purposes and to add more information about the composition of plastics, Table 4 presents the qualitative chemical content of PE, PP and PS determined by X-ray Fluorescence (XRF).

It can be seen that several other elements that were not determined by AAS were present in plastics, such as Titanium (Ti), Silicon (Si) and Strontium (Sr). Titanium dioxide is commonly used as pigment in plastics[174].

Table 4. Qualitative analysis of PE, PP and PS determined by XRF.

Qualitative groups	PE	PP	PS
Major elements (>1% wt)	Ti	Ca, Cl	-
Minor elements (0.1-1% wt)	Pb, S, Ca, Si, Al, Mg	Pb, Zn, Ti, Ca, S, K, Fe, Si, Al	S, Fe, Si, Al, Mg, Na
Trace elements (<0.1% wt)	Zn, Cl, K, Na	Sr, Cr, K, Mg	Ti, Zn, Cl

3.1.4 Conclusions

The characterisation performed on plastic blend, used tire rubber and pine biomass allowed to conclude that the tire rubber materials presented the highest ash content with a high level of metallic elements in its composition, particularly Zinc. Tire rubber was also the raw material that presented the highest decomposition temperature, due to its composition made of synthetic rubbers that degraded up to 750 ºC.

Plastic blend also presented a significant level of metallic contamination which is probably due to the additives used during plastic manufacturing. Plastic blend presented the highest fixed carbon content in the thermal analysis given the decomposition temperatures of PE, PP and PS lie between the range of temperatures defined for fixed carbon components, 350ºC and 550ºC.

Pine biomass was the material with the highest oxygen content which was expected given their lignocellulosic character. Pine presented alkali and alkaline-earth metals as the major metallic elements.

3.2 CHARS OBTAINED IN THE CO-PYROLYSIS OF PLASTICS AND PINE BIOMASS

Abstract: A mixture of 70% (w/w) pine biomass and 30% (w/w) plastics (mixture of PP, PE, and PS) was subjected to pyrolysis and the resulting char was submitted to a chemical and ecotoxicological characterisation. Part of the produced char was subjected to extraction with dichloromethane (DCM). The raw and extracted chars (chars A and B, respectively) were submitted to a thermal analysis and the results obtained demonstrated that the extraction of the pyrolysis char with DCM was an efficient method to remove organic matter with boiling points up to 200 ºC.

Chars A and B were submitted to the leaching test ISO/TS 21268-2 using two different leachant solutions: DCM (0.2% v/v) and $CaCl_2$ (0.001 mol/L). The concentrations of the heavy metals Cd, Cr, Ni, Zn, Pb and Cu were determined in both chars and eluates. The eluates were further characterized to determine 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. The ecotoxicological characterisation was performed by using the bio-indicator *Vibrio fischeri*. The chemical and ecotoxicological results were analysed according to the French proposal of Criteria on the Evaluation Methods of the Ecotoxicity of Waste (CEMEW). Char A was considered to be ecotoxic by the ecotoxicological criterion. The results indicated that the volatile organic compounds that remained trapped on the raw char and that are leached in the leaching tests induced high ecotoxicity levels. Char B was not considered to be ecotoxic by the ecotoxicological criterion (EC_{50} (30min) ≥ 10%), but it was considered to be ecotoxic by the chemical criterion due to the concentration of Ni ≥ 5 mg/kg wb.

The results presented in this section were published, partially or completely, in the following papers:

Bernardo, M.S., Lapa, N., Barbosa, R., Gonçalves, M., Mendes, B., Pinto, F., Gulyurtlu, I., Chemical and ecotoxicological characterisation of solid residues produced during the co-pyrolysis of plastics and pine biomass, *Journal of Hazardous Materials*, 166 (2009) 309–317. (doi: 10.1016/j.jhazmat.2008.11.031; IF: 4.173)

Bernardo, M.S., Gonçalves, M., Lapa, N., Barbosa, R., Mendes, B., Pinto, F., Gulyurtlu, I., Determination of aromatic compounds in eluates of pyrolysis solid residues using HS-GC–MS and DLLME–GC–MS, *Talanta*, 80 (2009) 104–108. (doi: 10.1016/j.talanta.2009.06.037; IF: 3.794)

Bernardo, M., Lapa, N., Gonçalves, M., Barbosa, R., Mendes, B., Pinto, F., Gulyurtlu, I, Evaluation of the environmental hazard of char residues produced in the co-pyrolysis of different wastes: chemical and ecotoxicological characterisation*, Book of Proceedings of the XII International Waste Management and Landfill Symposium*, Sardinia, Italy, 5-9 October 2009.

3.2.1 Introduction

The work presented in this section was in line with another work developed at UTCAE-LNEG[63,175] (former UEZ-LNEG) and in the framework of the FCT-MCES project POCTI/ENR163388/2004 “Valorisation of used tires, plastics and biomass wastes by pyrolysis to produce valuable end products”. In this stage of the project, in 2007, the main goal was to investigate the conditions that optimize the quantity and quality of bio-oils from pine biomass when co-processed with plastics; therefore tire rubber was not included at this stage in the pyrolysis feedstock mixture. A significant quantity of chars (solid fraction) was obtained in these experiments as by-products, mainly originated from the thermal decomposition of the lignocellulosic material.

The char produced with a feedstock mixture composed by 70% (w/w) of pine biomass and 30% (w/w) of plastics was chosen as a representative char sample from the co-pyrolysis process of these two raw materials, and the results of its chemical and ecotoxicological characterisation are presented in the following sections.

3.2.2 Experimental part

3.2.2.1 Pyrolysis experiments and char samples

A mixture composed by 70% (w/w) of pine biomass and 30% (w/w) of plastics (mixture of PP, PE and PS) was subjected to pyrolysis in a 1 L stirred batch autoclave (Figure 9) built in Hastelloy C276 (Parr instruments, model 4571) in the installations of UTCAE-LNEG[175], during 15 min at a temperature of 400 ºC with an initial pressure of 0.4 MPa, in the presence of nitrogen. Heating rates of around 4.6 ºC/min were achieved.

As refered in section 3.1.1, the composition of the mixture of plastics attempted to reflect the average composition, at the time the project began, found in the Portuguese Municipal Solid Wastes[175-176]: 56% (w/w) of PE, 27% (w/w) of PP and 17% (w/w) of PS.

Figure 9. Stirred batch autoclave of 1 L from Parr Instruments of UTCAE-LNEG[175].

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. The product yields were obtained as the ratio between the mass of product obtained and the initial mass of the feedstock mixture.

One part of the chars (solid fraction) was submitted to a Soxhlet extraction with dichloromethane (DCM) in order to remove and recover the pyrolysis liquids that remained soaked in the chars. The raw char (not extracted) was designated in this work as Char A and the char extracted with DCM was denominated as Char B (Figure 10). The DCM extract yield was around 50% (g/g_{char}).

Figure 10. Image of Char A (left image) and of Char B (right image).

3.2.2.2 Thermal analysis of chars

Chars A and B were submitted to a thermal analysis that consisted in measuring the progressive weight loss associated with the combustion of samples in a CEM microwave furnace MAS 7000, under an air atmosphere, from room temperature up to 600 ºC with increments of 50 ºC. The samples remained 10 min in 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. The mass of char used in the experiments was 0.5 g. This thermal analysis allowed defining the decomposition profile of the chars as a function of the temperature.

3.2.2.3 Determination of the metal content of chars

The char samples were placed in porcelain crucibles and digested with hydrogen peroxide 30% (v/v) in a heated bath at a temperature of 95 ºC and then digested with *aqua regia* ($HCl:HNO_3$, 3:1, v/v) at the same temperature. Finally, a microwave acid digestion adapted from the EPA 3015 method[177] was used to complete the solubilization of the inorganic components of the samples. The previously digested samples were dissolved in ultra-pure water (Milli-Q Academic, Millipore) up to a volume of 45 mL. These aqueous samples were digested with 5 mL of *aqua regia* in a Milestone ETHOS 1600 microwave heating system. The temperature of each sample achieved 170±5 ºC in 10 min, and remained at this temperature for 10 min. The digested samples were filtrated using Whatman filter paper grade 595 and a selected group of heavy metals were quantified in the digested samples using a Thermo UNICAM 929 Atomic Absorption Spectrometry (AAS) equipment: Cr was analysed using the acetylene-nitrous oxide flame technique, and Cd, Cu, Zn, Ni and Pb were analysed using the air-acetylene flame technique.

3.2.2.4 Leaching tests

The leaching methodology followed the standard leaching test ISO/TS 21268-2[142]. This standard has been developed to measure the release of inorganic and non-volatile organic constituents from soil and soil materials and the ecotoxicological levels of the eluates. In this work, an adaptation of this standard was made taking into account the physical similarities between the pyrolysis chars and soil materials (they are both granular materials). The adaptation was done because by the time this work was performed there were no standards specified for the determination of the leaching behaviour of organic compounds from chars.

Although this leaching standard is described as adequate for assessing the release of non-volatile organic contaminants, it was used in this work also to assess the release of volatile organic compounds. Therefore, the contact between the char samples and leaching solution was performed in closed vessels, allowing for a representative sampling of volatile organic compounds. This is not foreseen in the leaching test ISO/TS 21268-2[142] and corresponds to the adaptation introduced in the leaching test.

The chars were mixed with the leaching solutions in a single stage batch test performed at an L/S ratio of 10 L/kg, at a constant temperature of 20±2 ºC. The containers (capped glass bottles) were shaken in a roller-rotating device (Heidolph) at 10 rpm, for a period of 24±0.5 h. The leachants used were the following: a calcium chloride solution ($CaCl_2$) 0.001 mol/L (according to the standard ISO/TS 21268-2) and a dichloromethane (DCM) solution of 0.2% (v/v). The $CaCl_2$ solution can simulate a more real leaching environment with dilute concentrations of divalent cations that can act as the exchangeable fraction and inorganic ligands that can act as complexing agents, affecting the mobility of organic and inorganic species. The choice for 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 chars. The concentration chosen to the DCM aqueous solution was previously tested as the highest concentration that could be used without promoting a significant toxic effect in the bacterium *Vibrio fischeri* used in the ecotoxicological analysis of the eluates.

At the end of the leaching test, the mixtures were allowed to settle for 15 min and the eluates were filtrated over fibre glass filters GF/C Whatman to minimize the sorption of organics. Duplicates and blank tests were made for each sample.

The eluates were immediately analysed for pH (Crison, micropH 2001) and subsequently divided into sub-samples to be used in the different chemical and ecotoxicological analyses. The eluates used in the quantification of heavy metals were preserved with HNO_3 to a pH<2 and refrigerated at 4 ºC. For the ecotoxicological tests and quantification of organic contaminants, the eluates were preserved at a temperature of 4±1 ºC.

Table 5. Codes used for the different eluates obtained.

Eluate code	Type of eluate
1	Char A (not extracted) leached with $CaCl_2$ 0.001M solution
2	Char B (previously extracted with DCM) leached with CaCl2 0.001M solution
3	Char A (not extracted) leached with DCM 0.2% (v/v) solution
4	Char B (previously extracted with DCM) leached with DCM 0.2% (v/v) solution

3.2.2.5 *Chemical characterisation of the eluates*

3.2.2.5.1 *Metals content*

The acidified eluates were analysed for metal content using the Thermo UNICAM 929 Atomic Absorption Spectrometry (AAS) equipment. The metals determined in chars were the same analysed for the eluates: Cr (acetylene-nitrous oxide flame technique) and Cd, Cu, Zn, Ni and Pb (air-acetylene flame technique).

3.2.2.5.2 *Organic compounds*

The concentration of BTEX (Benzene, Toluene, Ethylbenzene and Xylenes) compounds in the eluates was evaluated by headspace static sampling (HS) 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 ºC; headspace volume and eluate solution volume, 25 mL; sample volume, 0.5 mL. The sample was injected in a TRACE^{TM} GC 2000 Series gas chromatograph equipped with a split–splitless injector, a RTX$^{®}$-VMS with 75m×0.53mm×3µm 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 ºC; the oven temperature program was as follows: 32 ºC (hold for 7 min), up to 80 ºC at a rate of 10 ºC/min, up to 150 ºC at a rate of 50 ºC/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 µg/L 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 analysed as described above and calibration curves were constructed for each analytes in both leaching solutions.

Other volatile aromatics present in the eluates were identified by headspace sampling (HS) and gas chromatography hyphenated with mass spectrometry (GC-MS). 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 30m×0.25mm×1.4µm. The carrier gas was helium at 1.5 mL/min; samples were injected, at 60 ºC, 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 ºC; the oven temperature program was as follows: 32 ºC (hold 5 min), heating ramp up to 100 ºC (5 ºC/min), heating ramp up to 250 ºC (10 ºC/min) and finally heating ramp up to 280 ºC (50 ºC/min, hold 1 min).

3.2.2.6 Ecotoxicological characterisation of the eluates

The ecotoxicological parameter analysed was the inhibitory effect of the eluates on the light emission of the marine bacterium *Vibrio fischeri* (Azur Environmental Microtox® system) according to the ISO standard 11348-3[178]. The luminescence inhibition of *V. fischeri* was evaluated for an exposure period of 5, 15, and 30 min. Blank tests were performed with both leaching solutions in order to determine the threshold luminescence inhibition caused by these solutions. The results of the ecotoxicity test were expressed as EC_{50} (% v/v) values which represents the effective concentration of the eluate analysed that causes a reduction of 50% of the *V. fischeri* bioluminescence.

3.2.2.7 Methodology used to assess the ecotoxicity of the pyrolysis chars

The Criteria and Evaluation Methods of the Ecotoxicity of Waste (CEMEW)[161] proposed by the French Ministry of Environment, in 1998, attempted to regulate the European classification of wastes defined in the Hazardous Waste Directive[149] under the code H14 (ecotoxic wastes). According to this methodology, the ecotoxicity of a waste shall be assessed through its chemical composition or its ecotoxicological characteristics. Both shall be performed on raw materials and on its eluate.

The chemical composition is used as a positive criterion which means that the presence of at least one pollutant in a concentration higher than the limits fixed on the CEMEW allows for the classification of ecotoxic. If the chemical characterisation is inconclusive, i.e. 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 must proceed with the ecotoxicological characterisation. The ecotoxicological characterisation is used as a positive criterion. The positive criterion of the ecotoxicological analysis means that if at least one of the biological tests is positive, the waste shall be classified as ecotoxic. The negative criterion presumes that only the negative response to all of the ecotoxicological tests performed allows the classification as non-ecotoxic.

The conceptual methodology that is applied in this work to assess the ecotoxicity of the pyrolysis chars is slightly different from the French proposal (Figure 11) and follows a suggestion of Lapa et al.[179]. The main difference is related with the importance that is attributed to the chemical and ecotoxicological characterisations. In this work, the chemical and ecotoxicological characterisation was performed for all eluates and the results were then used to classify the chars using the criteria adopted for this study. This methodology enabled to obtain information on the contribution of each class of chemical contaminants to the ecotoxic characteristics of the chars, and also to detect the eventual synergetic effects between chemical species that are present below their limit values.

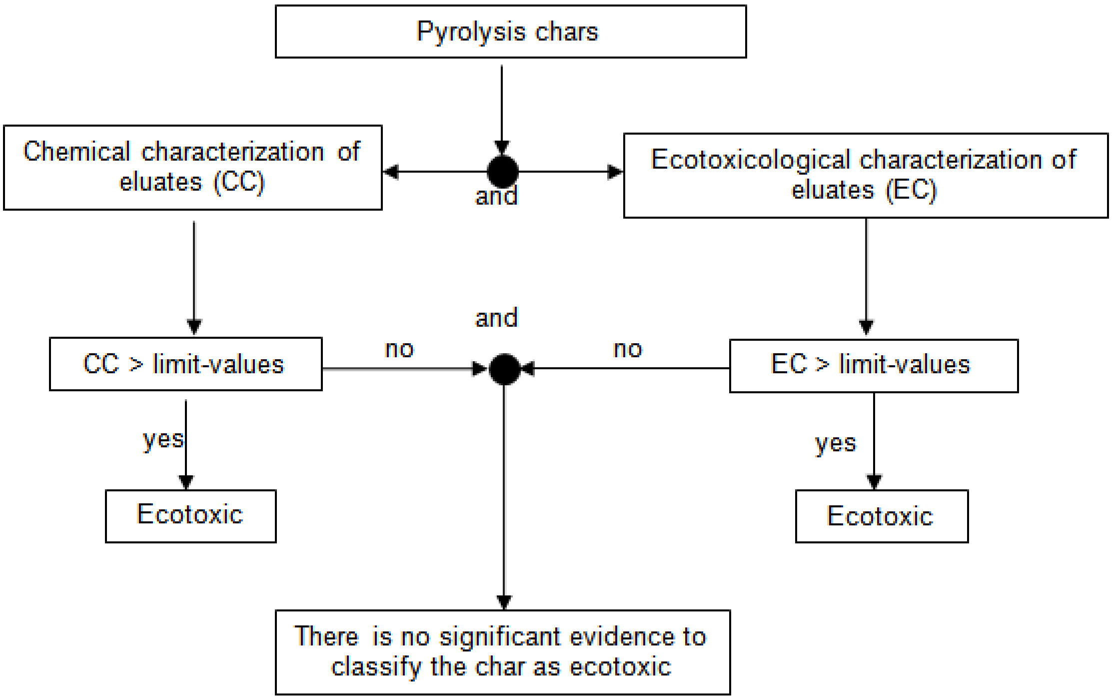

Figure 11. Criterion applied to assess the ecotoxicity of pyrolysis chars.

3.2.3 Results and discussion

3.2.3.1 Thermal analysis of chars

Figure 12 shows the weight loss for each char as a function of the temperature. Char B, the DCM extracted char, did not present a significant initial weight loss up to 200ºC, while Char A, the crude char, suffered a weight loss higher than 30% (w/w) in the same temperature range due to the volatilization of pyrolysis liquids that remained trapped in the char. This result suggests that the extraction with DCM was effective in the removal of organic matter with boiling points up to 200 ºC. Between 250 ºC and 450 ºC, both chars lost weight at a similar rate until stabilizing at a steady value of less than 1% of their initial weight. Both chars presented a stable residual weight above 450ºC indicating that at this temperature all the combustible matter was already decomposed. This behaviour indicates that the chars had identical contents of non-volatile organic compounds.

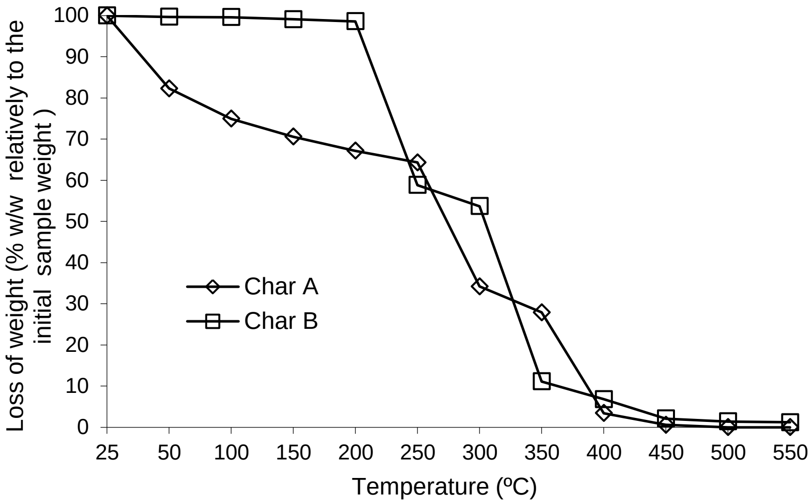

Figure 12. Loss of weight (% w/w relatively to the initial sample weight) of Chars A and B by combustion in air atmosphere.

3.2.3.2 Metal content of chars

Table 6 presents the heavy metal content of chars A and B. The selection of metals to be determined was made based on the mineral content of pine and plastics performed in section 3.1.3.3 and presented in Table 3. Pb, Zn and Cu were quantified in both raw materials. Cd, Cr and Ni were also selected because of their particularly high toxicity for human health and environment.

Both chars showed detectable amounts of Cr, Ni and Zn, while the concentrations of Cd, Cu and Pb were below the respective detection limits.

Cr and Ni were not detected in any of the raw materials (see Table 3). A possible explanation for the presence of these metals in the pyrolysis chars is a contamination from the pyrolysis reactor which is built in Hastelloy C276. This is a nickel-molybdenum-chromium wrought alloy. Pyrolysis of biomass creates an acidic environment inside the reactor that might be the cause of metals release from the reactor walls although no damage in the reactor walls was observed in plain sight.

Zn was quantified in the plastics and pine biomass with 9.2 mg/kg wb and 22.9 mg/kg wb, respectively (Table 3), and was subjected to a magnification factor in the raw char due to the division of the initial feedstock mass by three fractions (liquids, chars, and gases).

The higher concentrations of the quantified metals in Char B than in char A are due to a concentration effect caused by the removal of the light organic fraction during DCM extraction. Considering the DCM extraction yield, it should be expected a mass reduction of Char A of 50% which leads to a concentration factor of the metals in the extracted char B of around 2 when compared to char A. However, it was observed that Cr concentration in Char B was about 20 times higher than in Char A. In the raw char A, Cr might be strongly associated with the organic matrix and was not completely solubilised in the acidic digestion. Therefore, its content in the raw char was probably underestimated.

For Zn, the inverse was registered; its concentration in the extracted char B was only 1.2 times higher than in the raw char, indicating that probably the full Zn content in Char B was not determined or some of the Zn was extracted during DCM extraction.

Table 6. Metal content of chars A and B.

Metals (mg/kg) wb	Char A	Char B
Cd	<0.540	<0.540
Cr	4.98±2.32	102±28
Cu	<0.248	<0.248
Ni	44.1±5.2	91.1±1.6
Pb	<12.3	<12.3
Zn	47.2±9.2	57.0±9.5

wb – wet basis; The mean and standard deviation of triplicates are shown.

3.2.3.3 *Chemical characterisation of eluates*

3.2.3.3.1 *Metal content*

The pH values and concentrations of metals in the eluates are shown in Table 7. The results for metals concentration are presented in mass of leached substance per mass unit of char

Table 7. pH values and metal content in the eluates of Chars A and B.

Chemical parameters	Eluate 1 (Char A, $CaCl_2$ 0.001 M)	Eluate 2 (Char B, $CaCl_2$ 0.001 M)	Eluate 3 (Char A, DCM 0.2% (v/v))	Eluate 4 (Char B, DCM 0.2% (v/v))
pH	6.2	6.0	6.2	5.7
Metals (mg/kg wb)				
Cd	<0.120	<0.120	<0.120	<0.120
Cr	<1.15	<1.15	<1.15	<1.15
Cu	<0.110	<0.110	<0.110	<0.110
Ni	<1.03	30.6±8.0	<1.03	32.7±1.7
Pb	<5.00	<5.00	<5.00	<5.00
Zn	1.76±0.71	5.45±1.48	2.58±1.09	5.43±0.71

wb – wet basis; The mean and standard deviation of duplicates are shown

All the eluates showed pH values (from 5.7 to 6.2) similar to the pH values of the leaching solutions ($CaCl_2$ solution: pH=6.3; DCM solution: pH=5.9), which means that there was not a significant leaching of acidic or basic compounds from the chars.

All the metals analysed were below their detection limits, except for Ni and Zn, which were released in significant concentrations from the chars. Ni and Zn released from the extracted Char B in higher concentrations (Eluate 2 and 4) than from Char A, which can be explained by their high concentrations in Char B. No significant differences were observed in the amounts leached by $CaCl_2$ solution and by DCM solution.

As referred previously, the chars showed high concentrations of Cr (especially Char B) (Table 6), but this metal was not detected in the eluates, suggesting its presence in the chars in a very stable form resistant to mobilisation at relatively neutral pH values.

3.2.3.3.2 *BTEX compounds*

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 $CaCl_2$ and DCM leaching solutions and the corresponding detection and quantification limits were evaluated. All correlation coefficients were above 0.993 and the limits of detection (LOD) ranged between 17.6 and 25.7 µg/L for both leaching solutions; the limits of quantification (LOQ) were situated between 65.4 and 85.5 µg/L. The method precision was evaluated at two concentration levels (LOQ and 2xLOQ) and varied from 2.8 to 12.7% R.S.D. (Relative Standard Deviation), for the different analytes in both leaching solutions.

The validated method was used to determine the concentrations of BTEX compounds in the four eluates (Table 8). No BTEX compounds were detected in eluates 2 and 4 obtained from Char B, which confirms that the extraction with DCM was an efficient method for the removal of volatile organic contaminants.

Table 8. BTEX concentrations in the eluates of Chars A and B.

Eluates	Concentrations (µg/L)				
	Benzene	Toluene	Ethylbenzene	*m/p*-Xylenes	*o*-Xylene
1 (Char A, $CaCl_2$ 0.001M)	<21.9	511±9	277±2	<19.6	49±2
2 (Char B, $CaCl_2$ 0.001M)	<21.9	<22.6	<17.6	<19.6	<25.7
3 (Char A, DCM 0.2% (v/v))	197±7	726±14	382±4	<22.8	73±4
4 (Char B, DCM 0.2% (v/v))	<23.1	<23.7	<23.4	<22.8	<21.7

LOD are shown; The mean and standard deviation of triplicates are shown

Eluates 1 and 3 showed a contamination with toluene, ethylbenzene and o-xylene in concentrations from 49 µg/L to 726 µg/L with predominance for toluene. Toluene and ethylbenzene were also the compounds detected in the pyrolysis liquid fraction with the highest concentrations[176]. Eluate 3 presented higher concentrations of the analytes than eluate 1 and also had benzene at a concentration of 197 µg/L. The results obtained in this work showed that the presence of organic solvents in the leaching solution causes an increase in the amounts of organic contaminants leached from the chars. 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 behaviour 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 scenarios where the material can contact with relatively apolar organic solutions can be grossly underestimated.

3.2.3.3.3 *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 (HS-GC-MS). 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 the presence of BTEX, several other aromatic hydrocarbons (PAHs, furans and other benzene derivatives) and other organic compounds such as phenolics were also detected and identified (Table 9). These organic compounds are typical components of the liquid fraction obtained from the co-pyrolysis of plastics and biomass[176], so it is expected that they also can occur in the chars resulting from that pyrolysis process. The relative concentration of each compound decreased as the retention time increased, 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 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.

Table 9. List of the organic compounds identified in the eluates of Chars A and B.

		Relative peak area (%)			
Name	R.T. (min)	Eluate 1	Eluate 2	Eluate 3	Eluate 4
Benzene^1	9.12	2.05		1.75	
Toluene^1	13.73	41.0	1.35	32.4	0.64
Ethylbenzene^1	17.62	33.6	1.81	31.3	0.55
m/p-Xylenes^1	17.93	2.54	0.10	1.50	
o-Xylenes^1	18.96	2.48		1.17	
Cumene^1	19.86	9.12	0.31	4.27	0.08
Propylbenzene^1	20.77	1.49		0.73	
4-Ethyltoluene^1	20.98	0.82		0.39	
3-Ethyltoluene^2	21.17	0.08		0.03	
2-Ethyltoluene^2	21.56	0.50		0.17	
*t*ert-Butylbenzene^1	21.79	0.01		0.05	
1,2,4-Trimethylbenzene^1	21.90	0.43		0.16	
1-Methylpropylbenzene^1	22.23	0.19		0.10	
1-Methyl-4-(1-methylethyl)benzene^2	22.52	0.07		0.03	
Trimethylbenzene (isomer)^2	22.70	0.20		0.06	
2-propenylbenzene^2	22.83	0.15			
1-propenylbenzene^2	23.06	0.49		0.14	
Butylbenzene/1,4-Diethylbenzene^1	23.27	0.20		0.07	
1-butenylbenzene^2	24.09	0.20		0.08	
1,2,4,5-Tetramethylbenzene^1	24.60	0.03		0.01	
Methylphenol (isomer)^2	24.71	0.08		0.07	
3-Methylbenzofurane^2	24.76	0.12		0.11	
4-etenyl-1,2-dimethylbenzene^2	25.14	0.06		0.04	
Dimethylphenol (isomer)^2	25.35			0.05	
1-Methylpropenylbenzene^2	25.40	0.11		0.05	
Dimethylphenol (isomer)^2	26.23	0.06		0.08	
Naphtalene^2	26.40	0.14		0.23	
Trimethylphenol (isomer)^2	26.60	0.07			
Trimethylphenol (isomer)^2	26.90	0.02		0.04	
Trimethylphenol (isomer)^2	27.41	0.04		0.08	
2,3,5,6-Tetramethylphenol^2	27.95	0.01		0.04	
Methylnaphtalene^2	28.47	0.05		0.15	

1 – Compound identified by co-injection of standards; 2 – compound tentatively identified by comparison with the spectra of NIST and Wiley libraries and by comparison between isomer molecular structures; R.T. – Retention time

It was possible to detect several aromatic compounds in eluates 2 and 4, namely toluene, ethylbenzene, m/p-xylenes and cumene (Figure 13), which were not detected in GC-FID given the lower detection limits that can be achieved by GC-MS.

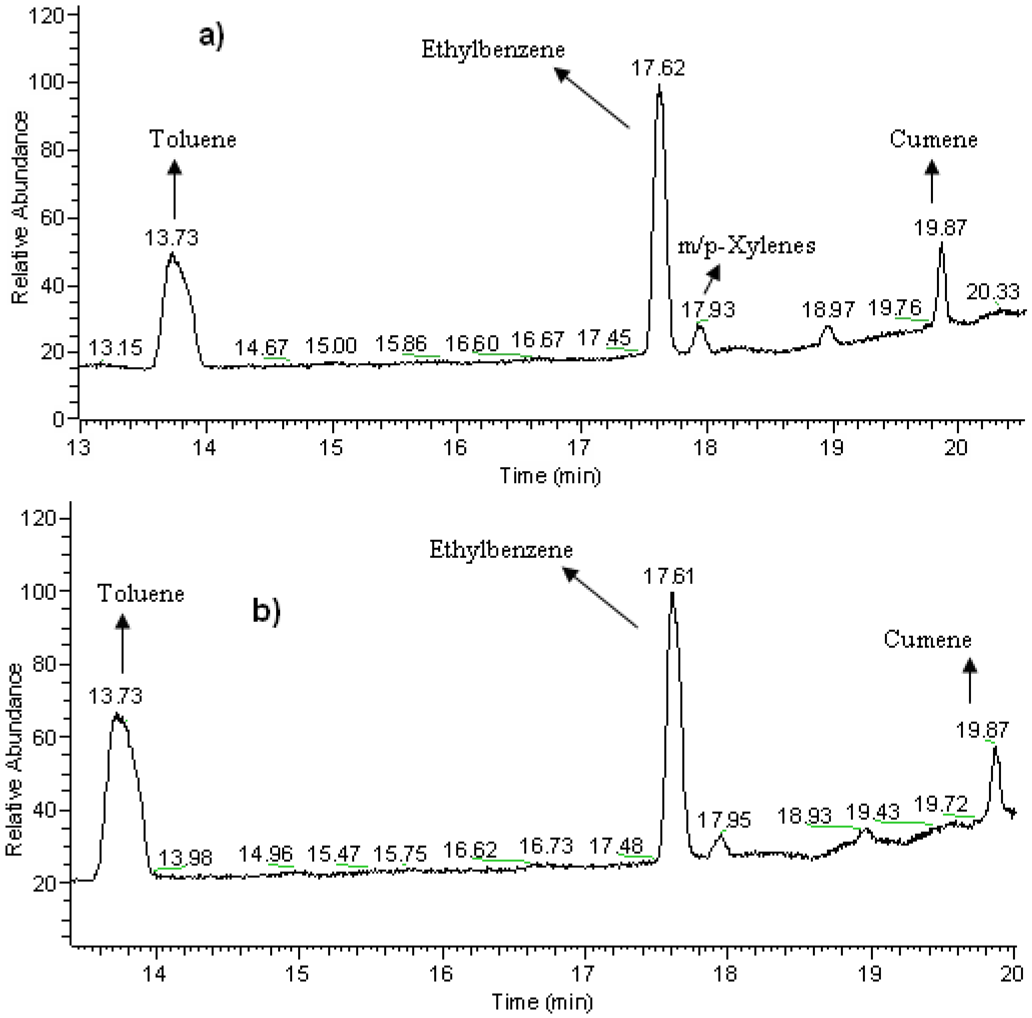

Figure 13. GC-MS chromatogram of a) eluate 2 and b) eluate 4, where it can be observed the presence of toluene, ethylbenzene, xylenes, and Cumene.

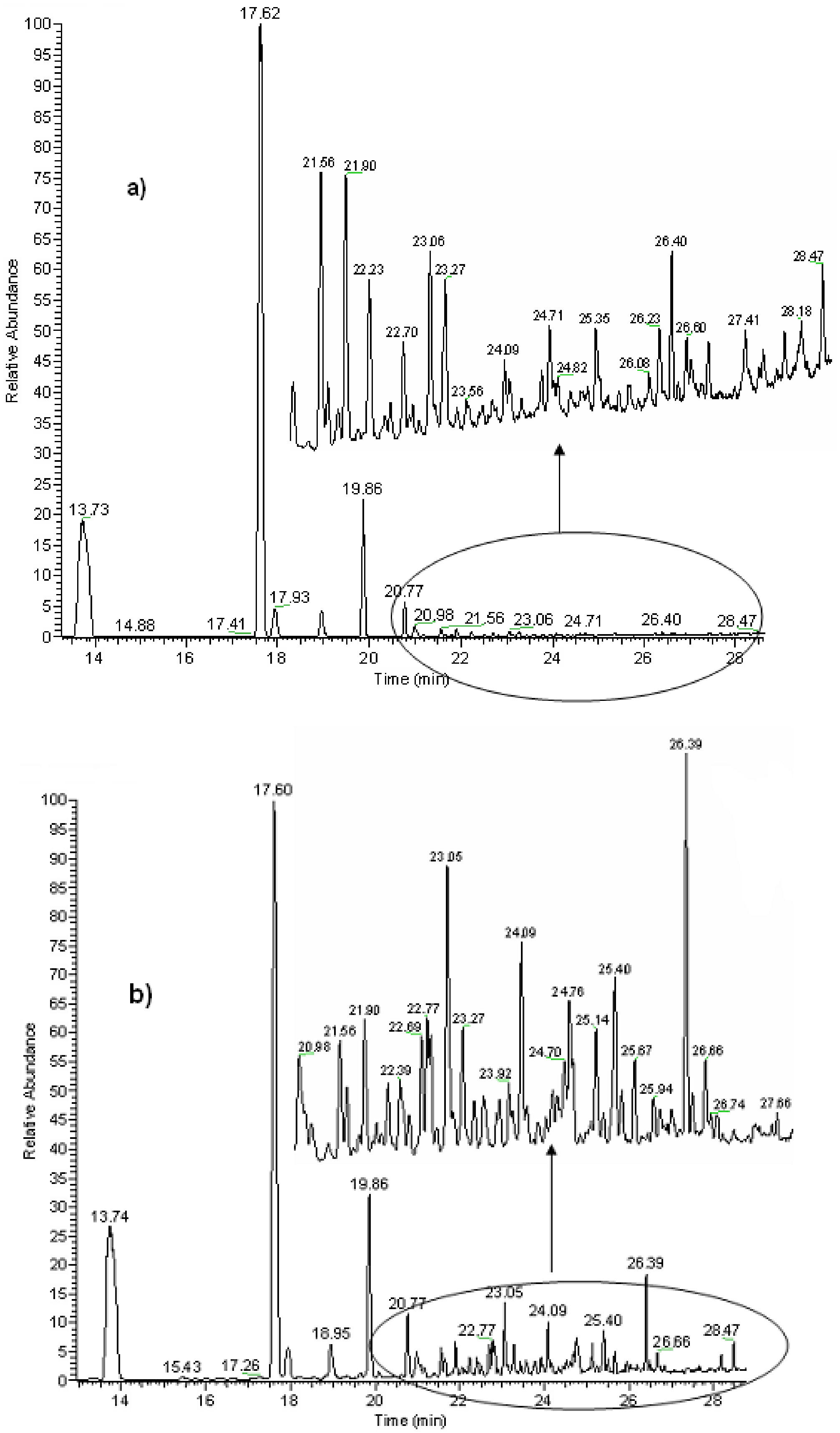

Figure 14. GC-MS chromatogram of a) eluate 1 and b) eluate 3, where it can be confirmed a high content in volatile organic compounds.

Eluates 1 and 3 were much more contaminated (Figure 14), as the GC-FID analyses had already indicated and it was possible to detect several other compounds at high enough concentrations to enable the acquisition of elucidative mass spectra. Eluate 3, resulting from the raw Char A leached with the DCM solution presented much more density of GC-MS peaks in the range of heavier volatile compounds (R.T above 20 min).

3.2.3.4 Ecotoxicological characterisation of eluates

The ecotoxicological data obtained in the eluates are shown in Table 10.

Table 10. Ecotoxicological levels of the eluates of Chars A and B.

	EC_{50} (%) (v/v)		
Eluate	5 min	15 min	30 min
1 (Char A, $CaCl_2$ 0.001M)	1.03	1.27	1.08
2 (Char B, $CaCl_2$ 0.001M)	>99	>99	70.4
3 (Char A, DCM 0.2% (v/v))	0.620	0.530	0.560
4 (Char B, DCM 0.2% (v/v))	>99	>99	73.6

Eluates 1 and 3 showed the highest ecotoxicity. Concentrations of these eluates of 0.560% and 1.08% (v/v) have induced a 50% luminescence inhibition to *V. fischeri* for an exposure period of 30 min, probably due to the high organic load in these eluates. The highest ecotoxicity levels of eluate 3 can be explained by the highest concentrations of BTEX compounds that were present in this eluate, but also by the ecotoxicity induced by DCM that was present in the leaching solution that by itself induced a 20% luminescence inhibition.

No significant ecotoxicity was detected in the eluates 2 and 4. Only for an exposure period of 30 min, these eluates caused 50% luminescence inhibition for concentrations of approximately 70% (v/v).

3.2.3.5 Ecotoxicity assessment of pyrolysis chars

CEMEW[161] proposal defines limit-values for metals that have been determined in the eluates of chars (Table 11). The presence of at least one heavy metal in a concentration higher than the respective limit-value leads to the classification of the char as ecotoxic.

All eluates showed concentrations of Cd, Cr, Cu, Pb and Zn (Table 7) below the limit-values defined in the CEMEW proposal. Eluates 2 and 4 showed Ni concentrations higher than the limit-value established in the proposal; therefore, Char B was classified as ecotoxic. Eluates 1 and 3 presented concentrations of all the metals analysed in this work below the limit-values defined in the French proposal; therefore, char A was classified as non-ecotoxic.

The ecotoxicological limit-value defined in CEMEW for the biological indicator *Vibrio fischeri* is EC_{50} (30 min) ≤ 10% (v/v). Comparing the results of the ecotoxicological characterisation with this limit-value, it can be concluded the following:

- Eluates 2 and 4 showed EC_{50} (30 min) values above 10% (v/v); therefore, according to the ecotoxicological criterion, Char B was classified as non-ecotoxic.
- Eluates 1 and 3 presented EC_{50} (30 min) values below 10% (v/v); therefore Char A was classified as ecotoxic.

Table 11. Limit-values of non-ecotoxic materials defined in CEMEW[161] for metals determined in the present work.

Metals	Limit-values (mg/kg)
Cd	2
Cr	5
Cu	5
Ni	5
Pb	5
Zn	20

3.2.4 Conclusions

The extraction of the pyrolysis chars with an appropriate organic solvent is an efficient method for the reduction of their content in organic matter promoting a reduction on their ecotoxicity. The solvent used in this work, DCM, showed a good capacity for the removal of volatile organic compounds with boiling points up to 200 ºC from the crude char.

The chemical analysis by GC-FID and by GC-MS showed that the crude char leached relatively high concentrations of volatile organic compounds, namely BTEX.

Char A was classified as ecotoxic by the ecotoxicological criterion of CEMEW and its ecotoxicity was attributed to the presence of a high load of organic contaminants.

Char B was classified as non-ecotoxic by the ecotoxicological criterion of CEMEW, but it was considered as ecotoxic by the chemical criterion due to the presence of Ni in concentrations above the limit-value for non-ecotoxic materials as defined in CEMEW.

3.3 CHARS OBTAINED IN THE CO-PYROLYSIS OF PLASTICS, USED TIRES AND PINE BIOMASS

Abstract: Chars produced in the co-pyrolysis of plastics, pine biomass and used tire rubber were characterized using chemical and ecotoxicity assays. One part of the solid char was submitted to extraction with dichloromethane (DCM) in order to reduce its toxic potential by removing organic contaminants. The raw and extracted char (chars A and B, respectively) were submitted to a thermal analysis and the results obtained demonstrated that the extraction of the pyrolysis char with DCM was an efficient method to remove organic compounds with boiling points up to 200 ºC.

Chars A and B were submitted to the leaching test ISO/TS 21268-2 and the concentrations of Cd, Pb, Zn, Cu, Hg and As were determined in both chars and eluates. The resulting eluates were also characterized to determine the concentrations of several organic compounds (volatile aromatic hydrocarbons and alkylphenols). An ecotoxicological characterisation was also performed on the eluates by using the bio-indicator *Vibrio fischeri*.

The chemical and ecotoxicological results were analysed according to the Council Decision 2003/33/EC and the Criteria on the Evaluation Methods of the Ecotoxicity of Waste (CEMEW).

The results obtained in this work indicated that the extraction with DCM is an effective method for the removal of organic contaminants of high to medium volatility from the pyrolysis char, thus decreasing its toxic potential. However, the chars (treated and non-treated with DCM) leached significant concentrations of Zn that were associated to the high ecotoxic levels of the eluates.

Both chars were classified as hazardous and ecotoxic materials.

The results presented in this section were published, partially or completely, in the following papers:

Bernardo, M., Lapa, N., Gonçalves, M., Barbosa, R., Mendes, B., Pinto, F., Gulyurtlu, I., Toxicity of char residues produced in the co-pyrolysis of different wastes, *Waste Management*, 30 (2010) 628–635. (doi: 10.1016/j.wasman.2009.10.015; IF: 2.428)

Bernardo, M., Gonçalves, M., Lapa, N., Mendes, B., Determination of alkylphenols in eluates from pyrolysis solid residues using dispersive liquid–liquid microextraction, *Chemosphere*, 79 (2010) 1026–1032. (doi: 10.1016/j.chemosphere.2010.03.062; IF: 3.206)

Bernardo, M., Lapa, N., Gonçalves, M., Barbosa, R., Mendes, B., Pinto, F., Evaluation of the toxicity of char residues produced in the co-pyrolysis of different wastes, *CD of Proceedings of the ISWA/APESB 2009 World Congress – Turning Waste into Ideas*, Lisbon, Portugal, 12-15 October 2009.

3.3.1 Introduction

In this work, the tire rubber was introduced in the pyrolysis feedstock mixture. The synergetic effects and advantages of the co-pyrolysis of tire rubber with pine and plastics in the fuel properties of gases and liquid products were studied[71,176]. The introduction of tire rubber in the pyrolysis feedstock led to the production of chars that theoretically would present different composition, leaching behaviour and ecotoxic properties from the chars obtained with the blends of plastics and pine biomass.

The strategy used in the previous section was extended and applied to the characterisation of the chars obtained in the pyrolysis of the ternary mixture. The results obtained are presented in this section.

3.3.2 Experimental part

3.3.2.1 Pyrolysis experiments and char samples

Pyrolysis experiments were carried out in the stirred batch autoclave of 1 L presented in Figure 9 (section 3.2.2.1). The autoclave was first loaded and then closed, purged and pressurised to 0.41 MPa with nitrogen. It was then heated at a rate of around 5 ºC/min until the desired reaction temperature was reached (420 ºC). This temperature was maintained for 15 min. At the end of this period, the autoclave was progressively cooled down to room temperature. Given the low heating rate and cooling period, the total residence time of the materials inside the reactor vessel was about 90 min.

The mixture subjected to pyrolysis was composed by 30% (w/w) pine biomass, 30% (w/w) used tires and 40% (w/w) plastics. Once again, the plastics were composed by a mixture of 56% (w/w) PE, 27% (w/w) PP and 17% (w/w) PS to reflect the average composition, at that time, found in the Portuguese MSW[175-176].

With these experimental conditions the reaction products were: 10% (w/w) gases, 60% (w/w) liquids and 25% (w/w) solid chars. About 5% of losses of the final pyrolysis products were determined. The product yields were obtained as the ratio between the mass of product obtained and the initial mass of the feedstock mixture.

The chars obtained in the pyrolysis experiments were a carbonized pasty residue covered with the pyrolysis oils and tars being very smelly. One part of the crude char obtained was extracted with dichloromethane (DCM) in an automatic Soxhlet extractor. The results obtained in the previous section 3.2 demonstrated that DCM is able to extract a large range of volatiles from the chars produced during the co-pyrolysis of plastics and biomass, decreasing their ecotoxicity and consequently their hazard potential. The extract yield was around 54% (g/g_{char}).

The raw char (not extracted) was designated in this work as Char A and the char extracted with DCM was denominated as Char B (Figure 15).

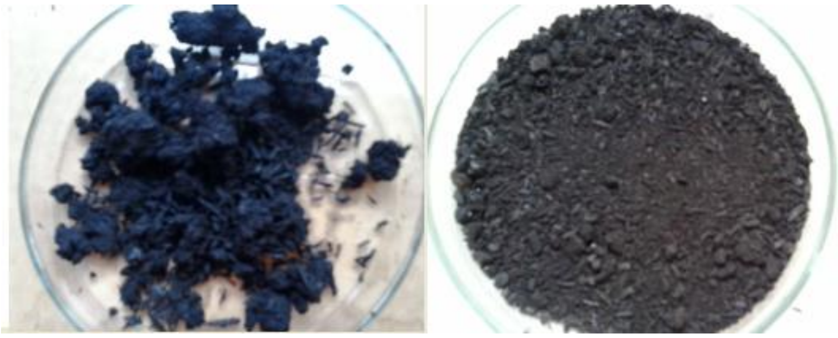

Figure 15. Image of Char A (left image) and of Char B (right image).

3.3.2.2 Thermal analysis of chars

Chars A and B were submitted to a thermal analysis that consisted in measuring the progressive weight loss associated with the combustion of samples in a CEM microwave furnace MAS 7000, under an air atmosphere, from room temperature up to 600 ºC with increments of 50 ºC. The samples remained 10 min in each temperature stage. At the end of each heating stage, the samples were removed from the furnace, cooled down to room temperature in a desiccator and weighed. The mass of char used in the experiments was 0.5 g. This thermal analysis allowed defining the decomposition profile of the chars as a function of the temperature.

3.3.2.3 Determination of the metal content of chars

The char samples were placed in porcelain crucibles and digested with hydrogen peroxide 30% (v/v) in a heated bath at a temperature of 95 ºC and then digested with *aqua regia* (HCl:HNO_3, 3:1, v/v) at the same temperature. Finally, a microwave acid digestion adapted from the EPA 3015 method[177] was used to complete the solubilization of the inorganic components of the samples. The previously digested samples were dissolved in ultra-pure water (Milli-Q Academic, Millipore) up to a volume of 45 mL. These aqueous samples were digested with 5 mL of *aqua regia* in a Milestone ETHOS 1600 microwave heating system. The temperature of each sample achieved 170±5 ºC in 10 min, and remained at this temperature for 10 min. The digested samples were filtrated using Whatman filter paper grade 595 and a selected group of heavy metals were quantified in the digested samples using a Thermo Elemental Solaar atomic absorption spectrometry (AAS) equipment: Cd, Cu, Zn, and Pb were analysed using the air-acetylene flame technique; Hg and As were analysed using the hydride generation technique.

3.3.2.4 Leaching tests

The leaching methodology followed the standard leaching test ISO/TS 21268-2[142] and the experimental conditions were the same as described in section 3.2.2.4: the chars were mixed with the leaching solutions in a single stage batch test performed at an L/S ratio of 10 L/kg, at a constant temperature of 20±2 ºC. The containers (capped glass bottles) were shaken in a roller-rotating device (Heidolph) at 10 rpm, for a period of 24±0.5 h. In this study, the leachant used was only the calcium chloride solution ($CaCl_2$) 0.001 mol/L as stated by the ISO/TS 21268-2 standard. At the end of the leaching test, the mixtures were allowed to settle for 15 min and the eluates were filtrated over fibre glass filters GF/C Whatman to minimize the sorption of organics. Duplicates and blank tests were made for each sample.

The eluates were immediately analysed for pH (Crison, micropH 2001) and conductivity (Mettler Toledo, MC226) and subsequently divided into sub-samples to be used in the different chemical and ecotoxicological analyses. The eluates used in the quantification of heavy metals were preserved with HNO_3 to a pH<2 and refrigerated at 4 ºC. For the ecotoxicological tests and quantification of organic compounds, the eluates were preserved at a temperature of 4±1 ºC.

3.3.2.5 Chemical characterisation of the eluates

3.3.2.5.1 *Metal content*

The acidified eluates were analysed for metal content using the Thermo Elemental Solaar AAS equipment. The following metals were determined: Cd, Cu, Zn and Pb (air-acetylene flame technique) and Hg and As (hydride generation technique).

3.3.2.5.2 *Organic compounds*

The organic compounds chosen to be monitored and quantified were a group of 15 aromatic hydrocarbons: benzene, toluene, ethylbenzene, o/*m/p/*-xylenes, cumene, propylbenzene, 4-ethyltoluene, *tert*-butylbenzene, 1,2,4-trimethylbenzene, 1-methylpropylbenzene, butylbenzene, 1,4-diethylbenzene and 1,2,4,5-tetramethylbenzene) and a group of 11 alkyl phenols: *o/m/p*-methylphenol, 3,4-dimethylphenol, 2,6-dimethylphenol, 2,3-dimethylphenol, 2,5-dimethylphenol, 2,4-dimethylphenol, 2,3,5-trimethylphenol, 2,4,6-trimethylphenol and 2,3,6-trimethylphenol.

The concentrations of the 15 aromatic volatile organic compounds in the eluates were determined by headspace static sampling and gas chromatography with mass spectrometry (HS-GC-MS). The headspace sampling technique was performed by using the following experimental conditions: equilibration time, 30 min; extraction temperature, 60 ºC; eluate solution volume, 25 mL; headspace volume, 25 mL. A volume of 0.5 mL of the headspace (gas) was collected with a syringe to be injected in GC system. The GC system was a Focus Gas Chromatograph equipped with a split-splitless injector, a TR-V1 capillary column (30m×0.25mm×1.4μm) and a Polaris Q mass spectrometer detector. The carrier gas was helium at 1.5 mL/min. Samples were injected at 60 ºC 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 ºC. The oven temperature program was as follows: 32 ºC (hold 5 min), up to 100 ºC (5 ºC/min), up to 250 ºC (10 ºC/min) and finally up to 280 ºC (50 ºC/min, hold 1 min). The MS system was operated in the full scan mode with a mass range from *m/z* 50 to 200.

A stock standard solution with a concentration of 1 g/L of each volatile component in methanol was prepared. Standard solutions prepared by dilution of an appropriate amount of the stock standard solution in the leaching solution were analysed as described above and calibration curves were constructed for each analyte in order to perform quantification.

The concentrations of the 11 alkyl phenols in the eluates were determined using dispersive liquid-liquid microextraction (DLLME) and gas chromatography with mass spectrometry (GC). The DLLME was performed using the following experimental conditions: sample volume, 4 mL; extraction solvent, 15 µL of trichloroethylene; disperser solvent, 1 mL of acetone. Analytes were separated and determined using a Focus Gas Chromatograph equipped with an auto-sampler AS2000, a split-splitless injector, a TR-5MS capillary column (30m×0.25mm×0.25µm) and a Polaris Q mass spectrometer detector. The carrier gas was helium at 1 mL/min. 1 µL of the samples were injected at 220 ºC 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 ºC. The oven temperature program was as follows: 35 ºC (hold 1 min), up to 100 ºC (5 ºC/min), up to 130 ºC (2 ºC/min) and finally up to 220 ºC (20 ºC/min, hold 3 min). The MS system was operated in the full scan mode with a mass range from *m/z* 45 to 200. Calibration standard solutions were prepared by spiking ultra-pure water with appropriated amounts of a 100 mg/L methanolic standard solution of the 11 alkyl phenols, and calibration curves for each analyte was constructed.

3.3.2.6 Ecotoxicological characterisation of the eluates

The ecotoxicological parameter analysed was the inhibitory effect of the eluates on the light emission of the marine bacterium *Vibrio fischeri* (Azur Environmental Microtox® system) according to the ISO standard 11348-3[178]. The luminescence inhibition of *V. fischeri* was evaluated for an exposure period of 5, 15, and 30 min. A blank test was performed with the leaching solution ($CaCl_2$ 0.001 mol/L). The results of the ecotoxicity test were expressed as EC_{50} (% v/v) values which represents the effective concentration of the eluate analysed that causes a reduction of 50% on the bioluminescence of *V. fischeri*.

3.3.2.7 Methodology used to assess the hazardous and ecotoxic potential of pyrolysis chars

The assessment of the ecotoxicity of pyrolysis chars followed the same conceptual methodology described in section 3.2.2.7 (Figure 11), according to an adaptation of the Criteria and Evaluation Methods of the Ecotoxicity of Waste (CEMEW)[161].

The classification of the chars as inert, non-hazardous and hazardous materials followed the Council Decision 2003/33/EC[180] that defines limit-values for several parameters in eluates obtained through the application of the leaching standard EN 12457-2[181] for the classification of wastes. The criteria defined in this European Decision are mostly based on the leaching concentrations of inorganic compounds and a few groups of organic compounds such as BTEX, mineral oil (C_{10} to C_{40}), polychlorinated biphenyls (PCB's) and polycyclic aromatic hydrocarbons (PAH's). However, the leaching standard EN 12457-2 specifies a scope which clearly excludes the leaching of organic contaminants, particularly volatiles. Nevertheless, BTEX, among others, are volatiles.

The leaching standard EN 12457-2 defines water as the leaching agent and has common experimental parameters with the leaching standard ISO/TS 21268-2, namely, the liquid/solid ratio (10 L/kg) and the contact time (24 h). The main differences are related with the leaching reservoirs (borosilicate glass and/or Teflon should be used) and the step of solid separation from the eluate, which should avoid organic compounds losses. Although in this work it was not applied the EN 12457-

2, the same limit-values defined in the Decision 2003/33/EC were considered, since, presently, there is no European legislation that includes leaching methodologies addressing the release of organics.

3.3.3 Results and discussion

3.3.3.1 Thermal analysis of chars

Figure 16 shows the weight loss for each char as a function of the temperature.

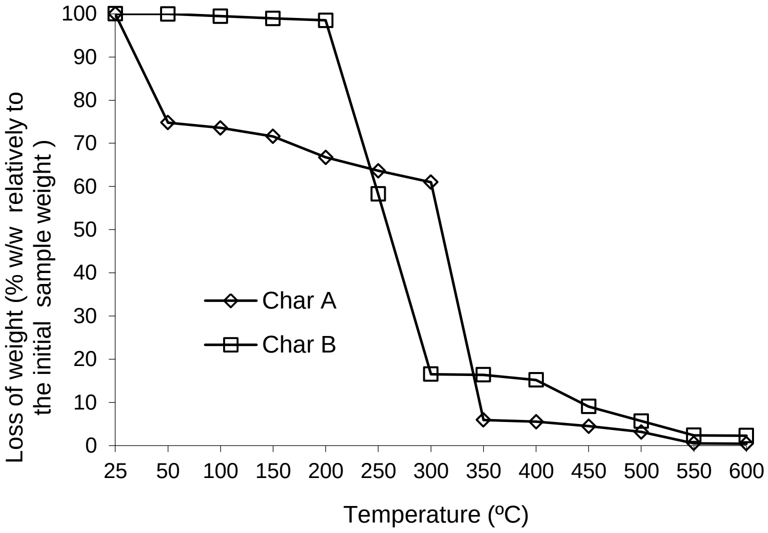

Figure 16. Loss of weight (% w/w relatively to the initial sample weight) of Chars A and B by combustion in air atmosphere.

Char A (non-extracted) showed a significant loss of weight at temperatures up to 50 ºC (from 100% to 75% of its initial weight) and a slowly weight decrease (from 75% to 60% of initial weight) at temperatures up to 300 ºC; the low to medium temperature weight loss corresponds to the volatilization of pyrolysis liquids that are present in the raw char. Char B (DCM extracted) did not present a significant initial weight loss up to 200 ºC. This result suggests that DCM extraction was efficient in the removal of compounds with boiling points up to 200 ºC. A similar result was obtained for the char resulting from the co-pyrolysis of pine and plastics, as referred in section 3.2.3.1.

At temperatures from 300 ºC up to 350 ºC, Char A suffered the highest weight loss (from 60% to 5% of its initial weight) followed by a slow weight decrease up to a final value of less than 1% of its initial weight at a temperature of 550 ºC. On the other hand, Char B showed a loss of weight from 100% to 15% of its initial weight in the range of temperatures from 200 ºC to 300 ºC. The weight of Char B suffered then a slow decrease from 15% to around 2% when temperature ranged from 300ºC to 550ºC. Therefore, at temperatures between 300ºC to 550ºC, Char A showed a higher weight loss than Char B. This difference may be attributed to a mobilization effect of the more volatile contaminants over the heavier ones: the lighter components have solvent properties that can reduce the interaction of the heavier components with the carbonaceous matrix and therefore make them more available for volatilization.

Both chars presented a stable residual weight between 550ºC and 600ºC.

3.3.3.2 Inorganic characterisation of chars and eluates

Table 12 presents the metal content of chars A and B and eluates A and B. Eluate A was produced through the leaching of Char A and eluate B resulted from Char B. For the eluates, the result is presented in mass of leached substance per mass unit of char.

Table 12. Metal content of chars A and B.

Chemical parameter	Char A	Char B	Eluate A	Eluate B
pH	-	-	4.94±0.03	4.81±0.05
Conduc. (µS/cm)	-	-	1100±0	820±0
Metals (mg/kg wb)				
Cd	<5.0	<5.0	<0.11	<0.11
Pb	<55.0	<55.0	0.76±0.09	<0.5
Zn	3615±539	6892±337	222±0.2	181±1.2
Cu	<7.5	<7.5	<1.9	<1.9
Hg	<0.3	<0.3	<0.01	0.08±0.01
As	<0.1	<0.1	<0.004	<0.004

wb – wet basis; Conduc. – Conductivity; the mean and standard deviation of duplicates are shown.

The selection of metals to be determined was based on the mineral content of the raw materials performed in section 3.1.3.3 (Table 3). Pb, Zn and Cu were quantified in the three raw materials. Cd, Hg and As were also selected because of their particularly high toxicity and because they have more restrict limit-values in the European Council Decision 2003/33/EC[180].

All the metals were below their detection limits, except for Zn which was quantified in significant concentrations in both chars. Zn was present in the tire rubber feedstock in major concentrations (Table 3), being this raw material its main source. The concentration of Zn in Char B was about 1.91 times higher than the concentration in Char A; this difference is due to the concentration effect associated with the extraction treatment with DCM, as the mass reduction of char A during the DCM extraction was about 54% which corresponds to a mass reduction factor of 1.85.

Although Cu, Hg and As were detected in pine biomass, plastics and tyres, respectively, these metals were not detected in the chars. In the case of Hg, it was lost probably by volatilization during pyrolysis given the fact that most mercury compounds when exposed to reducing conditions are readily decomposed to metallic Hg[182] that volatilizes around 350ºC; Cu and As might have dissolved in the pyrolysis liquid fraction.

As expected from its concentration in the chars, Zn is also the metal present in higher concentrations in the eluates. In what concerns the other metals analysed they were practically absent from the eluates as they were from the chars: a residual amount of Pb (0.76 mg/kg wb) was found in eluate A, a minor amount of Hg was found in eluate B and all the other metals were below their detection limits.

The pH and conductivity of the eluates are also shown in Table 12. Both eluates have similar pH values (4.81 and 4.94) and considerably lower than the pH of the $CaCl_2$ leaching solution (7.42) which means that there was a significant leaching of acidic components from both chars.

The conductivity of the eluates was higher than the conductivity of the leaching solution (214 µS/cm), indicating the substantial leaching of ionic species. The conductivity value obtained for eluate A (1100 µS/cm) is slightly higher than the conductivity value obtained for eluate B (820 µS/cm), what can be explained by the difference in the concentration of metals, particularly Zn, and other salts between eluates.

3.3.3.3 Organic compounds in eluates

Table 13 shows the concentrations of two groups of selected organic compounds in both eluates. The 15 aromatic hydrocarbons and the 11 alkyl phenols were selected taking into account the results presented in section 3.2.3.3.3 concerning the organic qualitative profile of eluates from chars obtained in the co-pyrolysis of plastics and pine biomass. The compounds detected in higher relative concentrations were those included in the present study. Moreover, these compounds are typical components of the liquid fractions obtained from the individual pyrolysis of plastics, biomass and tires or their mixtures[63,70-71,175-176,183], so it is expectable that they should be present in the chars resulting from the pyrolysis process.

The 15 aromatic hydrocarbons were determined in the eluates by using an optimized and validated HS-GC-MS method with the following performance: all analytes presented calibration curves with correlation coefficients above 0.990; the limits of detection (LOD) for each aromatic hydrocarbon ranged between 0.6 and 0.8 µg/L; the method precision varied from 4.8% to 13.2% with an average recovery for all analytes of 101%.

The 11 alkylphenols were determined in the eluates through an optimized and validated DLLME-GC-MS method: all calibration curves presented correlation coefficients above 0.999; The LODs were in the range of 0.07–0.17 µg/L; the precision for all analytes varied between 3.7% and 8.0% and the analytes presented an average recovery of 78%.

None of the 11 alkylphenol compounds were detected in eluate B obtained from Char B that was previously extracted with DCM. Concerning the aromatic volatile fraction, only toluene, ethylbenzene, *m/p*-xylene and butylbenzene/1,4-diethylbenzene were detected in eluate B, although in low concentrations. This means that the DCM extraction step was efficient for removing these organic compounds from the pyrolysis char.

Table 13. Concentrations of organic compounds in eluates A and B.

Analytes	R.T. (min)	Concentrations (µg/L)	
		Eluate A	Eluate B
o-methylphenol	14.30	2118±76	<0.16
m/p-methylphenol	14.95	3818±99	<0.17
2,6-dimethylphenol	16.07	1504±1	<0.13
2,4-dimethylphenol	17.43	4239±84	<0.15
2,5-dimethylphenol	17.51	1715±69	<0.13
2,3-dimethylphenol	18.56	2327±0	<0.14
3,4-dimethylphenol	19.27	2700±50	<0.07
2,4,6-trimethylphenol	19.81	1130±5	<0.16
2,3,6-trimethylphenol	21.04	1720±61	<0.16
2,3,5-trimethylphenol	22.84	1139±45	<0.16
Benzene	8.22	72.3±5.8	<0.8
Toluene	12.86	507.7±22.2	1.0±0.1
Ethylbenzene	16.75	297.0±11.7	1.0±0.1
m/p-xylene	17.08	116.4±7.8	1.1±0.0
o-xylene	18.10	7.4±0.3	<1.0
Cumene	19.11	127.1±8.6	<1.0
Propylbenzene	20.09	5.5±0.3	<1.2
4-ethyltoluene	20.36	10.8±0.6	<1.0
Tert-butylbenzene	21.16	<1.4	<1.4
1,2,4-trimethylbenzene	21.28	4.1±0.2	<1.1
1-methylpropylbenzene	21.61	<1.3	<1.3
Butylbenzene/1,4-diethylbenzene	22.70	1.6±0.2	1.4±0.0
1,2,4,5-tetramethylbenzene	24.05	1.3±0.1	<0.6

The mean and standard deviation of duplicates are shown.

On the other hand, eluate A showed a strong contamination (Figures 17 and 18) with relevance for the alkylphenol compounds quantified with values of 1.1 to 4.2 mg/L. These alkyl substituted phenols result, typically, from the thermochemical interaction between the biomass and aromatic-derived products. Eluate A also showed significant contamination with aromatics, in particular BTEX compounds and cumene. Several other minor peaks were also detected and tentatively identified as phenolic compounds, PAHs and other benzene derivatives.

Although the scope of the leaching standard used does not include volatile organics, since the contact between the chars and the leaching solution was performed in closed vessels, it was considered that representative samples of volatile organic compounds were taken. Moreover, in eluate B it was possible to detect small amounts of the more volatile contaminants, namely the BTEX group, indicating that this procedure is useful for studying the mobilization of the lighter organics.

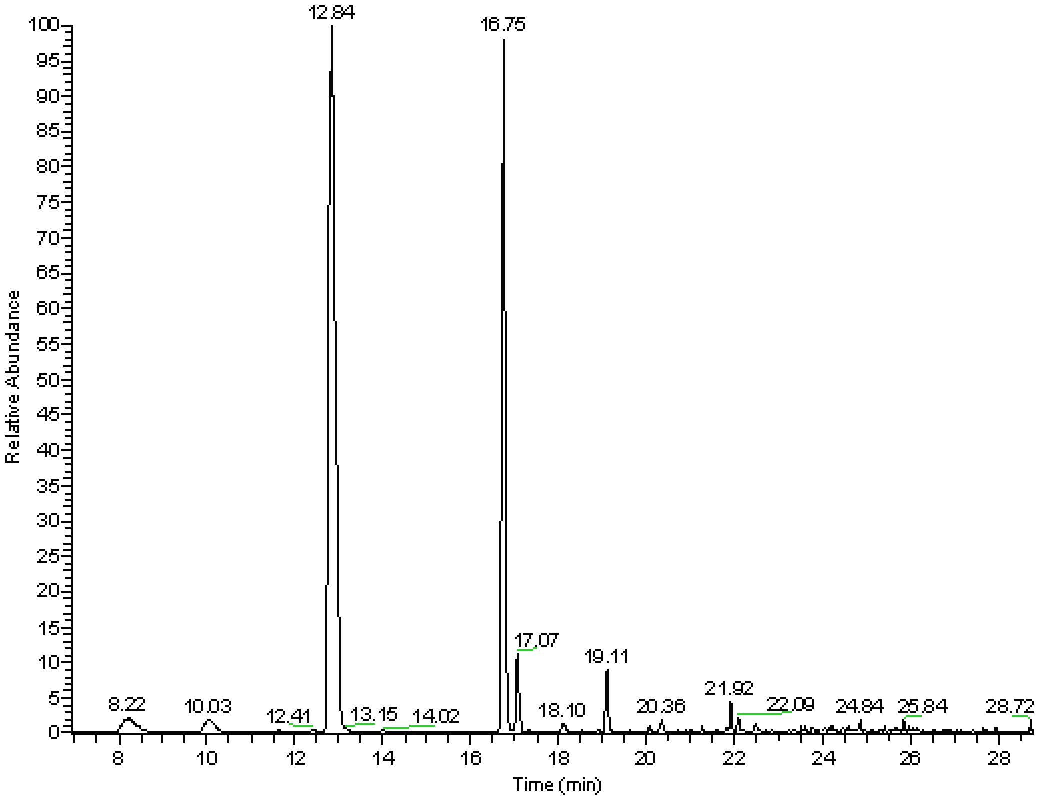

Figure 17. HS-GC-MS chromatogram of eluate A – aromatic volatile organic fraction.

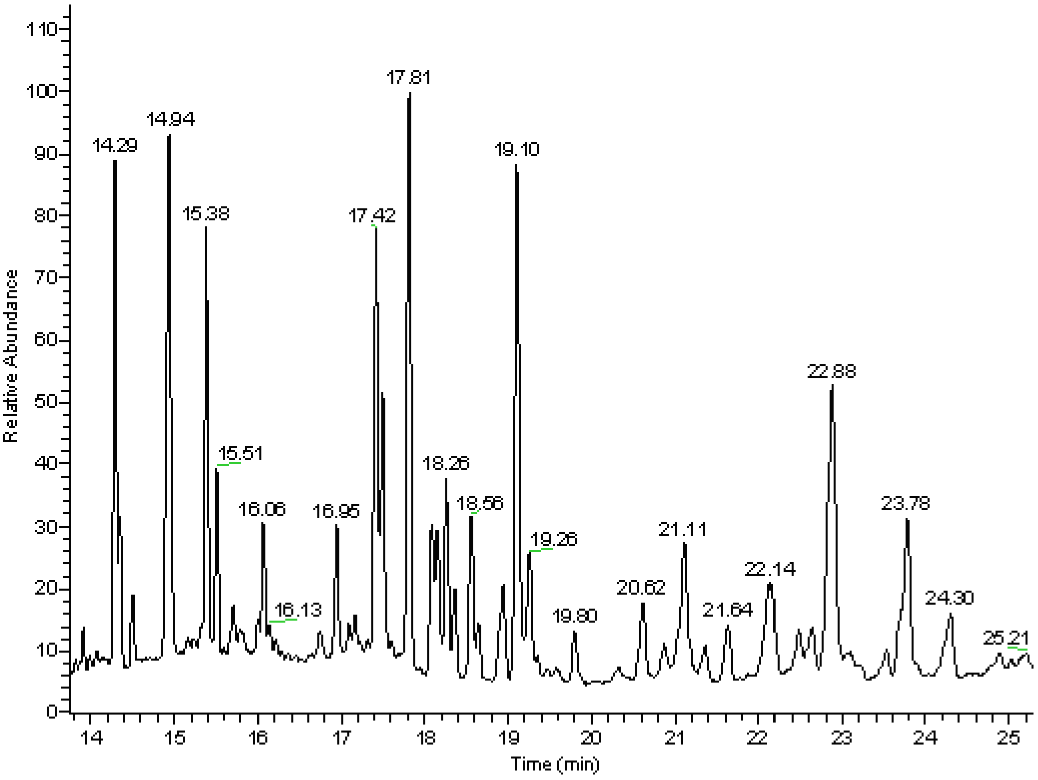

Figure 18. DLLME-GC-MS chromatogram of eluate A – alkylphenol compounds.

3.3.3.4 Ecotoxicological characterisation of eluates

The ecotoxicological data obtained in the eluates are shown in Table 14.

Table 14. Ecotoxicological levels of the eluates of Chars A and B.

Eluate	EC_{50} (%) (v/v)					
	5 min		15 min		30 min	
	Without pH_{corr}	pH_{corr} (pH = 7.4)	Without pH_{corr}	pH_{corr} (pH = 7.4)	Without pH_{corr}	pH_{corr} (pH = 7.4)
A	0.9	0.7	0.9	0.6	0.6	0.6
B	17.4	27.4	7.8	10.9	2.4	3.6

pH_{corr} – pH correction

The luminescence inhibition of *Vibrio fischeri* was evaluated with and without pH adjustment because the pH values of eluates A and B were outside the optimum value for the bacterium (between 6 and 8), which can contribute for ecotoxicity.

Eluate A presented the highest ecotoxicity levels with concentrations of 0.6-0.9% inducing 50% of bioluminescence inhibition. For this eluate, the pH correction did not cause a decrease in the ecotoxicity, probably because the inhibition effect of the high concentration of organic compounds was much higher than the ecotoxicity caused by pH.

Eluate B showed EC_{50} values for *Vibrio fischeri* of 2.4-27.4% for different exposure periods and for different pH values. In this eluate, a significant decrease in the ecotoxicity was observed after the pH correction, in particular for an exposure period of 5 min. It was observed, after the pH correction in this eluate, that a precipitate was formed. A decrease in the solubility of some metals probably occurred and their bioavailability also decreased. However, for the longer exposure period, no significant differences in the ecotoxicity were observed with and without pH correction.

In spite of the lower ecotoxicity presented by eluate B when compared to eluate A, which could be attributed to its lower organic content resulting from the extraction with DCM, eluate B still presented a significant ecotoxicity. This ecotoxicity of eluate B should result from contaminants that are not soluble in DCM and are soluble in the leaching solution and/or due to the metal content of the eluate. Eluate B presented significant concentrations of Zn and it is known that *V. fischeri* is very sensitive to low concentrations of Zn[178,184].

3.3.3.5 Ecotoxicity and hazard assessment of pyrolysis chars

Table 15 presents the classification of wastes according to the limit-values for eluates defined in CEMEW[161] and Council Decision 2003/33/EC[180] for the metals determined in the present work.

The Council Decision 2003/33/EC defines the limit-value for the group of BTEX compounds in eluates of inert wastes as 0.6 mg/L for a leaching ratio of 10 L/kg. Eluate B presented BTEX values of 3.1 μg/L that are far below the limit-value. However, eluate B as well as eluate A presented high Zn concentrations (222 and 181 mg/kg wb, respectively) that are quite above the limit-values for non-hazardous materials; therefore, according to the Council Decision 2003/33/EC, Chars A and B are classified as hazardous materials.

Comparing the metal content of the eluates with the limit-values defined in CEMEW, it can be observed the following:

- Both eluates presented Zn concentrations above the limit-value, being both chars classified as ecotoxic.

The ecotoxicological limit value defined in the CEMEW for *Vibrio fischeri* is EC_{50} (30min) ≤ 10% (v/v). Comparing the results of the ecotoxicological characterisation (Table 14) with this limit-value, it can be concluded that both eluates have shown EC_{50} values below 10%, leading to a classification of ecotoxic.

Globally, chars A and B were classified as hazardous and ecotoxic materials.

Table 15. Classification of wastes according to the limit-values defined in CEMEW[161] and Council Decision 2003/33/EC[180] for the metals determined in the present work.

Parameter (mg/kg)	Inert[a]	Non-hazardous[a]	Hazardous[a]	Ecotoxic[b]
Cd	0.04	1	5	2
Pb	0.5	10	50	5
Zn	4	50	200	20
Cu	2	50	100	5
Hg	0.01	0.2	2	0.5
As	0.5	2	25	0.5

[a] Limit values for the eluates according to Council Decision 2003/33/EC
[b] Limit values for the eluates according to CEMEW

3.3.4 Conclusions

The results obtained in this work indicated that the extraction with DCM is an effective method for the removal of organic contaminants of high to medium volatility from the pyrolysis chars obtained in the co-pyrolysis of tire rubber, pine biomass and plastics. The non-volatile organic fraction and the mineral matter remained in the chars after the DCM extraction. The non-volatile organic fraction (heavy hydrocarbons and derivatives) is hardly soluble in water or aqueous solutions so remained probably immobilized in the char during the leaching procedure. The inorganic fraction, composed by salts of different chemical elements among which it is possible to find metals, can be leached from the char and be responsible for the ecotoxicity of the eluates obtained from the char treated with DCM.

Globally, both chars, treated and not treated with DCM, were classified as hazardous and ecotoxic materials.

Regarding the release of heavy metals, Zn was the only heavy metal that exceeded the limit-values of the criteria used and whose presence was associated with significant ecotoxicity; this result suggests that the introduction of tires in the waste mixture submitted to pyrolysis can induce an increase on the ecotoxicity potential of the resulting char. Decontamination treatments of Zn must be evaluated and combined with solvent extraction to decrease the hazard level and ecotoxicity potential of the pyrolysis char.

The results of this study underline the need for relating ecotoxicological and chemical parameters, including inorganic and organic compounds, in the hazard assessment of a given material and the need of harmonization of the different procedures and classification criteria.

CHAPTER 4

4. DECONTAMINATION STUDY OF CHARS OBTAINED IN THE CO-PYROLYSIS OF PLASTICS, USED TIRES AND PINE BIOMASS

Abstract: The present work is devoted to the study of the organic decontamination of chars obtained in the co-pyrolysis of plastics, biomass and used tire rubber. The chars were extracted with several organic solvents of different polarities either individually and in sequence. The ability of each selected extractant to remove toxic organic compounds was evaluated by comparing the extraction yields and by characterizing the crude extracts with a combination of chemical analysis and toxicity bioassays.. The results obtained in this study indicated that hexane is the more efficient extraction solvent to be used in the organic removal of chars. The ecotoxicity of the raw pyrolysis char was mostly attributed to aromatic compounds like PAHs derivatives or phenyl derivatives and hexane was the organic solvent that had the highest selectivity and affinity towards these organic compounds.

A sequential extraction with solvents of increasing polarity can provide a better removal of the pyrolysis oils/tars that remained in the raw char than any individual extraction.

The compounds removed from the chars during the extraction process were mainly aliphatic and aromatic hydrocarbons that are important feedstocks for refining industries.

The results presented in this section were published, partially or completely, in the following papers:

Bernardo, M., Gonçalves, M., Lapa, N., Barbosa, R., Mendes, B., Pinto, F., Characterisation of chars produced in the co-pyrolysis of different wastes: decontamination study, *Journal of Hazardous Materials*, 207–208 (2012) 28–35. (doi: 10.1016/j.jhazmat.2011.07.115; IF: 4.173)

Bernardo, M., Lapa, N., Gonçalves, M., Barbosa, R., Mendes, B., Pinto, F., Characterisation of chars produced in the co-pyrolysis of different wastes: decontamination study, *Book of Proceedings of The Second International Conference Hazardous and Industrial Waste Management*, Crete, Greece, 5-8 October 2010.

Bernardo M., Lapa N., Gonçalves M., Mendes B. and Pinto F., Characterisation of chars produced in the co-pyrolysis of different wastes: decontamination and leaching studies, *Chemical Engineering Transactions*, 25 (2011) 521-526. (doi: 10.3303/CET1125087)

4.1 Introduction

The main conclusions of chapter 3 were that, globally, the crude chars obtained in the pyrolysis experiments can be classified as hazardous and/or ecotoxic materials, but when submitted to a treatment with an appropriate organic solvent, an efficient reduction of the content in organics was achieved and, therefore, a reduction on their hazardous level/ecotoxicity was observed.

In the present chapter, the use of several halogenated and non-halogenated solvents with different polarities, was examined for the solubilization/desorption of organic compounds from the matrices of chars. The ability of each selected extractant to remove toxic compounds was determined by comparing the extract yields and thoroughly characterizing the different extracts obtained.

A chemical fractionation of the crude solvent extracts 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 developed, mostly devoted to the characterisation of coal/petroleum tars and related material[132,185-188] as well as to biomass tars[189-191]. This type of approach applied to the characterisation of pyrolysis chars has not been reported before, particularly, with a detailed analysis of the individual organic compounds.

There are no specific methods or standards proposed for the analysis of pyrolysis chars. However, the common procedures used in the chemical fractionation of petroleum wastes, for example the 3611B Method recommended by EPA[192], can be adapted taking into account the physical and chemical similarities between petroleum wastes and the pyrolysis liquids/tars deposited in the surface of chars.

In this work, another tool was 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[193-195], air particulates[196] and contaminated sediments/soils[197-199]. To the author knowledge, this is the first time that BDF is applied and used in the characterisation of pyrolysis chars.

The main aim of this procedure was to define the solvents that have removed the organic compounds more efficiently.

4.2 Experimental part

4.2.1 Pyrolysis chars

The char samples were obtained in the co-pyrolysis of a feedstock mixture composed by 30% (w/w) pine biomass, 30% (w/w) used tyres and 40% (w/w) plastics (56% (w/w) PE, 27% (w/w) PP and 17% (w/w) PS). This mixture was the same as in chapter 3.3, and also the pyrolysis conditions were the same: stirred batch autoclave of 1 L (Figure 9), with an initial nitrogen pressure of 0.41 MPa, during 15 min at a temperature of 420 ºC and heating rates of around 5 ºC/min. The reaction products were: 10% (w/w) gases, 60% (w/w) liquids and 25% (w/w) solid chars. About 5% (w/w) losses of the final pyrolysis products were determined. The product yields were obtained as the ratio between the mass of product obtained and the initial mass of the feedstock mixture.

The chars obtained in the pyrolysis experiments were a carbonized pasty residue covered with the pyrolysis oils and tars with a strong odour (section 3.3.2.1, Figure 15).

4.2.2 Chars extraction: solvents selection

The pyrolysis chars were submitted to a Soxhlet extraction according to an adaptation of the EPA 3540C Method[200]. Several organic solvents with different polarities were used: hexane, dichloromethane (DCM), 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 -> ethanol was performed with the aim of achieving a higher extraction yield. Extraction was performed during 16 hours at a rate of 4 cycles/hour.

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.

4.2.3 Thermal analysis of chars

The raw and extracted chars were submitted to a thermal analysis that consisted in measuring the progressive weight loss associated with the combustion of samples in a CEM microwave furnace MAS 7000, under an air atmosphere, from room temperature up to 600 ºC with increments of 50 ºC. The samples remained 10 min in 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. The mass of char used in the experiments was 0.5 g. This thermal analysis allow to define the composition of the chars in terms of the volatility of their components: volatile organic compounds were those volatilized up to 250 ºC[163-164]; the weight loss registered between 250 ºC and 350 ºC was attributed to semi-volatile compounds[164]; the weight decrease observed from 350 ºC to 600 ºC was assigned to the volatilization and combustion of heavy compounds denominated as fixed residue[165]; the residue non-combusted above 600 ºC that presented a stable weight was considered as ashes[165].

4.2.4 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). The Microtox® toxicity test for organic extracts was followed in this work according the manufacturer's protocol[201]. The extract solutions were first solvent-exchanged to the organic solvent dimethylsulfoxide (DMSO) and properly diluted in the osmotically adjusted 2% NaCl solution (Microtox® diluent solution) in order to achieve ≤1% DMSO for all concentrations. This is the maximum DMSO concentration that can be applied to Microtox® without causing any toxic effect[201]. 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 50% decrease in bioluminescence) of the DMSO crude extracts were expressed as mass per litre of diluent.

4.2.5 Fractionation of the most ecotoxic extract - bioassay testing and chemical analysis

The crude extract that presented the highest toxicity was fractionated into aliphatic, aromatic and polar fractions according to the EPA 3611B Method[192]. 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 (GC) equipped with an auto-sampler, a split-splitless injector, a TR-5MS (Thermo Scientific) capillary column (30m×0.25mm×0.25μm) and a Thermo Scientific Polaris Q mass spectrometer detector (MS).

The carrier gas was helium at 1 mL/min; 1 μL of the samples were injected at 270 ºC 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 ºC and 250 ºC, respectively; the oven temperature program was as follows: initial temperature of 35 ºC (hold 1 min), up to 290 ºC at a temperature rate of 3 ºC/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 C_{10} to C_{30}) 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 subjected to a derivatisation procedure prior to its analysis on the Thermo Scientific GC-MS equipment. A given volume of the polar fraction was evaporated to dryness under a gentle flow of nitrogen. The dried fraction was then heated with 40 μL of *N*-methyl-*N*-trimethylsilyltrifluoroacetamide (MSTFA) at 50ºC during 30 min to promote silylation. After the derivatisation reaction, the sample was redissolved in heptane and 1 μL was injected in the GC-MS. A TR-V1 capillary column of Thermo Scientific (60m×0.25mm×1.4μm) was used and the carrier gas was helium at 1 mL/min. The sample was injected at 270 ºC in the splitless mode with a splitless time of 3 min and a split flow of 30 mL/min. The interface and ion source were kept at 220 ºC. The oven temperature program was as follows: 40 ºC (hold 1 min) up to 290 ºC (5 ºC/min, hold 5 min). The MS system was operated in the full scan mode with a mass range from m/z 50 to 200. The main components were tentatively identified by comparison of their mass spectra with references from the Wiley and NIST spectra libraries.

4.3 Results and discussion

4.3.1 Extract yield for different extraction solvents

4.3.1.1 Single extraction

The effects of organic solvents on the extraction yield were studied and the results are presented in Table 16. The extraction yields were determined as the ratio between the total mass of extract obtained and the mass of char sample.

Table 16. Extract yields of the pyrolysis char obtained with the different extraction solvents.

Extraction solvent	Extract yield (% g/g sample)
Hexane	58.1±3.9
DCM	54.9±2.0
Hexane:Acetone (1:1 v/v)	40.6±0.5
Ethanol	32.6±0.4

The mean and standard deviation of duplicates are shown.

The most effective extractants for single extractions were hexane and DCM with extract yields of 58.1% and 54.9%, respectively, which shows that most of the char organic components are non-polar or with low polarity. The extract yields decreased with the increase of solvent polarity, being ethanol the solvent with the worst recovery efficiency (32.6%). Also, the colour of this extract was much lighter than the other extracts (Figure 19). Solvent polarity plays an important role in decreasing the solubility of organic compounds from the pyrolysis char. Nevertheless, even with the increasing polarity of the solvents, the extracts yields were considerable high, reflecting the complexity and diversity of char composition with a wide range of organic compounds with different polarities and solubilities.

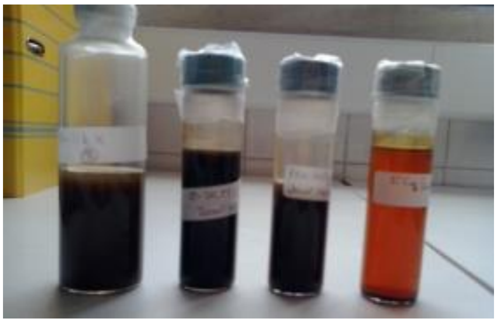

Figure 19. Extracts obtained with the different extraction solvents used individually. From the left to the right: hexane, DCM, hexane:acetone and ethanol extracts.

4.3.1.2 Sequential extraction

In order to achieve a more efficient removal of the different organics that might be present in the char, 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 17. The extraction yields were calculated as in section 4.3.1.1.

Table 17. Sequential extraction experiment and extract yields of the pyrolysis char obtained in each extraction step.

Extraction step	Extraction solvent	Extract yield (% 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
Total		65.9±4.4

The mean and standard deviation of duplicates are shown.

In the first step of extraction, hexane was chosen to extract mainly the non-polar compounds, since it was the less polar organic solvent that, individually, led to the highest extract yield (Table 16). In the second extraction step, the mixture of hexane with acetone still attained a significant removal of organic compounds 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 organics, with an extract yield not very significant (1.9%). Figure 20 presents the three extracts obtained in the sequential solvent extraction procedure.

Figure 20. Extracts obtained in the sequential solvent extraction. From the left to the right: hexane, hexane:acetone and ethanol extracts.

The global extract yield of the sequential extraction was around 65.9%, a higher value than that obtained for 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 compounds. The initial extraction with hexane removed a substantial fraction of the non-polar components leaving the more polar organic compounds available for extraction with solvents of medium to high polarity as acetone or ethanol.

4.3.2 Thermal analysis of chars

The relative mass composition of the raw and extracted chars based on the volatility of their components (volatile, semi-volatile, fixed residue and ashes) is presented in Figure 21.

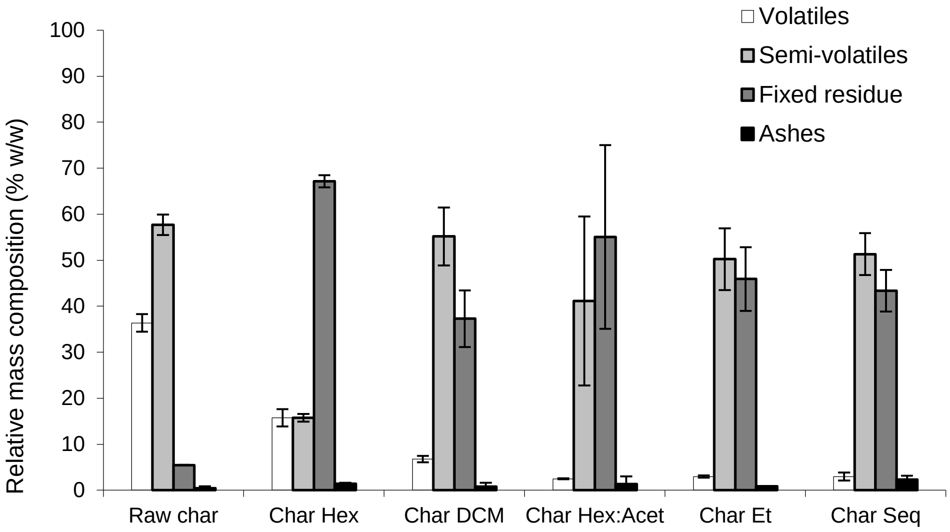

Figure 21. Relative mass composition (% w/w relatively to the initial weight) of the raw and extracted chars. (Char Hex – char extracted with hexane; Char DCM – char extracted with dichloromethane; Char Hex:Acet – char extracted with 1:1 (v/v) of hexane and acetone; Char Et – char extracted with ethanol; Char Seq – char sequentially extracted). The bars represent the standard deviations of duplicates.

The extractions with the different organic solvents removed mainly the light compounds from the raw char and, consequently, the heavier components, in particular the fixed residue, correspond 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 highest content in fixed residue, due to a concentration effect resulting from the removal of semi-volatile compounds.

The relative mass composition profiles of the chars extracted individually with DCM and ethanol, and sequentially with hexane, hexane-acetone and ethanol were very similar indicating that these solvents remove compounds with the same volatility characteristics.

The char treated with the mixture of hexane-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 the extraction of more volatiles.

4.3.3 Ecotoxicity of crude solvent extracts

4.3.3.1 Single extraction

The ecotoxicity levels of the crude solvent extracts obtained in the single solvent extractions are presented in Figure 22.

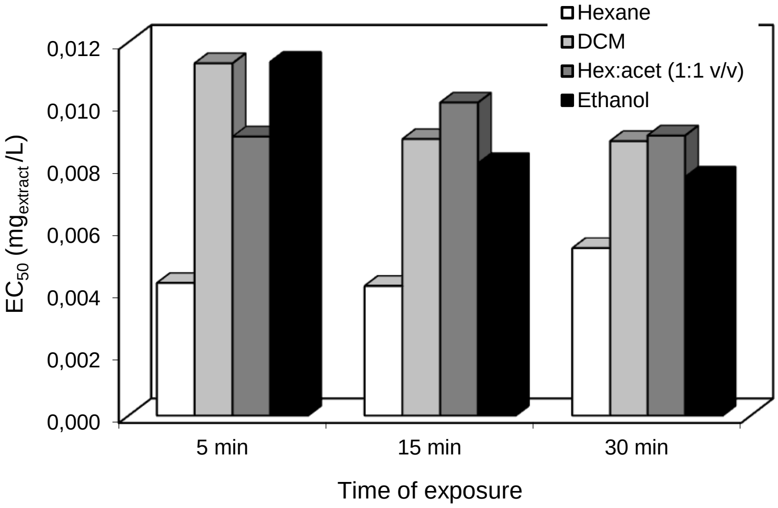

Figure 22. Ecotoxicity data of crude solvent extract solutions. (Hexane – hexane crude extract; DCM – dichloromethane crude extract; Hex:Acet (1:1 v/v) – crude extract obtained with 1:1 (v/v) of hexane and acetone; Ethanol – ethanol crude extract.

From Figure 22 it is clear that all the crude solvent extracts presented severe ecotoxic levels to *Vibrio fischeri* with EC_{50} values varying from 0.004 to 0.011 mg extract/L, being the hexane crude extract the most ecotoxic. Hexane was the solvent that allowed to achieve the highest extraction yield in the pyrolysis char (58.1%) and the highest amount of extract obtained can explain the highest ecotoxicity. Also, the classes of compounds that were extracted with this solvent as well as some synergistic effects between them can be responsible for higher ecotoxicity levels.

Although the extraction yield with dichloromethane was also high (54.9%), the ecotoxicity of the extract obtained was lower by comparison with hexane extract. The ecotoxicity of the dichloromethane extract is very similar to the ecotoxicity of the crude extracts obtained in the extractions with the more polar solvents, in spite of the lowest extractions yields obtained with these solvents. Hexane extracted mostly non-polar compounds and they may be the major cause of toxicity to *V. fischeri*. DCM, the mixture of hexane and acetone, and ethanol probably extracted the same classes of compounds, as it was already seen in the thermal analysis of the chars, and those compounds with higher polarity have low inhibitory effects on the bacterium.

4.3.3.2 Sequential extraction

The ecotoxicity levels of each crude extract obtained in each of the extraction steps in the sequential extraction are presented in Figure 23.

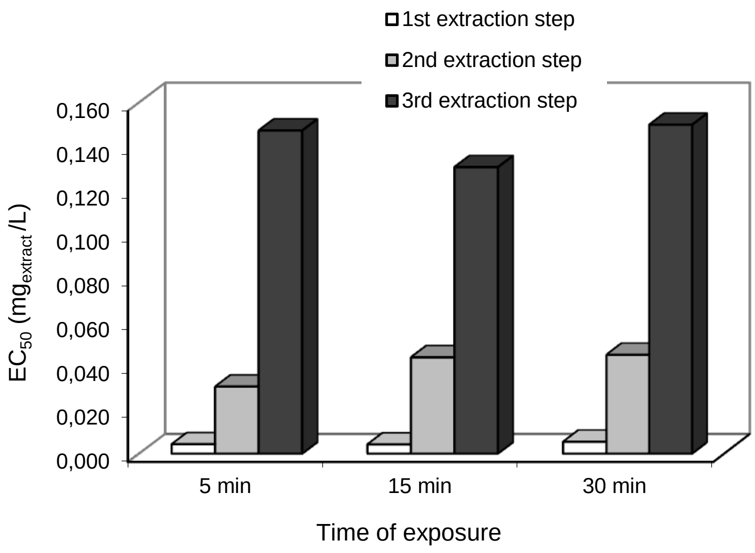

Figure 23. Ecotoxicity data of crude extracts in the sequential extraction.

As expected, the ecotoxicity decreased in each extraction step accordingly to the sequential lower extraction yields obtained. The 1^{st} extraction step with hexane allowed to remove the most ecotoxic compounds. The subsequently extraction steps with the more polar solvents allowed to eliminate the residual polar compounds that remained in the pyrolysis char that, according to the results, are less toxic to *V. fischeri*.

4.3.4 Characterisation of the hexane crude extract

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

4.3.4.1 Ecotoxicity of the aliphatic, aromatic and polar fractions from the hexane extract

The results concerning the ecotoxicity data of the aliphatic, aromatic and polar fractions of the hexane crude extract are presented in Figure 24.

It can be observed that the most ecotoxic fraction was 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 ecotoxicity of the crude extract.

In general, the ecotoxicity of the fractions decreased with time, in particular from 5 to 15 minutes and then stabilised. This was more evident to the aliphatic and polar fractions.

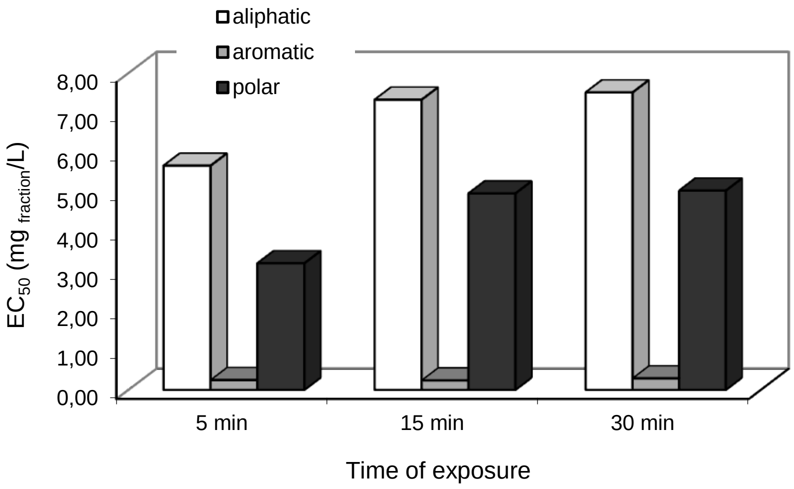

Figure 24. Ecotoxicity data for the aliphatic, aromatic and polar fractions of the hexane crude extract, for different times of exposure.

4.3.4.2 Composition of the aliphatic, aromatic and polar fractions from the hexane extract

The aliphatic fraction showed a qualitative profile of *n*-alkanes from decane (C_{10}) to triacontane (C_{30}) (Figure 25). 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 to 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 (Figure 26) showed several peaks that correspond 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 DCM allowed to elute the remain aliphatic hydrocarbons.

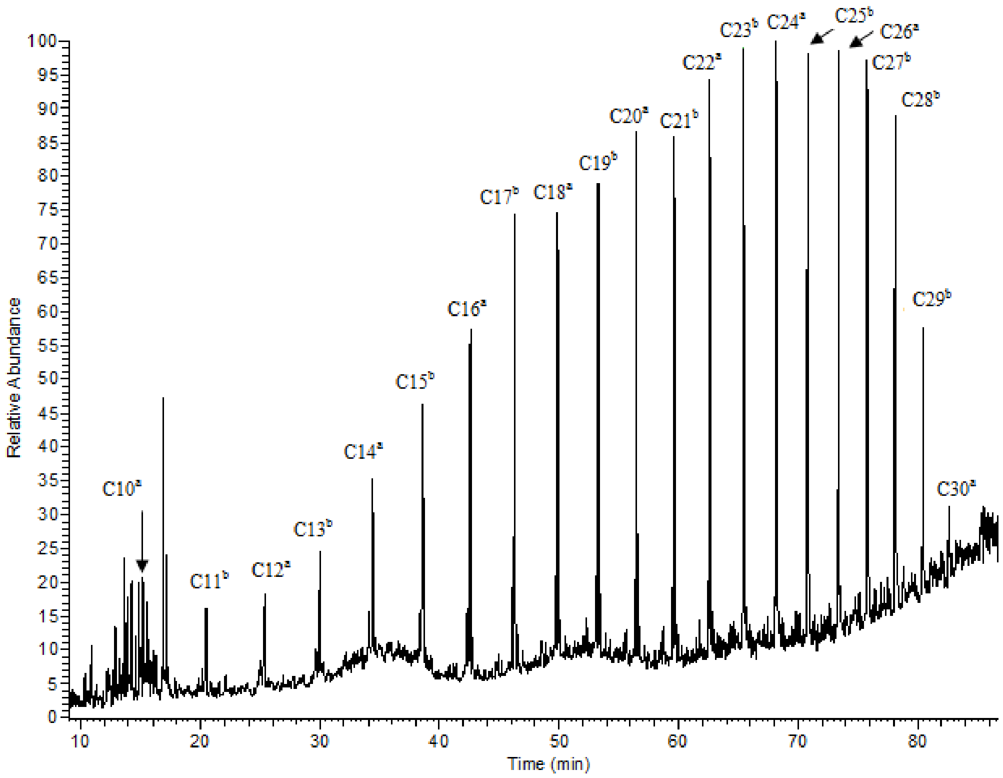

Figure 25. GC-MS chromatogram of the aliphatic fraction of the hexane crude extract. ^{a}Compound identified by co-injection of standards; ^{b}Compound tentatively identified by comparison with the spectra of NIST and Wiley libraries.

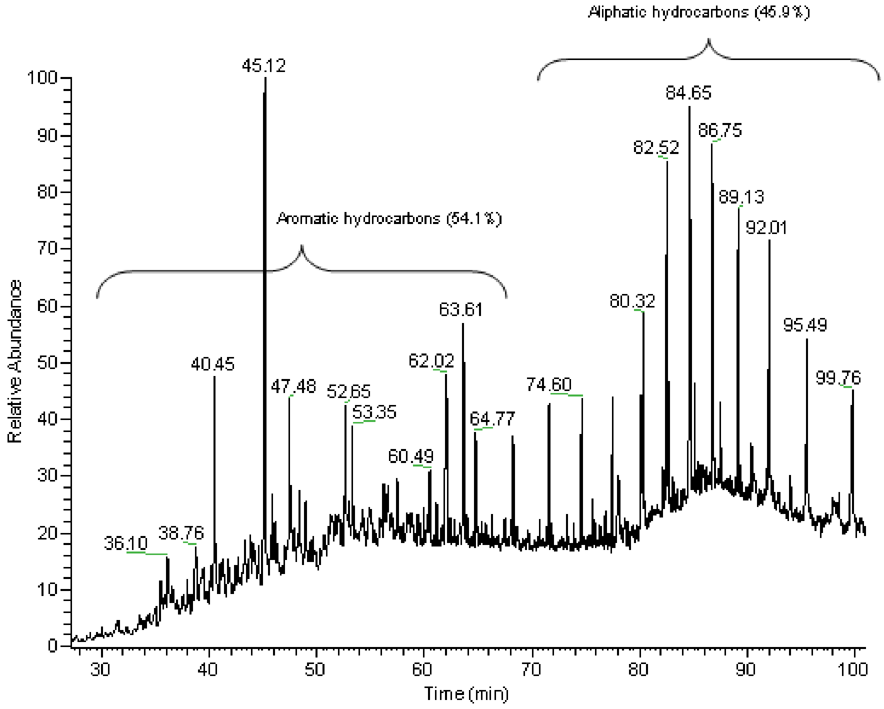

Figure 26. GC-MS chromatogram of the aromatic fraction of the hexane crude extract.

Table 18 shows the aromatic compounds identified in concentrations high enough to enable the acquisition of elucidative mass spectra. Several other minor peaks that correspond to substitute benzenes can be observed in the chromatogram. The aromatic compounds identified in this fraction were mainly PAHs derivatives as well as phenyl derivatives. Among the PAHs, naphthalene derivatives were the most representative compounds.

Table 18. List of aromatic compounds tentatively identified in the aromatic fraction of the hexane crude extract.

R. T. (min)	Compound	Relative peak area (%)
36.10	Dimethylnaphthalene	0.74±0.24
38.76	Diphenylmethane	1.04±0.15
40.16	Trimethylnaphthalene isomer	0.54±0.06
40.45	Trimethylnaphthalene isomer	2.74±0.0
41.02	Trimethylnaphthalene isomer	0.32±0.01
41.24	Trimethylnaphthalene isomer	0.53±0.01
43.79	Isopropylmethylnaphthalene	0.38±0.01
45.12	Diphenylpropane	5.19±0.25
45.84	Isopropyldimethylnaphthalene	1.09±0.08
47.48	Tetramethylnaphthalene	2.01±0.14
47.87	Dimethylbiphenyl	0.27±0.05
48.31	Isopropylbiphenyl	1.17±0.07
52.65	Phenyldodecane	1.68±0.20
53.35	Diphenylhexane	1.00±0.13
56.6	Phenylnaphthalene	0.54±0.12
60.49	Propenylanthracene	1.00±0.06
62.02	Terphenyl	2.45±0.21
63.61	Tetramethylphenanthrene	2.22±0.08

R. T. – Retention Time; The mean and standard deviation of duplicates are shown.

The GC-MS profile of the derivatized polar fraction is presented in Figure 27. Some alcohols were identified like propanediol (Retention Time, R.T. = 38.83 min) and esters of carboxylic acids such as propanoate (R.T. = 39.96 min). Above R.T. of 40 min, the dominant compounds were oxygen-containing aromatics such as phenyl methoxy compounds. Also, thiobenzoate compounds were identified (R. T. = 53.02 min). Oxygen-containing PAHs such as anthracene were also found for the longer retention times.

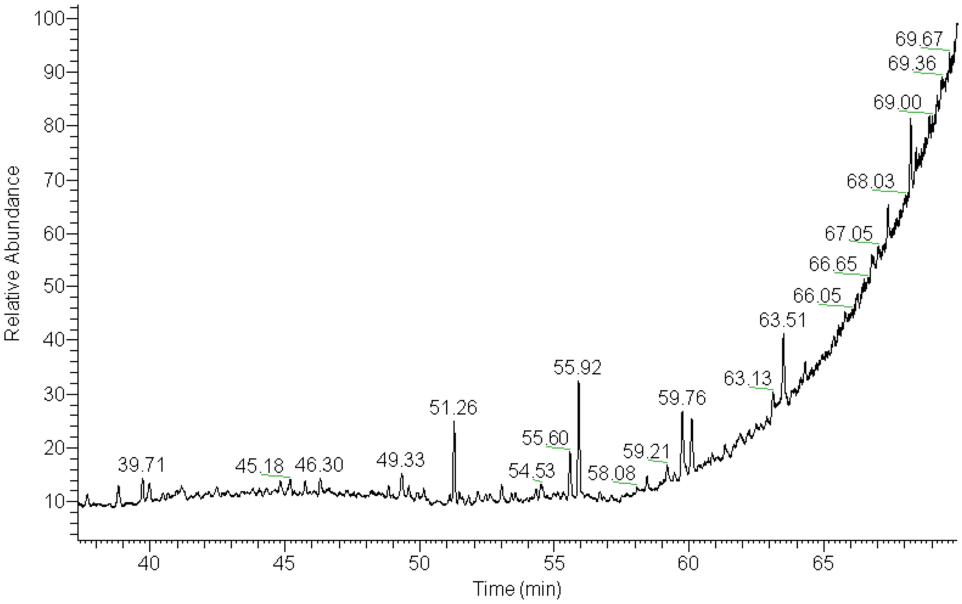

Figure 27. GC-MS chromatogram of the polar fraction of the hexane crude extract.

4.3.5 Comparison of chemical and ecotoxicity 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 ecotoxic 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 contributed to the observed ecotoxicity in the hexane crude extract.

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

Although the polar fraction also presented several aromatic compounds, mainly oxygen-containing hydrocarbons, the GC-MS chromatogram showed that they were present in low relative concentrations, and the ecotoxic behaviour of this fraction was not so marked.

The “petroleum like” profile of the aromatic fraction can explain the high ecotoxicity exhibited. It was previously demonstrated that organic extracts with a “petroleum like” hydrocarbon profile present more toxicity to *V. fischeri* than organic extracts where an aliphatic hydrocarbon profile prevails[198].

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[202]. So it could be argued that the highest ecotoxicity level of the aromatic fraction can be attributed to the presence of these compounds. Hartnik et al.[193] showed that

PAHs derivatives, in particular the alkylated naphthalene compounds that were also detected in high concentrations 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 that other 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 ecotoxicity in the case of compounds with relatively high concentration and some tentative explanations have to include antagonistic/synergistic behaviours.

4.4 Conclusions

The results obtained in this study indicated that the more efficient extraction solvent to be used in the removal of organic compounds from chars obtained in the co-pyrolysis of plastics, tire rubber and pine biomass waste is hexane. Higher extraction efficiency concerning extraction yield and removal of ecotoxic organic compounds was achieved with this solvent.

A sequential extraction with solvents of increasing polarity can provide a better removal of the pyrolysis oils/tars that remained in the raw char than any individual extraction.

The compounds removed from the char during the extraction process are mainly aliphatic and aromatic hydrocarbons that are important feedstocks for the refining industries. The char extracts that are mainly composed by pyrolysis tars, can be further separated in different fractions and be used for energetic applications or in the industry of speciality chemicals[148].

The bioassay-directed fractionation applied in this work led to the conclusion that the ecotoxicity of the raw pyrolysis char might be mostly attributed to aromatic compounds like PAHs derivatives or phenyl derivatives, and probably hexane was the organic solvent that had the highest selectivity and affinity towards these organic compounds.

CHAPTER 5

5. LEACHING BEHAVIOUR AND ECOTOXICITY EVALUATION OF THE DECONTAMINATED PYROLYSIS CHARS

Abstract: Three chars obtained from the pyrolysis of three waste blends composed by plastics, used tire rubber and pine biomass were studied in this chapter, after being submitted to an appropriate decontamination treatment that allowed the maximum removal/recover of the pyrolysis tars that remained in the chars. The leaching behaviour and potential environmental impact associated with the use or valorisation of the chars was assessed in this chapter by combining chemical analyses with ecotoxicological tests. Possible relations within chemical and ecotoxicological data were made to identify contaminants responsible for the ecotoxicity levels. A washing step with Ethylenediamine tetraacetic acid (EDTA) was applied to the chars to selectively remove metals that can be responsible for the ecotoxicity. The results indicated that the introduction of biomass on the pyrolysis feedstock enhanced the acidic character of chars promoting the mobilization of inorganics. Chars resulting from the blends of pine and plastics did not produce ecotoxic eluates. A relationship between zinc concentrations in eluates and their ecotoxicity behavior was found for chars obtained from mixtures with tires. A significant ecotoxicity reduction when the chars were treated with EDTA was registered, because a significant reduction in zinc leaching was also observed.

The results presented in this section were published, partially or completely, in the following papers:

Bernardo, M., Lapa, N., Gonçalves, M., Mendes, B., Pinto, F., Fonseca, I., Lopes, H., Physico-chemical properties of chars obtained in the co-pyrolysis of waste mixtures, *Journal of Hazardous Materials*, 219–220 (2012) 196 – 202. (doi: 10.1016/j.jhazmat.2012.03.077; IF: 4.173)

Bernardo, M., Mendes, S., Lapa, N., Gonçalves, M., Mendes, B., Pinto, F., Lopes, H., Leaching behaviour and ecotoxicity evaluation of chars from the pyrolysis of forestry biomass and polymeric materials, submitted to *Ecotoxicology and Environmental Safety*, 2013.

Bernardo, M., Lapa, N., Gonçalves, M., Mendes, B., Pinto, F., Physico-chemical properties and adsorption characteristics of chars produced in the co-pyrolysis of biomass, plastic and Tire wastes, *Proceedings of the 1st International Conference: WASTES: Solutions, Treatments and Opportunities*, Guimarães, Portugal, 12-14 September 2011.

Bernardo, M., Lapa, N., Gonçalves, M., Mendes, B., Pinto, F., Study of the organic extraction and acidic leaching of chars obtained in the pyrolysis of plastics, tire rubber and forestry biomass wastes*, Procedia Engineering*, 42 (2012) 1909–1916. (doi: 10.1016/j.proeng.2012.07.567)

Bernardo, M., Lapa, N., Gonçalves, M., Mendes, B., Pinto, F., Fonseca, I., Lopes, H., Characterisation and potential applications of chars from the pyrolysis of polymeric residues, *Proceedings of The 4th International Conference on Engineering for Waste and Biomass Valorisation*, Porto, Portugal, 10-13 September 2012.

5.1 Introduction

Three chars obtained from the pyrolysis of three waste blends composed by plastics, used tire rubber and pine biomass were studied in this chapter, after being submitted to an appropriate decontamination treatment that allowed the maximum removal/recover of the pyrolysis tars. This treatment was selected based on the results obtained in chapter 4.

One of the studied chars was the sample obtained in section 3.3: char from the co-pyrolysis of 30% (w/w) pine biomass + 30% (w/w) used tire rubber + 40% (w/w) plastics. Two new waste mixtures were introduced in this work in order to obtain different chars: 50% (w/w) pine + 50% (w/w) plastics and 50% (w/w) used tire rubber + 50% (w/w) plastics.

Plastics were the common raw material in the three feedstocks. The main objective was to improve the quantity and quality of the liquid fraction through the H-donor effect of plastics[70-71].

Foreseeing the application of the treated chars to environmental matrices, particularly aqueous media, the leaching behaviour and potential environmental impact associated with the use or valorisation of these materials were assessed in this chapter by using the integrated strategy of combining chemical analyses with ecotoxicological tests as described in the previous chapters. Metallic contaminants and their contribution to the ecotoxicity levels of the chars are in focus in this chapter. A washing step with EDTA was applied in this work to selectively remove metals that can be responsible for the ecotoxicity levels of the chars.

5.2 Experimental part

5.2.1 Pyrolysis experiments

Pyrolysis experiments were carried out in the stirred batch autoclave of 1 L presented in Figure 9 (section 3.2.2.1) and also in a stirred batch autoclave of 5 L (Parr Instruments) built in Hastelloy C276 (Figure 28). These facilities belong to and the experiments were performed by UTCAE-LNEG[175-183]. The experiments were developed in similar ways as described in the previous chapters of this thesis. The autoclaves were purged and pressurised to 0.41 MPa with nitrogen. Heating rates around 5ºC/min were used until the desired reaction temperature of 420ºC was reached. This temperature was maintained for 15 min. At the end of this period, the reactor vessels were cooled down to room temperature. Given the low heating rate and cooling period, the total residence time of the materials inside the reactor vessel was about 90 min.

Figure 28. Stirred batch autoclave of 5 L from Parr Instruments of UTCAE-LNEG[183].

5.2.2 Char samples

The char samples were obtained from the pyrolysis of 3 different mixtures:

- 30% (w/w) pine biomass + 30% (w/w) used tire rubber + 40% (w/w) plastics;
- 50% (w/w) pine + 50% (w/w) plastics;
- 50% (w/w) used tire rubbers + 50% (w/w) plastics

The plastics used in the three feedstocks were a mixture of 56% (w/w) PE, 27% (w/w) PP and 17% (w/w) PS.

Given the batch operation of the pyrolysis process, the resulting solids were a carbonized pasty residue covered with oils and tars. As concluded in chapter 4, the high concentrations of pyrolytic liquids in the chars are of concern given their rich composition in aromatic, oxygenated and aliphatic hydrocarbons, some of them of high environmental mobility and toxicity. Moreover, the physical characteristics of the chars (viscosity and intensive odour) make them difficult to handle. Thus, it is crucial to remove and recover these liquids, due to the environmental risks they pose and also because these oils are potential sources of valuable chemical compounds for chemical industry.

The pyrolytic solids were submitted to a sequential solvent extraction with solvents of increasing polarity, namely, hexane, a mixture of 1:1 (v:v) hexane:acetone and acetone, according to an adaptation of the EPA 3540C Soxhlet method[200]. The strategy of using a sequential extraction procedure with solvents of increasing polarity was demonstrated in chapter 4 as being the best for the removal of several organic compounds from different classes. Acetone was chosen for the last extraction step instead of ethanol due to its higher polarity.

The solvents were eliminated from the crude extract solutions using a vacuum rotary evaporator, and the resulting solids were dried at a temperature of 80 ºC, during 24 h, in a vacuum oven.

5.2.3 Thermal and elemental analysis

The chars were submitted to the thermal analysis already used in the previous works, that consisted in measuring the progressive weight loss associated with the combustion of samples in a muffle furnace (Heraeus, KR170E), under an air atmosphere, from room temperature up to 750 ºC with increments of 50 ºC, remaining 10 min at each temperature stage. The mass of char used in the experiments was 0.5 g. This thermal analysis allowed to define the composition of the chars in terms of the volatility of their components: volatile organic compounds were those volatilized up to 250 ºC[163-164]; the weight loss registered between 250 ºC and 350 ºC was attributed to semi-volatile compounds[164]; the weight decrease observed from 350 ºC to 600 ºC was assigned to the volatilization and combustion of heavy compounds denominated as fixed residue[165]; the residue non-combusted above 600 ºC that presented a stable weight was considered as ashes[165].

The chars were also submitted to an elemental analysis at UTCAE-LNEG which was performed in a LECO elemental analyser. Carbon, hydrogen and nitrogen were determined according to the ASTM D5373 standard[203] and sulphur determination followed the ASTM D4239 standard[204].

5.2.4 Determination of the metal content of chars

The char samples were placed in porcelain crucibles and digested with hydrogen peroxide 30% (v/v) in a heated bath at a temperature of 95 ºC and then digested with *aqua regia* ($HCl:HNO_3$, 3:1, v/v) at the same temperature. Finally, a microwave acid digestion adapted from the EPA 3015 method[177] was used to complete the solubilisation of the inorganic components of the samples. The previously digested samples were dissolved in ultra-pure water (Milli-Q Academic, Millipore) up to a volume of 45 mL. These aqueous samples were digested with 5 mL of *aqua regia* in a Milestone ETHOS 1600 microwave heating system. The temperature of each sample achieved 170±5 ºC in 10 min, and remained at this temperature for 10 min. The digested samples were filtrated using Whatman filter paper grade 595 and a broad group of metals were quantified in the digested samples using a Thermo Elemental Solaar atomic absorption spectrometry (AAS) equipment: Cadmium (Cd), Lead (Pb), Zinc (Zn), Copper (Cu), Nickel (Ni), Potassium (K), Manganese (Mn), Iron (Fe), Sodium (Na) and Magnesium (Mg) were analysed using the air-acetylene flame technique; Calcium (Ca), Aluminium (Al), Chromium (Cr), Molybdenum (Mo) and Barium (Ba) were analysed using the acetylene-nitrous oxide flame technique; Mercury (Hg), Arsenic (As), Selenium (Se) and Antimony (Sb) were determined using the hydride generation technique.

5.2.5 Leaching tests

The chars were leached according to the leaching standard ISO/TS 21268-2[142] and the experimental conditions were the same as described in sections 3.2 and 3.3: the chars were mixed with the leaching solution ($CaCl_2$ 0.001 M) in a single stage batch test performed at a L/S ratio of 10 L/kg, at a constant temperature of 20±2 ºC. The containers (borosilicate glass bottles) were shaken in a roller-rotating device (Heidolph) at 10 rpm, for a period of 24 ± 0.5 h. At the end of the leaching test, the mixtures were allowed to settle for 15 min and the eluates were filtrated over fibre glass filters GF/C Whatman to minimize the sorption of organics. Blank tests with $CaCl_2$ 0.001 mol/L and without chars were made for each sample. The eluates were immediately analysed for pH (Crison, micropH 2001) and electrical conductivity (Mettler Toledo, MC226) and for Total Organic Carbon (TOC) and Inorganic Carbon (IC) using a Shimadzu 5000 TOC analyser operating with the combustion-infrared method. The eluates were subsequently divided into sub-samples to be used in the different chemical and ecotoxicological analyses. The eluates used in chemical analyses were preserved with HNO_3 to a pH<2 and refrigerated at 4ºC. For the ecotoxicological tests, the eluates were preserved at a temperature of 4 ºC in air tight vessels.

5.2.6 Chemical characterisation of eluates

The acidified eluates were analysed for the same group of metals determined in the char samples: Cd, Pb, Zn, Cu, Ni, K, Mn, Fe, Na and Mg were analysed using the air-acetylene flame technique; Ca, Al, Cr, Mo and Ba were analysed using the acetylene-nitrous oxide flame technique; Hg, As, Se and Sb were determined using the hydride generation technique. The equipment was also the Thermo Elemental Solaar AAS.

5.2.7 Ecotoxicological characterisation of eluates

The ecotoxicological parameter analysed in the eluates resulting from the ISO/TS 21268-2 leaching test was the inhibitory effect on the light emission of the marine bacterium *Vibrio fischeri* (Azur Environmental Microtox® system) according to the ISO standard 11348-3[178]. The luminescence inhibition of *V. fischeri* was evaluated for an exposure period of 5, 15, and 30 min. A blank test was performed with the leaching solution ($CaCl_2$ 0.001 mol/L). The results of the ecotoxicity test were expressed as EC_{50} (% v/v) values which represents the effective concentration of the eluate analysed that causes a reduction of 50% on the *V. fischeri* bioluminescence.

5.2.8 EDTA washing of chars

In order to remove and identify the metals responsible for the ecotoxicity of chars, a selective chelant extraction of heavy metals was performed on the chars. The chars were treated with 0.05 M disodium EDTA, at 60 ºC, during 2 hours, with continuous stirring. The EDTA to char ratio was of 100 mL/g. At the end of the washing process, the mixtures were allowed to settle and then filtrated using a Whatman filter paper grade 595 to separate the char from the eluate. The char was further washed several times with ultra-pure water to remove the residual chelant until the pH of the washing water was neutral. The amount of metals leached with the EDTA washing solution was monitored by using the Thermo Elemental Solaar AAS equipment. The metals analysed were the following: Cd, Pb, Zn, Cu, Ni, K, Mn, Fe, Na and Mg were analysed using the air-acetylene flame technique; Ca, Al, Cr, Mo and Ba were analysed using the acetylene-nitrous oxide flame technique; Hg, As, Se and Sb were determined using the hydride generation technique.

Finally, the washed chars were dried in a vacuum oven at 80 ºC for 24 h. The EDTA washed chars were then submitted to the ISO/TS 21268-2 leaching test, and the eluates were analysed for pH, Zn content and ecotoxicity according to the methodologies described in the previous sub-sections.

5.2.9 Methodology used to assess the hazardous level and ecotoxic potential of pyrolysis chars

The assessment of the ecotoxicity of pyrolysis chars followed the same conceptual methodology described in section 3.2.2.7 (Figure 11), according to an adaptation of the Criteria and Evaluation Methods of the Ecotoxicity of Waste (CEMEW)[161].

The classification of the chars as inert, non-hazardous and hazardous materials followed the Council Decision 2003/33/EC[180] as described in section 3.3.2.7.

5.3 Results and discussion

5.3.1 Char samples – sequential solvent extraction yields

Table 19 presents the product yields (ratio between the mass of product obtained and the initial mass of the feedstock mixture) obtained in each of the pyrolysis experiments. The chars obtained from the pyrolysis of mixtures 1, 2 and 3 were named as chars 1, 2 and 3, respectively.

The yield of liquids corresponds to the liquids settled from the pyrolysis reactor. Comparing the results, it can be concluded that the addition of used tire rubber to the waste mixture increased the chars yield. The pyrolysis of mixture 3 did not produce any free liquid products since they were all soaked in the char.

Table 19. Composition of the three blends submitted to pyrolysis and product yields.

Mixture	Composition (w/w)	Pyrolysis reaction products (w/w)
1	30% pine + 30% tires + 40% plastics	10% gases + 60% liquids + 25% chars
2	50% pine + 50% plastics	12% gases + 54% liquids + 22% chars
3	50% tires + 50% plastics	2% gases + 97% chars

Figure 29 shows pictures of the three crude chars obtained in the pyrolysis experiments.

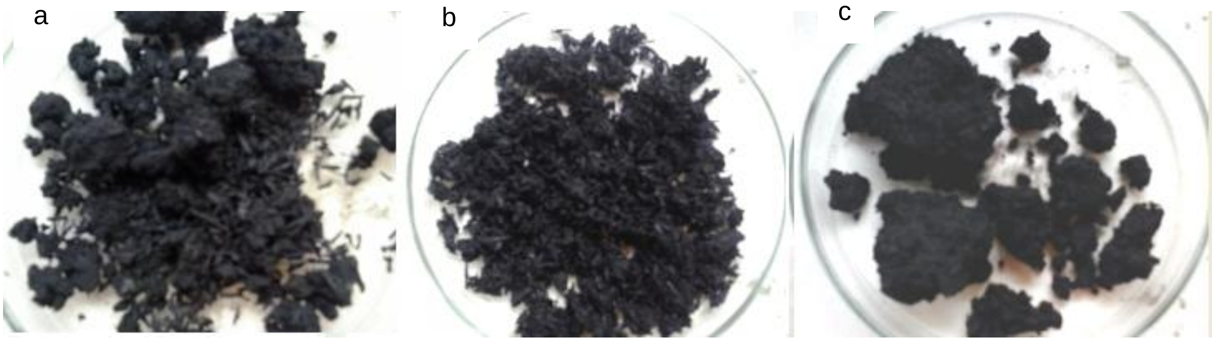

Figure 29. Crude chars obtained in the pyrolysis experiments (a: char 1, b: char 2; c: char 3).

The extraction yields obtained in the extraction steps for the three chars are presented in Figure 30. The extraction yields were determined as the ratio between the total mass of extract obtained and the mass of char sample.

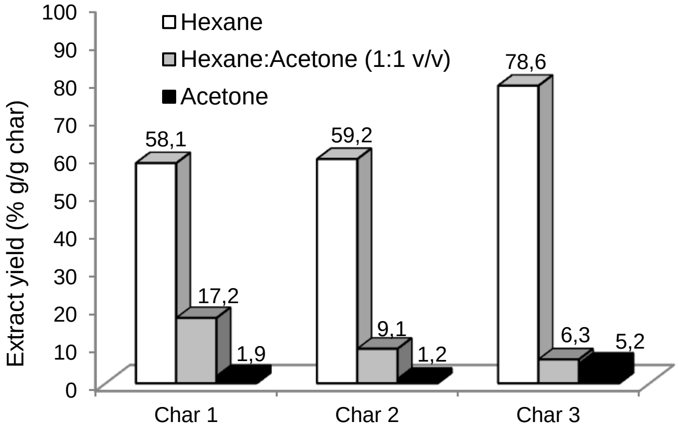

Figure 30. Extract yields of chars obtained in each extraction step.

The extraction yields showed that most of the oils/tars present in the three chars are non-polar and therefore soluble in pure hexane. Only residual amounts are polar enough to resist the extraction with hexane:acetone being recovered with pure acetone.

The total extraction yields (ratio between the total mass of extracts obtained in the three extraction steps and the mass of char sample) of the sequential extractions was of 66% for char 1, 63% for char 2 and 81% for char 3. The highest extraction yield obtained for char 3 corresponds to the complete impregnation of the pyrolysis liquids in the char.

These results showed that this procedure not only ensures a high decontamination of chars from organic compounds, but also it allows the recovery of a significant fraction of the pyrolysis condensed volatiles improving the liquid yields.

Figure 31 shows pictures of the chars after the sequential solvent extraction procedure.

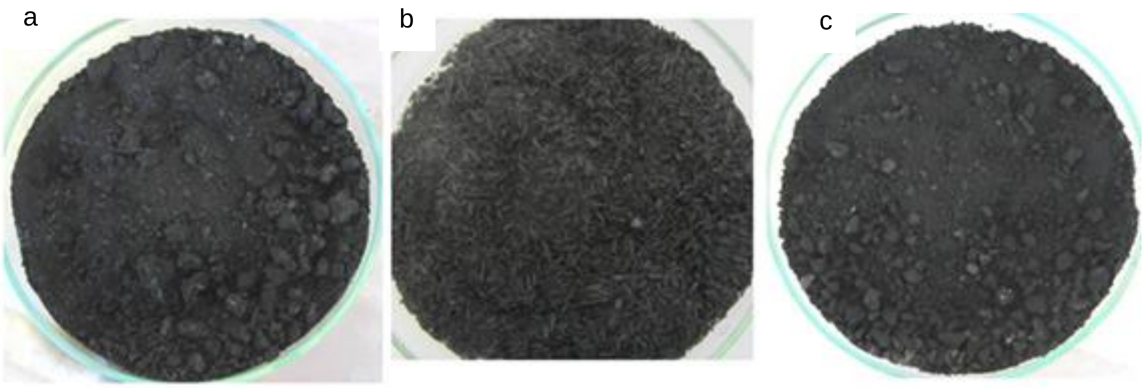

Figure 31. Extracted chars after the sequential solvent extraction procedure (a: char 1, b: char 2; c: char 3).

The chars obtained were mainly originated as primary products from the thermal decomposition of pine biomass and/or used tire rubber as the production of char from thermoplastics pyrolysis, particularly polyolefins, is quite low and resulting only from secondary tar-cracking reactions[41,84]. The visual observation of chars from mixture 1 (Figures 29a and 31a) showed that they appear to be a mixture of chars from mixtures 2 and 3, which may lead to the conclusion that interactions between the feedstocks during pyrolysis were negligible; however, only a more detailed analysis can elucidate if synergisms occur in the formation of chars.

5.3.2 Thermal and elemental analysis of chars

Table 20 presents the composition of the extracted chars based on the thermal and elemental analyses. The three chars presented residual amounts of volatiles, but significant amounts of semi-volatile matter (volatility between 250ºC and 350ºC). These semi-volatiles are, probably, asphaltene tars (complex polyaromatic hydrocarbons mixtures with alkyl side chains and heteroatoms side-chain functional groups) that are not soluble in the solvents used in the organic extractions, namely hexane and/or acetone, but are soluble in aromatic solvents such as toluene. However, the aromatic solvents were not used, because the goal of the sequential solvent extraction was the recovery of the pyrolysis oils/tars using solvents of low environmental impact including low toxicity.

The chars obtained from mixtures with tires in their composition presented the highest ash contents.

The carbon contents of the three chars were quite similar and the differences lie mostly on heteroatoms content, particularly sulphur and oxygen. The highest O/C ratio for char 2 suggests the presence of polar surface functional groups in this char. Char 3 showed the lowest H/C ratio being the most aromatic and hydrophobic char.

The high sulphur content in char 3 is originated from tires, which was the feedstock that presented the major content for this element (section 3.1.3.2, Table 2).

Table 20. Composition of chars according to their volatility and elemental analysis.

Parameters	Char 1	Char 2	Char 3
Thermal analysis			
Volatiles (% w/w)	2.62	5.36	1.18
Semi-volatiles (% w/w)	12.4	9.92	14.2
Fixed residue (% w/w)	81.3	83.3	75.9
Ashes (% w/w)	3.66	1.39	8.68
Elemental analysis (ar)			
Carbon Content (% w/w)	82.9	79.2	82
Hydrogen Content (% w/w)	7.1	6.2	5.7
Nitrogen Content (% w/w)	0.7	1.1	0.5
Sulphur Content (% w/w)	0.75	0.08	1.35
Oxygen Content (% w/w)[a]	4.89	12.03	1.77
H/C atomic ratio	1.03	0.94	0.83
O/C atomic ratio	0.044	0.114	0.016

ar – as-received basis; [a]by difference (include the oxygen in the free moisture associated with the sample and errors).

5.3.3 Metal content of chars

Table 21 presents the metal content determined in the solvent extracted chars.

Table 21. Metal content of extracted chars.

Metals (mg/kg wb)	Char 1	Char 2	Char 3
Cd	<4.78	<4.78	13.7±0.6
Pb	76.6±5.9	15.8±4.3	88.1±16.0
Zn	9128±183	99.6±1.9	28685±1022
Cu	4.50±2.5	<4.3	<4.3
Cr	<4.5	36.4±5.4	14.0±0.3
Ni	<6.5	70.0±47.2	<6.5
Mo	<8.8	123±37	<8.8
Ba	<16.8	<16.8	<16.8
Hg	0.250±0.05	<0.13	<0.13
As	0.290±0.01	0.320±0.03	0.510±0.05
Se	0.160±0.11	1.10±0.7	0.100±0.004
Sb	0.760±0.34	<0.07	0.210±0.02
K	407±61	570±83	1011±119
Mn	11.5±0.3	22.5±0.1	3.50±1.5
Fe	174±15	309±22	367±7
Na	256±40	8.70±5.4	42.4±18.0
Ca	3723±412	594±233	182±18
Al	180±67	<34.0	209±14
Mg	341±91	1794±66	1033±238

wb – wet basis; The mean and standard deviation of duplicates are shown.

Generally, char 3 presented higher amounts of metallic elements which is consistent with its higher ash content (Table 20) being the used tires the major source of metals. Also, the used tires were the source of Zn (section 3.1.3.3, Table 3), the element dominant in chars 1 and 3. As already said in section 3.1.3.3, zinc oxide as well as magnesium oxide are generally used as activators during the sulphur vulcanization of tires[172]. It was previously reported that sulphidation of metal oxides occurs in this process as well as in tires pyrolysis, due to the reaction between metals and the hydrogen sulphide generated[205-206].

In char 1, Ca is the element more abundant after Zn. Ca is added as carbonate during tire manufacturing to act as filler[173]. Therefore, it could be assumed that the source of Ca in char 1 is the tires; however, the concentration of Ca in char 3, which resulted from a mixture with higher mass of tires, is significantly lower. There is the possibility that Ca is underestimated in char 3 or overestimated in char 1.

In char 2 the prevalent metal was Mg. The principal source of Mg was the pine biomass (section 3.1.3.3, Table 3). Also, Ca, K and Fe are significant elements in this char. Char 2 also presented quantifiable amounts of Cr, Ni and Mo which were not detected in the raw materials (section 3.1.3.3, Table 3). The autoclaves where pyrolysis experiments were performed are built in Hastelloy C276 which is a nickel-molybdenum-chromium wrought alloy. A possible explanation, already exposed in section 3.2.3.2, for the presence of these metals is the contamination of the pyrolysis products by some release of heavy metals from the pyrolysis autoclaves walls.

5.3.4 Chemical and ecotoxicological characterisation of eluates

The solvent extracted chars were then submitted to the leaching standard ISO/TS 21268-2. Table 22 shows the results of the chemical characterisation of eluates. Eluates 1, 2 and 3 resulted from chars 1, 2 and 3, respectively. The results in mg/kg express the mass of leached substance per mass unit of char.

It can be seen that the chars obtained from mixtures with pine biomass (chars 1 and 2) gave origin to more acidic eluates, probably due to the release of acidic functionalities such as carboxylic and phenolic groups incorporated in the char matrix as a result of the incomplete thermal decomposition of the lignocellulosic matter. This hypothesis is strengthened by the significant Total Organic Carbon (TOC) content of eluates 1 and 2. Mukherjee et al.[207] has previously demonstrated that the pH of lignocellulosic chars is strongly dependent on pyrolysis temperature, being quite acidic for low pyrolysis temperatures (250ºC), slightly acidic for temperatures around 400ºC and become alkaline for higher pyrolytic temperatures.

Eluate 2 showed the highest conductivity value which means that char 2 leached higher levels of salts that dissociated in solution.

Inorganic Carbon (IC) of eluate 3, was significantly higher when compared to the other eluates, which puts in evidence a significant leaching of carbonates from char 3.

From the concentrations of heavy metals, zinc leached in the highest amounts from the three chars, but particularly from chars 1 and 3 that were the ones also with higher concentrations of this metal. Although char 3 presented a Zn concentration 3 times higher than char 1, it was not observed a linear correlation between the initial quantity of Zn in the chars and the concentration of Zn eluted. There are several possible explanations for this fact: the more hydrophobic character of char 3 that creates aggregates which expose a lower surface area than that of dispersed particles; the slightly more acidic eluate 1 may lead to higher Zn leaching; also the speciation of this metal in both chars might have influenced its mobility. Char 3 presented a higher sulphur content (Table 20), and some zinc may be in the form of zinc sulphide (ZnS) originated in the sulphidation of zinc oxide, being this metallic sulphide quite insoluble for pH values above 6-7[208]. Also Pb, which was present in significant concentrations in chars 1 and 3 was not detected in the eluates, suggesting its presence in the chars in a quite stable form. Pb might be present in these chars also as sulphide presenting a very low solubility for pH values above 4[208].

Table 22. Chemical characterisation of eluates.

Parameters	Eluate 1	Eluate 2	Eluate 3
pH	6.07	5.11	6.68
Conductivity (µS/cm)	451	760	347
TOC (mg/kg wb)	1673	2885	204
IC (mg/kg wb)	5.34	3.57	28.1
Metallic elements (mg/kg wb)			
Cd	<0.057	<0.057	<0.057
Pb	<0.091	<0.091	<0.091
Zn	593	8.35	29.5
Cu	<0.036	<0.036	<0.036
Cr	<0.064	<0.064	<0.064
Ni	<0.119	3.99	0.244
Mo	<0.513	8.19	1.52
Ba	1.58	1.65	<0.758
Hg	<0.004	<0.004	<0.004
As	<0.022	<0.022	<0.022
Se	<0.024	<0.024	<0.024
Sb	<0.021	<0.021	<0.021
K	443	256	185
Mn	1.34	1.09	0.152
Fe	<0.14	<0.14	<0.14
Na	96.1	<0.065	<0.065
Ca	586	879	55.8
Al	1.14	<0.869	<0.869
Mg	97.8	156	21.9

Char 2 (from 50% pine and 50% plastics) leached quantifiable amounts of Mo and Ni, but Cr was not detected. The high stability and high immobilisation of Cr in the char matrix have been already observed for the char resulting from 70% pine and 30% plastics studied in section 3.2.

Alkali and alkaline-earth metals leached more readily from chars resulting from the mixtures with biomass, which is consistent with the high conductivity presented by eluates 1 and 2.

Table 23 shows the ecotoxicological levels of eluates.

Table 23. Ecotoxicological levels of eluates.

	EC_{50} (%) (v/v)		
	Eluate 1	Eluate 2	Eluate 3
5 min	66.7	>100	>100
15 min	13.5	>100	74.1
30 min	7.28	>100	35.9

Eluate 2 did not present toxicity to *V. fischeri* for all the exposure periods. Eluate 1 presented the highest ecotoxicity level, particularly at 30 minutes of exposure, in which a concentration of 7.28% of the eluate caused 50% bioluminescence inhibition.

Eluate 3 started to present ecotoxic effect only above 15 min of exposure period; nevertheless, at the higher exposure time (30 min) a concentration of 36% of eluate 3 induced 50% bioluminescence inhibition.

The ecotoxicity levels of eluates 1 and 3 seemed to be mainly associated with the presence of Zn in these eluates with significant concentrations, particularly in eluate 1 which was also the eluate with the highest ecotoxic effect. A possible relation with Zn in the eluates and their ecotoxicity had been already suggested in section 3.3.3.4.

5.3.5 Ecotoxicity and hazard assessment of pyrolysis chars

Table 24 presents the classification of wastes according to the limit-values for eluates defined in CEMEW[161] and Council Decision 2003/33/EC[180] for the parameters determined in the present work.

Table 24. Classification of wastes according to the limit-values defined in CEMEW[161] and Council Decision 2003/33/EC[180] for the metals determined in the present work.

Parameter (mg/kg)	Inert[a]	Non-hazardous[a]	Hazardous[a]	Ecotoxic[b]
TOC	30000	-	-	-
Cd	0.04	1	5	2
Pb	0.5	10	50	5
Zn	4	50	200	20
Cu	2	50	100	5
Cr	0.5	10	70	5
Ni	0.4	10	40	5
Mo	0.5	10	30	-
Ba	20	100	300	-
Hg	0.01	0.2	2	0.5
As	0.5	2	25	0.5
Se	0.1	0.5	7	-
Sb	0.06	0.7	5	-

[a] Limit values for the eluates according to Council Decision 2003/33/EC
[b] Limit values for the eluates according to CEMEW

Comparing the chemical characterisation of eluates (Table 22) with the limit-values defined in the Council Decision 2003/33/EC (Table 24), it can be concluded the following:

- Eluate 1 presented concentrations for all the parameters, except for Zn, below the limit-values for inert materials. However, the high Zn concentration in this eluate (593 mg/kg wb) were quite above the limit-value for hazardous materials; therefore, char 1 was classified as hazardous material.
- Eluate 2 presented concentrations for all the parameters below the limit-values defined for non-hazardous wastes; therefore, char 2 was classified as a non-hazardous material.
- Eluate 3 presented concentrations for all the parameters below the limit-values defined for non-hazardous wastes; therefore char 3 was classified as a non-hazardous material.

Comparing the chemical characterisation of eluates (Table 22) with the limit-values defined in CEMEW (Table 24), it can be concluded the following:

- Eluate 1 presented concentrations for all the parameters, except for Zn, below the limit-values of an ecotoxic material. Due to Zn concentration, char 1 was classified as an ecotoxic material.
- Eluate 2 presented concentrations for all the parameters below the limit-values of an ecotoxic material; therefore, char 2 was classified as non-ecotoxic.
- Eluate 3 presented concentrations for all the parameters, except for Zn, below the limit-values of ecotoxic materials; thus, char 3 was classified as an ecotoxic material.

Comparing the results of the ecotoxicological characterisation (Table 23) with the ecotoxicological limit-value defined in the CEMEW for *Vibrio fischeri* (EC_{50} (30min) $\leq 10\%$ (v/v)), only eluate 1 does not fulfil this criterion, leading to a classification of char 1 as ecotoxic material.

Globally, char 1 was classified as hazardous and ecotoxic material, char 2 as non-hazardous and non-ecotoxic material and char 3 as non-hazardous, but ecotoxic material. It can be concluded that not always the chemical criteria fit in ecotoxicological criteria.

5.3.6 Influence of EDTA extraction on the ecotoxicity of chars

The hypothesis that Zn is the main responsible for the ecotoxicity of eluates 1 and 3 is supported by the absence or trace amounts of the majority of the known toxic metals and by the presence of Zn in both eluates with concentrations susceptible to cause toxic effects to *V. fischeri*. Zinc sulphate ($ZnSO_4$) is used as inorganic reference toxicant in the Microtox test used in the present work and the EC_{50} values for 15 min are typically between 1.5 and 3.0 mg/L[178,184,209]. However, it is necessary to confirm this relationship between Zn and the ecotoxicity results.

Ethylene Diamine Tetraacetic Acid (EDTA) is widely recognized as a very effective chelating agent to remove heavy metals from soils and soil materials[210-211]. To author's knowledge, this is the first time that the same strategy was applied to pyrolytic chars with the aim to selectively sequester metal ions that can be responsible for their ecotoxicity.

EDTA washing procedure was only applied to chars 1 and 3 as they were the ones that produced ecotoxic eluates. The choice of EDTA was due to its high affinity to zinc, the metallic element supposed to cause the ecotoxicity of eluates 1 and 3.

Table 25 presents the detectable amounts of metals that were removed from the chars during the EDTA washing procedure. Zn was effectively extracted with significant amounts from char 1 (27.5% of Zn removal) and char 3 (35.3% of Zn removal) during the EDTA treatment.

Table 25. Concentrations of metals extracted from chars 1 and 3 during the EDTA washing procedure.

Metallic elements (mg/kg wb)	Char 1 (EDTA)	Char 3 (EDTA)
Zn	2509	10134
Cu	<1.15	1.23
Ni	<2.57	5.57
K	156	500
Mn	<0.3	2.03
Fe	21.6	118
Ca	512	1517
Mg	59.7	196

Some competition among other cations that have affinity to form chelates with EDTA was observed, but these were identified mainly as being Ca^{2+}, Mg^{2+} and K^{+}. The amount of Ca removed from char (1517 mg/kg wb) is quite above the concentration that had been determined in the char (182 mg/kg) and presented in Table 21, confirming the hypothesis that Ca was underestimated in char 3 using the digestion procedure described in section 5.2.4.

Table 26 presents the results of the characterisation of eluates of the EDTA treated chars. Only zinc was monitored in the eluates.

Table 26. Chemical and ecotoxicological characterisation of eluates from chars 1 and 3 treated with EDTA.

	Eluate 1	Eluate 3
pH	5.77 (6.07)	6.38 (6.68)
Zn (mg/kg wb)	24.76 (593)	3.59 (29.54)
EC_{50} (%) (v/v)		
5 min	>100 (66.7)	>100 (>100)
15 min	>100 (13.5)	>100 (74.1)
30 min	49.1 (7.28)	>100 (35.9)

Values between parentheses – before EDTA treatment

The pH difference of eluates was not significant so it can be concluded that this parameter did not influence the leachability of zinc. On the other hand, the concentrations of zinc leached from the treated chars were much lower than those leached before the EDTA treatment; the concentration of zinc leached from char 1 decreased 95.8% and from char 3 decreased 87.8%, which shows that the EDTA washing process was efficient in the removal of zinc from the chars and affected its mobility.

This substantial decrease of zinc concentration in the eluates of chars was reflected in the ecotoxicological data with a corresponding significant increase in the EC_{50} values. Eluate 3 did not present ecotoxicity for all the exposure periods. Eluate 1 only presented ecotoxic effect for the longer exposure period (30 minutes), which is consistent with the fact that it was the eluate with the highest concentration of zinc.

The classification of chars 1 and 3 according to the Council Decision 2003/33/EC and CEMEW proposal after the EDTA treatment is as follows:

- Eluate 1 presented a Zn concentration below the limit-value for non-hazardous materials. Therefore, the treated char 1 is classified as non-hazardous material. Eluate 1 also fulfilled the ecotoxicological criteria of CEMEW, however, Zn concentration slightly overpassed the limit-value of the CEMWE chemical criterion. Char 1 is therefore classified as ecotoxic.
- Eluate 3 fulfilled the chemical criterion of the Council Decision for non-hazardous materials and the chemical and ecotoxicological criteria of CEMEW; char 3 was classified as non-hazardous and non-ecotoxic material.

5.4 Conclusions

This work allows concluding that the composition of the feedstock submitted to pyrolysis has a considerable influence on chars characteristics: the highest is the ratio of tire rubber in feedstock, the highest is the aromatization, hydrophobicity degree, and ash content of the resulting chars. On the other hand, the introduction of pine biomass on the feedstock composition enhanced the acidic character of chars promoting the mobilization and release of inorganic elements.

Chars resulting from the pyrolysis of mixtures with pine and plastics did not produce ecotoxic eluates, which is a good indicator for the environmental application of this type of chars.

A concentration-dependent relationship between zinc concentrations in eluates and their ecotoxicity behaviour was found for chars obtained from mixtures with tires in their composition, suggesting the necessity of a previous treatment for zinc removal. A significant ecotoxicity reduction was registered when the chars were treated with EDTA, because a significant reduction in zinc leaching was also obtained. On the other hand, if chars from the pyrolysis of mixtures composed by used tire rubber were considered to be used in environmental applications, particularly water applications, the best condition of use is for pH above 6-7, as there is a significant risk of zinc mobilization in the case of lower pH values for which this metal is highly soluble.

CHAPTER 6

6. STUDY OF THE POTENTIAL OF CHARS TO BE VALORISED AS ADSORBENTS: REMOVAL OF Pb^{2+} FROM AQUEOUS MEDIUM

Abstract: The sorption and textural properties of the three chars studied in chapter 5 were evaluated in the present work. Lead (Pb2+) removal efficiency of the chars from aqueous solutions was determined as an example of a particular application of these chars as adsorbents.

The chars were predominantly of macroporous nature, but the introduction of tires in the pyrolysis feedstock enhanced their mesoporous content as well as surface area.

Pb2+ sorption onto the chars was a slow and unstable process in which sorption-desorption seems to be competing.

The char with the best overall performance for Pb2+ uptake resulted from the pyrolysis of the mixture of 50% tire rubber + 50 % plastics (char 3), achieving almost 100% of Pb2+ removal on the study of the effect of adsorbent dose. Mixing the three raw materials (pine biomass + tire rubber + plastics) for pyrolysis had no advantage for the resulting char concerning the removal efficiency of Pb2+. The sorption mechanisms varied according to the pyrolysis feedstock: in chars from feedstock with pine, chemisorption involving complexation with oxygenated surface functional groups followed by cation exchange were the presumable mechanisms. In char 3, cation-exchange with Ca2+, K+ and Zn2+ played the major role on Pb2+ sorption.

The results presented in this section were published, partially or completely, in the following papers:

Bernardo, M., Mendes, S., Lapa, N., Gonçalves, M., Mendes, B., Pinto, F., Lopes, H., Fonseca, I., Removal of lead (Pb2+) from aqueous medium by using chars from co-pyrolysis, *Journal of Colloid and Interface Science*, 409 (2013) 158–165. (doi: 10.1016/j.jcis.2013.07.050; IF: 3.172)

Bernardo, M., Mendes, S., Lapa, N., Gonçalves, M., Mendes, B., Pinto, F., Fonseca, I., Sorption of Lead (Pb2+) from aqueous solutions using chars obtained in the pyrolysis of forestry pine, rubber tires and plastics*, Book of Congress of VIII Jornadas Técnicas Internacionais de Resíduos - Waste Management for Resources Sustainability*, Lisbon, Portugal, 16-18 July 2013.

6.1 Introduction

The present chapter evaluates the potential of the three chars studied in chapter 5 to be used as adsorbents. A characterisation of the adsorption and textural properties of the solvent extracted chars was performed and the results are presented.

The efficiency of chars for the removal of a toxic heavy metal from aqueous medium was determined as an example of a particular application of these chars as adsorbents.

Lead (Pb^{2+}) was selected as a representative toxic metal because is considered as one of the priority substances in the framework of the European water policy[212-213] presenting a significant risk to biota and humans, given its persistence, toxicity and bioaccumulation characteristics.

Chars resulting from thermochemical processes are emerging as low-cost sorbents for metallic contaminants. Their effectiveness was already demonstrated in several studies[98-105]. Chars may have several characteristics that make them effective as heavy metals sorbents, but those characteristics depend on the feedstock from which they derived and the conditions of the thermal process used. The presence of an aromatic carbon matrix with relatively porous structures, of functional groups (carbonyl, carboxyl, hydroxyl, etc.) or inorganic forms (exchangeable cations, mineral oxides, etc.) in the adsorbent surface provide active sites capable to interact with polar and charged chemical species, such as metallic cations [108,214-216].

Previous studies demonstrated the efficiency of using chars produced in the pyrolysis of several feedstocks for the sorption of Pb^{2+}: manure[217-219], broiler-litter[214,220], tire rubber[118,120,221], wood residues[108,216,222], agricultural/crop residues[217,222-225], and sewage sludge[215,226].

Tire rubber chars are known for their well-developed mesopore structures with a high sorption capacity to bulky molecules[48,89,116,227], but their surface chemistry characterized by high sulphur content and inorganic inclusions is likely to play a major role in heavy metals sorption. Studies of the removal of heavy metals by tire chars are still limited and the mechanisms involved are not well understood.

In the lignocellulosic biomass chars, the oxygenated functional groups and the alkali and alkaline-earth cations can act as active sites for heavy metals adsorption, as the surface area and porosity in these non-activated carbons are negligible[82,106,108,216].

Given the aforementioned, it was anticipated that the use of chars from the pyrolysis of feedstock mixtures composed by both lignocellulosic biomass and tire rubber would represent an advantage since these chars could present the combined sorption characteristics of both materials.

To the author knowledge, no data is available for Pb^{2+} sorption or other metal with the chars used in the present work as well as the related mechanisms. The influence of several experimental parameters in Pb uptake was evaluated.

6.2 Experimental part

6.2.1 Pyrolysis experiments and char samples

Pyrolysis experiments and char samples are the same as in chapter 5. The description of the experiments is presented in section 5.2.1. The char samples used in the present work are described in section 5.2.2 and resulted from the following mixtures:

- 30% (w/w) pine biomass + 30% (w/w) used tire rubber + 40% (w/w) plastics – Char 1
- 50% (w/w) pine + 50% (w/w) plastics – Char 2
- 50% (w/w) used tire rubbers + 50% (w/w) plastics – Char 3

The plastics used in the three feedstocks were a mixture of 56% (w/w) PE, 27% (w/w) PP and 17% (w/w) PS.

The char samples were submitted to the sequential solvent extraction procedure explained in section 5.2.2. In the present chapter, whenever mentioned the char samples they concern the solvent extracted chars.

6.2.2 Characterisation of chars

6.2.2.1 Textural properties

The textural properties of the chars were evaluated by adsorption of N_2 at 77K using an ASAP 2010 Micromeritics apparatus. Adsorption measurements were made after outgassing the samples under vacuum for at least 3h, at 300ºC.

The isotherms were used to calculate the apparent surface area (S^{BET}) through the B.E.T. equation and the total pore volume, mesopore volume and pore size distribution through the Barrett, Joyner, and Halenda (BJH) method (ASAP 2010 Micromeritics software version 4.0).

The volume and pore size distribution for meso and macropores were determined with a mercury (Hg) intrusion porosimeter Micromeritics AutoPore IV 9500 with the software version 1.07.

All these analyses were performed in the Chemistry Department of Faculdade de Ciências e Tecnologia (Faculty of Sciences and Technology), Universidade Nova de Lisboa (New University of Lisboa).

6.2.3 Lead uptake experiments – general conditions

The preparation of Lead (Pb) solutions (synthetic wastewaters) used in the uptake studies was performed by appropriate dilutions in ultra-pure water of a stock Lead nitrate solution, $Pb(NO_3)_2$, with the concentration of 1000 mg/L (Merck).

Batch experiments were conducted in polypropylene flasks and the mixtures of adsorbent-adsorbate were agitated at a speed of 100 rpm/min in a thermostatic orbital shaker bath (Tuttnauer, Model 14-310) at 25±5ºC. After the agitation period, the mixtures were separated by filtration using Whatman® grade 40 cellulose filters.

The pH of filtrate was immediately determined by using a pH meter (Crison, micropH 2001) and, subsequently, the filtrate was acidified to pH<2 with concentrated HNO_3 (65% v/v) and refrigerated at 4 ºC in polypropylene flasks for chemical analysis. Concentrations of Pb in the filtrate were determined by AAS with the Thermo Elemental Solaar equipment using the air-acetylene flame technique. Blank tests with Lead solution and without chars were performed simultaneously.

The metal ion retained in the char, q_t (mg/g), also designated by uptake capacity was determined according to equation 1:

$$q_t = \frac{(C_0 - C_t)}{W} \times V$$

(Equation 1)

And the Lead removal efficiency (in %) was determined according to the equation 2:

$$Removal\ efficiency = \frac{(C_0 - C_t)}{C_0} \times 100$$

(Equation 2)

where C_0 and C_t are the initial and final metal ion concentrations (mg/L), respectively, V is the volume of the solution (L) and W is the char mass (g).

6.2.3.1 Study on the effect of pH

The effect of pH on Lead uptake was investigated with an initial pH range between 2.0 and 9.0. In these experiments, 0.2 g of each char was mixed with 50 mL of Lead solution with an initial concentration of 5 mg/L for an agitation period of 24 h. The initial pH of Lead solutions was adjusted to the required values by using NaOH 1M or concentrated HNO_3 (65% v/v).

6.2.3.2 Effect of contact time

The effect of contact time in the uptake capacity of Pb was assessed for agitation periods that ranged from 0 to 120 h. For the kinetic experiments, 0.2 g of each char was mixed with 50 mL of Lead solution with an initial concentration of 5 mg/L and an adjusted pH value of 6.0.

6.2.3.3 Effect of the initial concentration of Lead (Pb)

The effect of initial Pb concentration in the uptake capacity of the chars was evaluated for a concentration range of 5-100 mg/L, using 0.2 g of each char mixed with 50 mL of Lead solution with an initial adjusted pH value of 6.0, and an agitation period of 48 h.

6.2.3.4 Effect of sorbent mass

The effect of changing the sorbent dose in the removal of Lead was tested for a range of char mass between 0.1 and 1.5 g. These tests were conducted by mixing the char samples with 50 mL of Lead solution with an initial concentration of 20 mg/L, an initial adjusted pH value of 6.0 and an agitation period of 48 h.

6.2.3.5 Study on the sorption mechanism

The concentrations of several metals in the filtrate after the uptake of Lead were determined to elucidate the mechanism of Lead sorption. In this study, the uptake experiment was performed with 1.5 g of char mixed with 50 mL of Lead solution with an initial concentration of 20 mg/L, an initial adjusted pH value of 6.0, and an agitation period of 48 h. A blank test with the char sample and ultra-pure water was conducted.

The following metallic elements were analysed by AAS with the Thermo Elemental Solaar equipment: Cadmium (Cd), Zinc (Zn), Copper (Cu), Nickel (Ni), Potassium (K), Manganese (Mn), Iron (Fe), Sodium (Na), and Magnesium (Mg) (analysed using the air-acetylene flame technique); Calcium (Ca), Aluminium (Al), Chromium (Cr), Molybdenum (Mo), and Barium (Ba) (analysed using the acetylene-nitrous oxide flame technique).

6.3 Results and discussion

6.3.1 Characterisation of chars

6.3.1.1 Textural properties

The N_2 isotherms obtained for the three chars are presented in Figure 32.

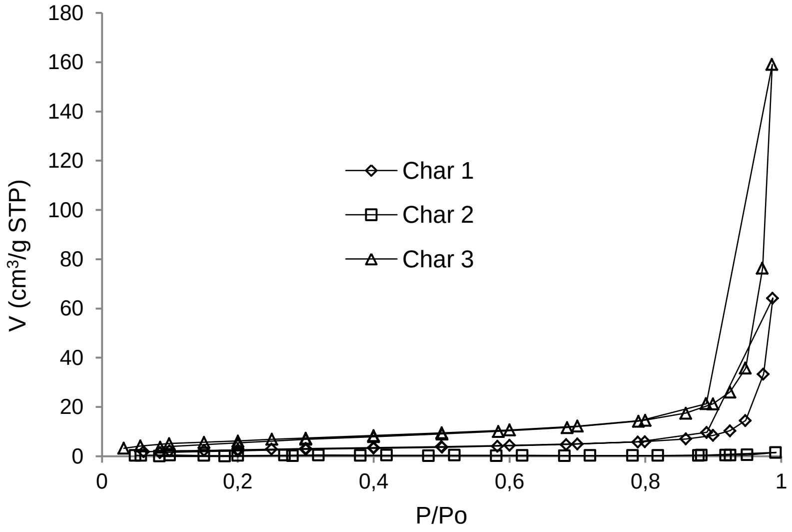

Figure 32. N_2 adsorption–desorption isotherms of chars at 77 K.

Char 2 had a very low adsorption capacity for N_2 gas (less than 1 cm^3/g for the entire relative pressure, P/P_0, range) which might mean that char 2 is a non-porous material in the micro and mesopore range, or the pores are extremely narrow and small being not accessible to N_2 at 77 K. Another hypothesis is that the pores may be blocked with condensed volatiles. Although char 2 had resulted from the pyrolysis of pine mixed with plastics, it is expected that the carbonaceous structure of this char was mainly originated by the thermal decomposition of the lignocellulosic materials. It is known that the pyrolysis of lignocellulosic biomass at mild temperatures generally causes low surface areas and frequently biomass chars are characterized by micro-macroporous structured particles[16,82, 108,232-233].

Table 27 shows the textural parameters given by the technique of N_2 adsorption-desorption.

Table 27. Textural parameters given by N_2 adsorption-desorption isotherms.

	S_{BET} (m^2/g)	Total pore volume (cm^3/g)	Mesopore volume (cm^3/g)	Average pore diameter (µm)
Char 1	9.82	0.099	0.099	0.040
Char 2	n.c.	n.c.	n.c.	n.c.
Char 3	23.7	0.246	0.246	0.042

n.c. – not calculated

Given the fact that Char 2 does not present micro and mesopores, it is not possible its characterization by N_2 adsorption. Thus, mercury porosimetry was used as a complementary technique. Table 28 and Figure 33 present the results obtained with mercury porosimetry.

Char 2 presented porosity in the macropore range, more specifically it is an interparticle porosity due to the high pore size diameter at which occurs the mercury intrusion.

Table 28. Textural parameters given by Hg intrusion porosimetry.

	Total intrusion volume (cm^3/g)	V_{mes} (cm^3/g)	V_{mac} (cm^3/g)	Average pore diameter (µm)
Char 1	1.49	0.150	1.34	0.189
Char 2	2.07	0.030	2.04	0.656
Char 3	1.84	0.250	1.59	0.142

Chars 1 and 3 presented similar N_2 isotherms (Figure 32) of type II according to the IUPAC classification[234] that are typical of non-porous or macroporous materials and represents unrestricted monolayer-multilayer adsorption. The presence of a hysteresis loop between the adsorption and the desorption isotherms is associated with the presence of mesoporous in these two chars. This type of hysteresis loop, which does not exhibit any limiting adsorption at high P/P_0, is observed with aggregates of plate-like particles giving rise to slit-shaped pores. The average pore diameter of 0.04 µm (Table 27) confirms the presence of mesopores (mesopores are in the range 0.002–0.05 µm). The BET surface area (Table 27) of char 3 is higher than that for char 1, which is consistent with the total pore volumes obtained for each char. These low values of surface areas were expected for these non-activated pyrolysis chars. The results obtained with Hg intrusion porosimetry for these two chars are in good agreement with those obtained by N_2 isotherms since peaks of mercury intrusion in the mesopore and macropore range are observed. The average pore diameter for these chars (0.142-0.189 µm) obtained with the Hg technique agrees with the predominance of macropores.

Both chars 1 and 3 were obtained from pyrolysis of feedstock with used tire rubber and they showed to have textural and porosity properties similar to those of tire char[48,89,116,118,221,227], which are largely affected by the carbon black from the original tire material that remains in the chars after pyrolysis.

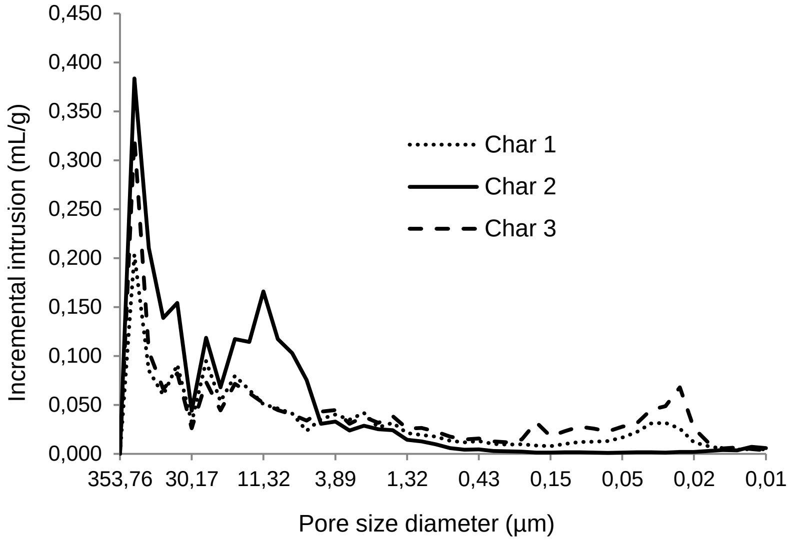

Figure 33. Incremental intrusion vs pore size for mercury porosimetry.

6.3.2 Lead uptake experiments

6.3.2.1 Effect of pH solution

The effect of the initial pH on the removal efficiency of Lead by each char is presented in Figure 34.

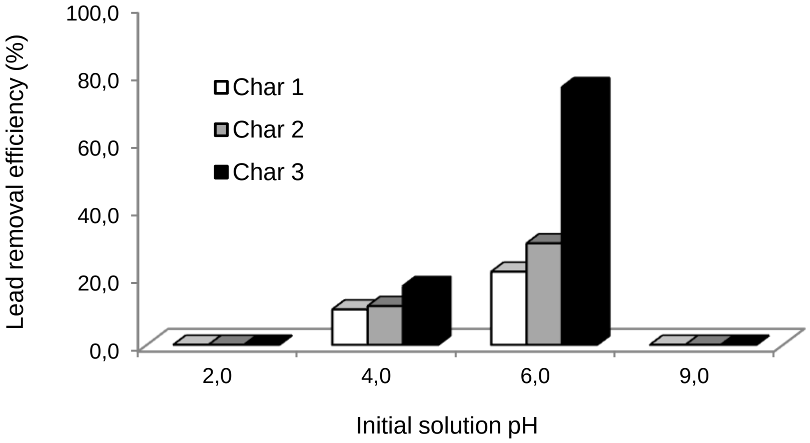

Figure 34. Effect of solution pH on Pb2+ removal efficiency. Conditions: Adsorbent dose, 4 g/L; Initial Lead concentration, 5 mg/L; contact time, 24 h.

Four different pH values were tested (2.0, 4.0, 6.0 and 9.0). The removal of Lead from aqueous solution increased with the increase of pH from acidic conditions up to relatively neutral conditions, being the maximum removals achieved for the pH of 6.0 (21.7%, 30.1% and 76.2% for chars 1, 2 and 3, respectively). On the other hand, there was no sorption at alkaline pH value of 9.0. Similar results were previously obtained by different authors that also tested the effect of pH on the sorption of Lead with biomass chars[108,215-216,218,222].

The pronounced effect of pH in the removal efficiencies of Lead can be partly explained by the metal speciation at different pH values[235], and also the variation of the surface charge of chars with pH. At very strong acidic conditions, Lead is present in solution as free Pb^{2+} ion, but there is also a high concentration of H^+ ions that protonate the surface of chars causing a strong positive charge, which blocks the sorption of Lead ion by electrostatic repulsion. At alkaline conditions, particularly for pH above 8, Lead precipitate as hydroxide. From moderately acidic to neutral conditions, Lead still exists mostly as free ion, but the competition effect with H^+ for chars markedly decreases. For an initial pH value of 6.0, no significant changes in the final pH solution after the uptake were observed, which means that the release of protons from chars was negligible, as well as the release of basic species, or the parallel release of both acidic and basic species occurred.

It is not likely that the differences between the three chars at a pH of 6.0 are related with the surface charges. Chars 1 and 2 resulted from pyrolysis of mixtures with pine biomass that presented the highest oxygen content and char 3 was produced with a blend of used tire rubber and plastics, and presented the highest sulphur content (Table 20). Sulphur and nitrogen groups behave as Lewis bases and contribute to carbon basicity, whilst oxygen and hydrogen functional groups attribute acidic properties to the carbon surfaces[236]. Thus, it is expected that char 2 should be the most acidic one and char 3 the most alkaline. It is widely known that acidic sites are usually related to negative charged sites[236-237]. Therefore, it will be expected that chars 1 and 2 had more electrostatic affinity to the positively charged Pb^{2+} ions. However, char 3 is the least acidic char and led to the highest Lead removal, showing that electro-sorption is not the dominant mechanism.

Given these results, in the following studies, solutions with an initial pH value of 6.0 were tested.

6.3.2.2 Effect of contact time

The uptake capacities of the three chars for Pb^{2+} as a function of contact time are presented in Figure 35.

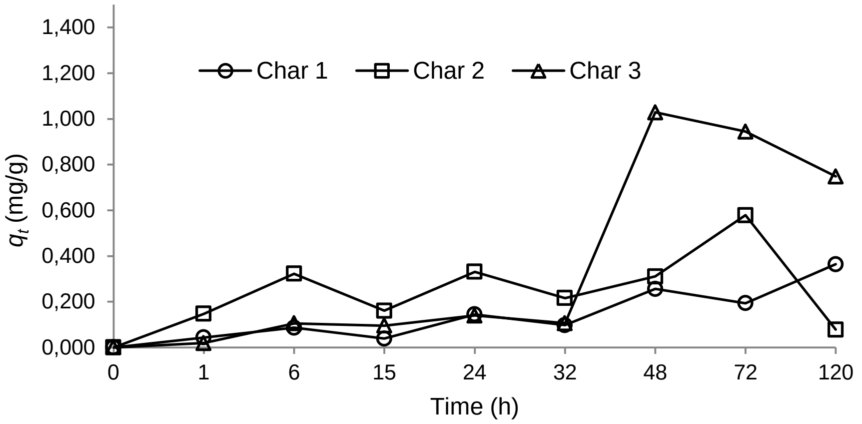

Figure 35. Effect of contact time on Pb2+ uptake capacity. Conditions: Adsorbent dose, 4 g/L; Initial Lead concentration, 5 mg/L; initial solution pH, 6.

All chars present an increasing capacity for Pb^{2+} removal from the aqueous solution during the first 6 hours, due to the interaction between Lead ions and free binding sites available on the external surface of chars and on large pores. During this period, char 2 presented the highest uptake rate for Lead, probably due to its marked macropore nature which facilitates the sorbate diffusion. It was previously demonstrated that an increase of the pore size of carbon yields to an increase in Lead uptake[236].

After this period, the chars presented a slow and unstable ion removal in which sorption-desorption seems to compete. Char 2 remained as the one with the highest uptake capacity. However, between 32-48 h of contact time, char 3 presented a significant shift in its uptake capacity suggesting that a barrier was overcome and active sites became available and/or the sorption mechanism has changed.

For longer contact times (above 48 h), the low stability of the uptaked Pb^{2+} was even more significant for chars 2 and 3, but char 1 still presented a very slow approach to equilibrium. The data dispersion can be related with the low Lead initial concentration or the low adsorbent dose used in these experiments that did not provide the necessary driving force for Lead uptake and a stable sorbed state. Similar results were reported for Lead removal with low doses of pine chars[108].

The slow kinetics of chars 1 and 2, resulting from pyrolysis of mixtures with pine biomass, could be associated with chemisorption involving complexation with oxygenated surface functional groups. Given the significant content of light cations in these two chars (Table 21), chemisorption by cation exchange is also a presumable mechanism. Char 2 presented higher content of oxygen (Table 20) than char 1 that can also explain the highest uptake capacities along the time.

For char 3, the sorption mechanism will be discussed in detail later on.

The highest Lead removal efficiency (88%) and uptake capacity (1.03 mg/g) was attained in char 3 for 48 h of contact time. By comparison, chars 1 and 2 presented lower removal percentages at 48 h of contact time and beyond. Therefore, this was the contact time chosen for the subsequent experiments.

6.3.2.3 Effect of the initial concentration of Pb^{2+}

The effect of the initial concentration of Pb^{2+} on the removal efficiency is presented in Figure 36.

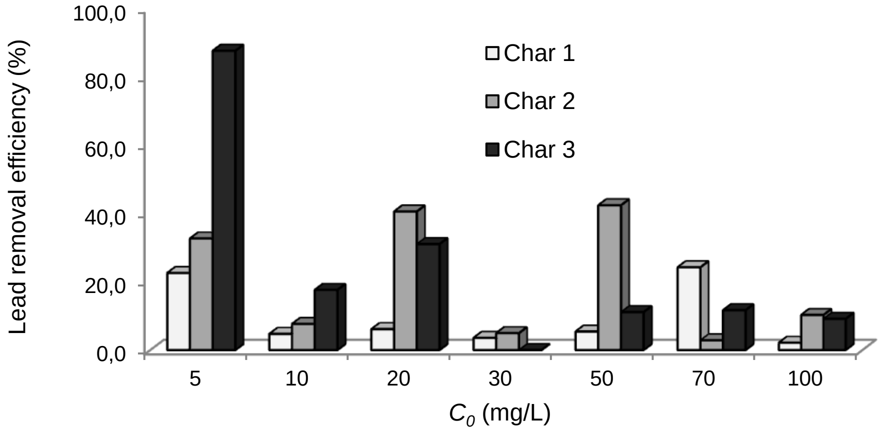

Figure 36. Effect of initial Pb2+ concentration (C0) on chars' removal efficiency. Conditions: Adsorbent dose, 4 g/L; contact time, 48 h; initial solution pH, 6.

It was observed a decreasing tendency in the removal efficiency of Pb^{2+} with the increase of the initial concentration of Lead. This was expected as the chars have a limited number of binding sites that become saturated for a certain Lead concentration. Inversely, the uptake capacity of the chars tended to rise with the increase of Lead concentration (Figure 37) because the resulting driving force minimizes the mass transfer resistances between the solution and char.

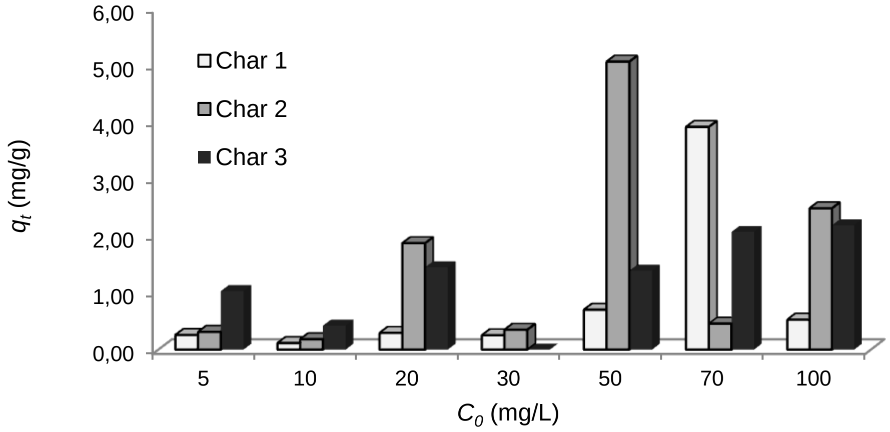

Figure 37. Effect of initial Pb^{2+} concentration (C_0) on uptake capacity. Conditions: Adsorbent dose, 4 g/L; contact time, 48 h; initial solution pH, 6.

The results can also be explained by Pb speciation with the increase of the initial concentration at a given pH. For the pH tested, Lead exists mostly as free ion for low concentrations as already referred in section 6.3.2.1. However at high concentrations there is a tendency for species such as Pb_2OH^{3+}, $Pb_3OH_4^{2+}$, among others[235] to be formed that significantly difficult the sorption process due to their bigger sizes than Pb^{2+}.

6.3.2.4 Effect of sorbent mass

Figure 38 illustrates the effect of the sorbent mass on Lead removal efficiency. Generally, the percentage of Lead removal increased with the increase of the char dosage. This may be attributed to an increase of surface area available for sorption, as well as of more active sites accessible as a result of the increase of char dosage. The tendency was more visible up to a sorbent dose of 20 g/L. Afterwards only a slight increase for chars 2 and 3 and a decrease in the Lead removal efficiency for char 1 with the increase of the sorbent dosages were observed. This may be explained by an effect of aggregation of char particles that was visually observed with the increase of char amount, which reduces the surface area for sorption.

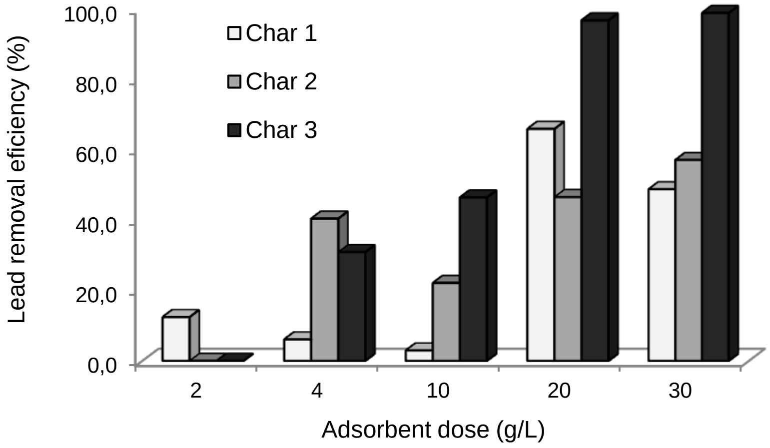

Figure 38. Effect of chars dose on Pb^{2+} removal efficiency. Conditions: Initial Lead concentration, 20 mg/L; contact time, 48 h; initial solution pH, 6.

The maximum removal percentage of Pb^{2+} for char 2 (57.2%) was registered for the highest solid to liquid ratio (30 g/L). Char 3 presented the best performance with a removal efficiency of 98.9% for the highest sorbent mass (30 g/L). Char 1 showed the second best performance with a removal percentage of Pb^{2+} of 66.0% for a sorbent dose of 20 g/L.

The uptake capacity of chars showed a reverse trend (Figure 39), decreasing with the increase of the char dosage. This was expected as the ratio between the mass of Pb^{2+} per unit mass of sorbent decreased with the increase of the sorbent mass, because the initial concentration of Pb^{2+} remained constant in all these experiments.

The highest observed uptake capacities were 1.18 mg/g for char 1 for the lowest sorbent dose, 1.87 mg/g and 1.45 mg/g for chars 2 and 3, respectively, for a sorbent dose of 4 g/L.

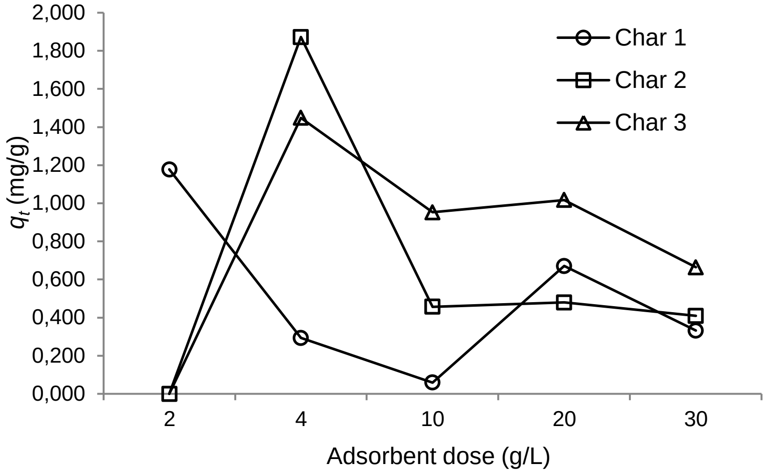

Figure 39. Effect of chars dose on Pb^{2+} uptake capacity. Conditions: Initial lead concentration, 20 mg/L; contact time, 48 h; initial solution pH, 6.

6.3.2.5 Sorption mechanisms of char 3 (50% Tire rubber + 50% Plastics)

As char 3 presented the best performance in Lead removal, the sorption mechanisms of this char were further investigated. The mechanisms involved on the removal of heavy metals by tire rubber derived chars are not well understood and seems to be a sequence of different phenomena. According to the kinetic study performed in this work (Figure 35), during the first 32 h, char 1 and char 3 presented very similar sorption behaviours with low uptake capacities (around 0.1 mg/g). The common feature between these two chars is the fact that both resulted from feedstock mixtures with tire rubber in their composition. After 32 h, the uptake capacity of char 3 increased around 10 times which can be partly explained by the higher mineral content of this char (Table 20).

The importance of exchange reactions on Lead sorption by this char was evaluated by measuring the amounts of metals present in solution after the sorption assays. Figure 40 presents the sorbed Lead by char 3 and the corresponding released cations that were present in quantifiable amounts.

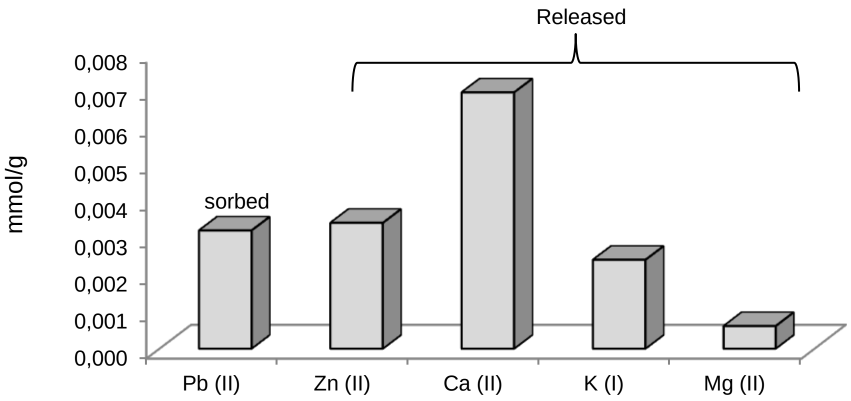

Figure 40. Lead ion sorbed and released cations from char 3. Conditions: Initial Lead concentration, 20 mg/L; contact time, 48 h; initial solution pH, 6; adsorbent dose, 30 g/L.

Significant amounts of Zn, Ca and K were released, and in less extent Mg was also involved on Pb^{2+} sorption. Char 3 is able to leach significant concentrations of carbonates, as demonstrated in section 5.3.4 (Table 22), and a fraction of these metals must be present in the char as carbonates, so Lead precipitation in the carbonate form may have occurred as removal mechanism. The amount of calcium released is much higher than the amount of Lead sorbed indicating that a competition between cations for sorption might have occurred.

The role of cations such as Ca, Mg and K in the sorption of Lead was already demonstrated[108,215-216].

Zinc was probably the differentiation element in Lead sorption mechanism occurring in char 3. Zinc was present in tire derived chars in high concentrations, particularly in char 3, as oxide and/or sulphide and it is known that Zn takes part on Lead ions sorption[221,238]. Co-precipitation and/or complexation involving cation exchange might have occurred as well as the chemisorption of Lead with sulphur, which are both typically slow processes being compatible with the obtained kinetics (Figure 35). Sulphur enriched carbons such as char 3 can show a good performance for Lead ions sorption, because Lead chemical species show affinity towards sulphur[239-241].

Furthermore, char 3 may have its sorption sites more inaccessible since it is the more hydrophobic char taking more time to become wet, and the char with the smallest pore diameter (Table 28). The shift in Lead removal for this char observed at 32 h may be related with the reaching of Lead to the hindered binding sites.

As calcium, the amount of zinc released overcomes the amount of Lead sorbed indicating that competition phenomena during sorption might have occurred.

6.4 Conclusions

The sorption and textural properties of the tars-free chars obtained from the co-pyrolysis of mixtures of pine biomass, used tire rubber and plastic wastes were evaluated in the present work.

The efficiency of the organically treated chars for the removal of Lead (Pb^{2+}) from aqueous solutions was determined as an example of a particular application of these chars as adsorbents.

Chars from the pyrolysis of feedstocks with biomass in their composition are predominantly of macroporous nature; the introduction of tire rubber in the pyrolysis feedstock enhanced the mesoporous content and surface area of the resulting chars.

Pb^{2+} uptake kinetics with the pyrolysis chars was a slow process in which seems to occur Lead sorption-desorption phenomena, due to competition between cations for the binding sites.

The sorption mechanisms for Lead ion varied according to the chars origin: in the case of chars from the pyrolysis feedstock with pine, chemisorption involving complexation with oxygenated surface functional groups followed by cation exchange were the presumable mechanisms.

In tire rubber derived chars the mineral composition played the major role in Lead uptake. The sorption of Pb^{2+} by char from the mixture with 50% tire + 50% plastics was accompanied by a significant release of Ca^{2+} and Zn^{2+}. Lead precipitation as carbonate with Ca^{2+} exchange must have occurred and complexation involving oxides and/or sulphides with Zn^{2+} exchange was the most probable and dominant mechanisms. Concerning Zn, the release of this heavy metal from tire-derived chars must be monitored and controlled since it was previously demonstrated that high concentrations of Zn contributes to the hazardous level and ecotoxicity of the chars. In these chars, the pH is critical, as the optimum solution pH value for Lead sorption was 6, and Zn leaching is significantly reduced for pH above 6-7. Equilibrium must be found in this experimental condition in order to achieve optimal sorption without jeopardise the environmental performance of char as adsorbent avoiding secondary problems of environmental pollution.

CHAPTER 7

7. CONCLUSIONS AND FUTURE WORK

Overview of the main conclusions that arise from the work developed in the thesis as well as suggestions for future research.

7.1 OVERVIEW AND MAIN CONCLUSIONS

The main aim of the present thesis was to study the physico-chemical and ecotoxicological properties, decontamination, and use of chars obtained as by-products in the co-pyrolysis of blends containing plastic wastes, used tire rubber and pine biomass in order to assess their toxicity and potential valorisation as adsorbents.

The char samples used in this thesis were all obtained in batch pyrolysis processes at relatively low temperatures (around 400ºC), short reaction times (15 min), and low heating rates (around 5 ºC/min) that lead to a total residence time of the materials inside the reactor of around 90 min. These experimental conditions are typical of a slow pyrolysis process and were chosen focused in the quality of the liquid product which was the main goal of other studies occurring in parallel. Under these conditions and considering the raw materials used, particularly the woody biomass and used tire rubber, it would be expected significant amounts of carbonaceous solid products with high content of tars. The present thesis aimed to exploit the potential value of those pyrolysis solid products and aspires that the results obtained and presented here can be extensive and applicable to the generality of char materials obtained in the thermochemical processes of wastes obtained under similar conditions of operation.

From chapter 3 it was concluded that the extraction of the tars deposited on the surface of chars is rather important for two main reasons: (i) the decontamination of the chars and (ii) the recovery of an important feedstock of aliphatic and aromatic chemicals, for fuel applications or for other chemical uses.

When plastics are co-processed with pine biomass, the resulting chars can be effectively decontaminated from organics which significantly reduces their ecotoxic behaviour. However, the introduction of used tire rubber in the pyrolysis feedstock demonstrated that raw materials with a high content of metallic elements produce chars that after the treatment to remove tars, still have hazardous and ecotoxic properties due to the presence of metallic contaminants in their matrices. Chapter 3 pointed out that the high concentrations of Zn in tire derived chars were the main responsible by the hazardous and ecotoxic properties of those chars.

Chapter 3 puts in evidence the necessity to combine decontamination treatments directed both to the organic fraction and inorganic fraction of chars. Simultaneously, this chapter emphasized the need for relating ecotoxicological and chemical parameters, including inorganic and organic compounds, in the hazard assessment of chars or other materials and the need of harmonization of the different procedures and classification criteria, because not always the chemical criteria fits the ecotoxicological criteria.

Chapter 4 was centred in the optimization of the organic removal from the chars resulting from the co-pyrolysis of three raw materials (pine biomass + used tire rubber + plastics). It was concluded that hexane is the most efficient extraction solvent to be used because a high extraction yield and removal of ecotoxic compounds were achieved. However, the importance of performing sequential extractions

with solvents of increasing polarity was also put in evidence. The sequential extraction can provide a better removal of the pyrolysis oils/tars that remained in the raw char than any individual extraction.
Chapter 4 also made possible to conclude that the compounds extracted from the chars are mainly aliphatic and aromatic hydrocarbons. The latest ones, composed mainly by PAHs derivatives and phenyl derivatives, were the compounds that mainly contributed to the ecotoxic behaviour of the crude chars. This was an important finding as it allows establishing methodologies with the use of extraction agents directed to those compounds.

Chapter 5 confirmed the substantial contribution of the inorganic fraction and metallic contaminants of the chars for their ecotoxic behaviour. The use of different feedstock mixtures led to the conclusion that chars resulting only from pine biomass co-processed with plastics did not present ecotoxic properties when submitted to an appropriate treatment to reduce the tars content; although this char was the most acidic one with the highest release of inorganic and organic elements, it was classified as non-hazardous and non-ecotoxic material according to the classification criteria used. This is a good indicator for environmental applications of this type of chars.
On the other hand, chapter 5 demonstrated that effectively there was a relationship between zinc and the ecotoxicity of chars obtained from mixtures with tires in their composition. A significant ecotoxicity reduction was registered when these chars were treated with EDTA, being this treatment directed to Zn removal. If these tire-derived chars were considered for environmental applications, particularly water applications, conditions that minimise Zn mobility from the chars should be chosen, for example, pH conditions above 6-7. As alternative, a treatment for Zn removal has to be considered.

In chapter 6, the textural properties of the organically treated chars studied in chapter 5 were evaluated. The main conclusions were that chars from the pyrolysis of feedstocks with biomass in their composition are predominantly of macroporous nature; the introduction of tire rubber in the pyrolysis feedstock enhanced the mesoporous content and surface area of the resulting chars. This is an important indication for the type of molecules that can be accommodated by these materials.
In Chapter 6 it was also presented a particular application of the chars as adsorbents for Lead (Pb^{2+}) in aqueous medium in order to gain some insight about the sorption properties of these materials for heavy metals as well as the related mechanisms. The sorption mechanisms for Lead ion varied according to the feedstock used to produce the char: in the case of chars from the pyrolysis feedstock with pine, chemisorption involving complexation with oxygenated surface functional groups followed by cation exchange were the presumable mechanisms. In tire rubber derived chars, cation exchange must have played the major role, since a significant release of Ca^{2+}, K^{+} and Zn^{2+} accompanied the Lead sorption by char from tire rubber and plastics. This was also the char with the best overall performance for Pb^{2+} sorption.
Also from chapter 6, it can be concluded that these chars have potential to be used as heavy metals sorbents; however, for tire-derived chars, Zn participates actively in the sorption process being important to control its release from the chars in order to avoid secondary environmental pollution problems.

7.2 SUGGESTIONS FOR FUTURE WORK

The use of char materials for several applications rather than energetic valorisation by combustion is growing very fast. Particularly, the increasing trend of using the chars as materials for soil amendment and as adsorbents of pollutants demand additional research related with the overall impacts on health and environment in all stages of their life cycle. This is especially important for complex and heterogeneous feedstocks as it was concluded in the present thesis. In this context, it is suggested to use Municipal Solid Wastes (MSW) samples as pyrolysis feedstocks and the resulting chars should be thoroughly characterised, since the next great step that pyrolysis/carbonization will take in a short future is its industrial implementation for the treatment of MSW.

There are no specific regulations concerning the characterisations and use of char materials, but their huge potential to be used in a variety of applications and the prospect of large scale production will press the development of official methods and classification criteria. This thesis constituted a first step in that framework by employing existing methodologies and criteria adapted to this purpose.

In the present thesis, some representative chemical and ecotoxicological parameters were used to characterize the chars. However, and particularly for chars resulting from more complex feedstocks, the characterisation should also include other classes of organic compounds also known to be formed in pyrolysis processes such as polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Also, other ecotoxicological tests should be used and preferably a test battery with organisms from different trophic levels should be employed in order to give more complete information about the ecotoxic effects.

This thesis also made use of a leaching test that contemplates the release of both organic and inorganic constituents as a tool to assess the environmental hazard assessment of the pyrolysis chars. Not all of the important aspects of the leaching behaviour of a given material can be addressed in one single test. Therefore, as future work it is also suggested that leaching studies of char materials at different experimental conditions can be performed, for example with different leaching solutions, different pHs, among others, to compare mainly the influence in the leaching of organic compounds; this will help the standardization of leaching tests adequate to organic rich-materials.

As final suggestion and considering the porosity and sorption properties of the chars studied in the present thesis, it would be interesting to study their sorption properties for bulky organic molecules as well as for other heavy metals.

8. REFERENCES

[1] Directive 2008/98/EC of the European Parliament and of the Council of the European Union of 19 November 2008 on waste and repealing certain Directives.

[2] Vamvuka, D., Bio-oil, solid and gaseous biofuels from biomass pyrolysis processes - An overview, *International Journal of Energy Research*, 35 (2011) 835–862.

[3] Quek, A., Balasubramanian, R., Liquefaction of waste tires by pyrolysis for oil and chemicals - A review, *Journal of Analytical and Applied Pyrolysis*, 101 (2013) 1–16.

[4] Al-Salem, S.M., Lettieri, P., Baeyens, J., The valorization of plastic solid waste (PSW) by primary to quaternary routes: From re-use to energy and chemicals, *Progress in Energy and Combustion Science*, 36 (2010) 103–129.

[5] Cordero, T., Marquez, F., Rodriguez-Mirasol, J., Rodriguez, J.J., Predicting heating values of lignocellulosics and carbonaceous materials from proximate analysis, *Fuel*, 80 (2001) 1567-1571.

[6] Henrich, E., Bürkle, S., Meza-Renken, Z.I., Rumpel, S., Combustion and gasification kinetics of pyrolysis chars from waste and biomass, *Journal of Analytical and Applied Pyrolysis*, 49 (1999) 221–241.

[7] Janse, A.M.C., de Jonge, H.G., Prins, W., van Swaaij, W.P.M., Combustion kinetics of char obtained by flash pyrolysis of pine wood, *Industrial & Engineering Chemistry Research*, 37 (1998) 3909-3918.

[8] Ryu, C., Sharifiz V.N., Swithenbank, J., Waste pyrolysis and generation of storable char, *International Journal of Energy Research,* 31 (2007) 177–191.

[9] Di Blasi, C., Combustion and gasification rates of lignocellulosic chars, *Progress in Energy and Combustion Science,* 35 (2009) 121–140.

[10] Hwang, I.H., Matsuto, T., Tanaka, N., Sasaki, Y., Tanaami, K., Characterisation of char derived from various types of solid wastes from the standpoint of fuel recovery and pretreatment before landfilling, *Waste Management*, 27 (2007) 1155–1166.

[11] Hwang, I.H., Ouchi, Y., Matsuto, T., Characteristics of leachate from pyrolysis residue of sewage sludge, *Chemosphere*, 68 (2007) 1913–1919.

[12] Hwang, I.H., Matsuto, T., Evaluation of carbonization as a thermal pretreatment method for landfilling by column leaching tests, *Waste Management*, 28 (2008) 3–14.

[13] Karayildirim, T., Yanik, J., Yuksel, M., Bockhorn, H., Characterisation of products from pyrolysis of waste sludges, *Fuel*, 85 (2006) 1498–1508.

[14] Manchón-Vizuete, E., Macías-García, A., Gisbert, A. N., Fernández-González, C., Gómez-Serrano, V., Adsorption of mercury by carbonaceous adsorbents prepared from rubber of tyre wastes, *Journal of Hazardous Materials B,* 119 (2005) 231–238.

[15] Méndez-Liñán, L., López-Garzón, F.J., Domingo-García, M., Pérez-Mendoza, M., Carbon Adsorbents from Polycarbonate Pyrolysis Char Residue: Hydrogen and Methane Storage Capacities, *Energy Fuels,* 24 (2010) 3394–3400.

[16] González, J.F., Román, S., Encinar, J.M., Martínez, G., Pyrolysis of various biomass residues and char utilization for the production of activated carbons, *Journal of Analytical and Applied Pyrolysis,* 85 (2009) 134–141.

[17] Jindarom, C., Meeyoo, V., Kitiyanan, B., Rirksomboon, T., Rangsunvigit, P., Surface characterisation and dye adsorptive capacities of char obtained from pyrolysis/gasification of sewage sludge, *Chemical Engineering Journal*, 133 (2007) 239–246.

[18] Zhang, C., Liang, X., Liu, S., Hydrogen production by catalytic dehydrogenation of methylcyclohexane over Pt catalysts supported on pyrolytic waste tire char*, International Journal of Hydrogen Energy*, 36 (2011) 8902-8907.

[19] Muradov, N., Fidalgo, B., Gujar, A.C., Garceau, N., T-Raissi, A., Production and characterisation of Lemna minor bio-char and its catalytic application for biogas reforming, *Biomass and Bioenergy*, 42 (2012) 123-131.

[20] Ko, J.H., Kwak, Y., Yoo, K., Jeon, J., Park, S.H., Park, Y., Selective catalytic reduction of NOx using RDF char and municipal solid waste char based catalyst*, Journal of Material Cycles and Waste Management*, 13 (2011) 173–179.

[21] Manyá, J.J., Pyrolysis for Biochar Purposes: A Review to Establish Current Knowledge Gaps and Research Needs, *Environmental Science Technology*, 46 (2012) 7939−7954.

[22] Lehmann, J., Rillig, M.C., Thies, J., Masiello, C.A., Hockaday, W.C., Crowley, D., Biochar effects on soil biota - A review, *Soil Biology & Biochemistry*, 43 (2011) 1812-1836.

[23] Griessacher, T., Antrekowitsch, J., Steinlechner, S., Charcoal from agricultural residues as alternative reducing agent in metal recycling. *Biomass and Bioenergy*, 39 (2012) 139-146.

[24] Adrados, A., Lopez-Urionabarrenechea, A., Solar, J., Requies, J., De Marco, I., Cambra, J.F., Upgrading of pyrolysis vapours from biomass carbonization, *Journal of Analytical and Applied Pyrolysis*, 103 (2013) 293–299.

[25] Kumar, M., Gupta, R.C., Industrial Uses of Wood Char, *Energy Sources*, 20:7 (1998) 575-589.

[26] Malkow, T., Novel and innovative pyrolysis and gasification technologies for energy efficient and environmentally sound MSW disposal, *Waste Management*, 24 (2004) 53–79.

[27] Meier, D., van de Beld, B., Bridgwater, A.V., Elliott, D.C., Oasmaa, A., Preto, F., State-of-the-art of fast pyrolysis in IEA bioenergy member countries, *Renewable and Sustainable Energy Reviews,* 20 (2013) 619–641.

[28] United Nations Framework Convention on Climate Change, Kyoto Protocol, 1998. Available online at: http://unfccc.int/resource/docs/convkp/kpeng.pdf

[29] Bernardo, M.S., Lapa, N., Barbosa, R., Gonçalves, M., Mendes, B., Pinto, F., Gulyurtlu, I., Chemical and ecotoxicological characterisation of solid residues produced during the co-pyrolysis of plastics and pine biomass, *Journal of Hazardous Materials*, 166 (2009) 309–317.

[30] Bernardo, M.S., Gonçalves, M., Lapa, N., Barbosa, R., Mendes, B., Pinto, F., Gulyurtlu, I., Determination of aromatic compounds in eluates of pyrolysis solid residues using HS-GC–MS and DLLME–GC–MS, *Talanta*, 80 (2009) 104–108.

[31] Bernardo, M., Lapa, N., Gonçalves, M., Barbosa, R., Mendes, B., Pinto, F., Gulyurtlu, I, Evaluation of the environmental hazard of char residues produced in the co-pyrolysis of different wastes: chemical and ecotoxicological characterisation, Book of Proceedings of the XII International Waste Management and Landfill Symposium, Sardinia, Italy, 5-9 October 2009.

[32] Hoornweg, D., Bhada-Tata, P., What a waste: a global review of solid waste management. Urban development series; knowledge papers nº15. Washington D.C.-The World bank, 2012. Available online at: http://documents.worldbank.org/curated/en/2012/03/16537275/waste-global-review-solid-waste-management

[33] Bridgwater, A.V., Waste incineration and pyrolysis, *Resource Recovery and Conservation*, 5 (1980) 99-115.

[34] DEFRA - Department for Environment, Food & Rural Affairs – UK government, Incineration of Municipal Solid Waste, 2013. Available online at: https://www.gov.uk/government/publications/incineration-of-municipal-solid-waste

[35] C-Tech Innovation Ltd, Thermal methods of municipal waste treatment - report of the Biffaward Programme on Sustainable Resource Use, UK, 2003. Available online at: http://www.ctechinnovation.com/thermal.pdf

[36] California Integrated Waste Management Board, Technology Evaluation and Economic Analysis of Waste Tire Pyrolysis, Gasification, and Liquefaction, California, USA, 2006. Available online at: http://www.calrecycle.ca.gov/publications/Detail.aspx?PublicationID=1174

[37] http://images01.olx.com.pk/ui/19/58/81/1357984121_471335781_1-Pictures-of--Fuel-Oil-Furnace-Oil-Tire-Oil-Rubber-Oil-Pyrolysis-Oil-Tyre-Oil-Cheap-Oil-Trading.jpg

[38] http://www.ecn.nl/uploads/RTEmagicC_biochar.jpg.jpg

[39] Martínez, J.D., Puy, N., Murillo, R., García, T., Navarro, M.V., Mastral, A.M., Waste tyre pyrolysis–A review, *Renewable and Sustainable Energy Reviews*, 23 (2013) 179–213.

[40] Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the incineration of waste.

[41] Scheirs, J., Kaminsky, W., Feedstock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels, Wiley series in Polymer science, John Wiley & Sons Ltd, Chichester, UK, 2006.

[42] Al-Salem, S.M., Lettieri, P., Baeyens, J., Recycling and recovery routes of plastic solid waste (PSW): A review, *Waste Management,* 29 (2009) 2625–2643.

[43] Panda, A.K., Singh, R.K., Mishra, D.K., Thermolysis of waste plastics to liquid fuel. A suitable method for plastic waste management and manufacture of value added products - A world prospective, *Renewable and Sustainable Energy Reviews,* 14 (2010) 233–248.

[44] BIO Intelligence Service, Plastic waste in the environment, Final report prepared for European Commission DG ENV with the specific contract 07.0307/2009/545281/ETU/G2 under Framework contract ENV.G.4/FRA/2008/0112, 2011. Available online at: http://ec.europa.eu/environment/waste/studies/pdf/plastics.pdf

[45] European Commission, Joint Research Centre, Institute for Prospective Technological Studies, Assessment of the environmental advantages and drawbacks of existing and emerging polymers recovery processes, 2007. Available online at: http://ftp.jrc.es/EURdoc/eur22939en.pdf

[46] Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste.

[47] ETRMA – European Tyre and Rubber Manufacturer's Association, Annual Report 2011/2012. Available online at: http://www.etrma.org/uploads/Modules/Documentsmanager/etrma-annual-report-2012_8_def.pdf

[48] Antoniou, N., Zabaniotou, A., Features of an efficient and environmentally attractive used tyres pyrolysis with energy and material recovery, *Renewable and Sustainable Energy Reviews,* 20 (2013) 539–558.

[49] OECD/IEA, Technology roadmap - Biofuels for transport, France, 2011. Available online at: http://www.iea.org/publications/freepublications/publication/Biofuels_Roadmap_WEB.pdf

[50] Isahak, W.N.R.W., Hisham, M.W.M., Yarmo, M.A., Hin, T., A review on bio-oil production from biomass by using pyrolysis method, *Renewable and Sustainable Energy Reviews,* 16 (2012) 5910–5923.

[51] ICNF - Instituto da Conservação da Natureza e das Florestas, IFN6 – Áreas dos usos do solo e das espécies florestais de Portugal continental. Resultados preliminaries, Lisboa, 2013. Available online at: http://www.icnf.pt/portal/florestas/ifn/resource/ficheiros/ifn/ifn6-res-prelimv1-1

[52] AEBIOM – European Biomass Association, Procurement of forest residues - RESTMAC project 'Creating Markets for Renewable Energy Technologies - EU RES technology marketing campaign, 2007. Available online at: http://www.aebiom.org/wp/wp-content/uploads/file/Publications/Forest_residues_August2007.pdf

[53] Ingram, L., Mohan, D., Bricka, M., Steele, P., Strobel, D., Crocker, D., Mitchell, B., Mohammad, J., Cantrell, K., Pittman, C.U., Pyrolysis of Wood and Bark in an Auger Reactor: Physical Properties and Chemical Analysis of the Produced Bio-oils, *Energy & Fuels,* 22 (2008) 614–625.

[54] Amutio, M., Lopez, G., Artetxe, M., Elordi, G., Olazar, M., Bilbao, J., Influence of temperature on biomass pyrolysis in a conical spouted bed reactor, *Resources, Conservation and Recycling,* 59 (2012) 23– 31.

[55] Thangalazhy-Gopakumar, S., Adhikari, S., Ravindran, H., Gupta, R.B., Fasina, O., Tu, M., Fernando, S.D., Physiochemical properties of bio-oil produced at various temperatures from pine wood using an auger reactor, *Bioresource Technology*, 101 (2010) 8389–8395.

[56] DeSisto, W. J., Hill, N., Beis, S.H., Mukkamala, S., Joseph, J., Baker, C., Ong, T., Stemmler, E.A., Wheeler, M.C., Frederick, B.G., van Heiningen, A., Fast pyrolysis of pine sawdust in a fluidized-bed reactor, *Energy Fuels*, 24 (2010) 2642–2651.

[57] Puy, N., Murillo, R., Navarro, M.V., López, J.M., Rieradevall, J., Fowler, G., Aranguren, I., García, T., Bartrolí, J., Mastral, A.M., Valorisation of forestry waste by pyrolysis in an auger reactor, *Waste Management*, 31 (2011) 1339–1349.

[58] Jacobson, K., Maheria, K.C., Dalai, A.K., Bio-oil valorization: A review, *Renewable and Sustainable Energy Reviews*, 23 (2013) 91–106.

[59] Xiu, S., Shahbazi, A., Bio-oil production and upgrading research: A review, *Renewable and Sustainable Energy Reviews,* 16 (2012) 4406–4414.

[60] Sharypov, V.I., Marin, N., Beregovtsova, N.G., Baryshnikov, S.V., Kuznetsov, B.N., Cebolla, V.L., Weber, J.V., Co-pyrolysis of wood biomass and synthetic polymer mixtures. Part I: influence of experimental conditions on the evolution of solids, liquids and gases, *Journal of Analytical and Applied Pyrolysis*, 64 (2002) 15–28.

[61] Marin, N., Collura, S., Sharypov, V.I., Beregovtsova, N.G., Baryshnikov, S.V., Kutnetzov, B.N., Cebolla, V., Weber, J.V., Copyrolysis of wood biomass and synthetic polymers mixtures. Part II: characterisation of the liquid phases, *Journal of Analytical and Applied Pyrolysis*, 65 (2002) 41–55.

[62] Rutkowski, P., Influence of zinc chloride addition on the chemical structure of bio-oil obtained during co-pyrolysis of wood/synthetic polymer blends, *Waste Management*, 29 (2009) 2983–2993.

[63] Paradela, F., Pinto, F., Gulyurtlu, I., Cabrita, I., Lapa, N., Study of the co-pyrolysis of biomass and plastic wastes, *Clean Technologies and Environmental Policy*, 11 (2009) 115-122.

[64] Zhou, L., Wang, Y., Huang, Q., Cai, J., Thermogravimetric characteristics and kinetic of plastic and biomass blends co-pyrolysis, *Fuel Processing Technology*, 87 (2006) 963–969.

[65] Bhattacharya, P., Steele, P.H., Hassan, E.B.M., Mitchell, B., Ingram, L., Pittman Jr, C.U., Wood/plastic copyrolysis in an auger reactor: Chemical and physical analysis of the products, *Fuel*, 88 (2009) 1251–1260.

[66] Brebu, M., Ucar, S., Vasile, C., Yanik, J., Co-pyrolysis of pine cone with synthetic polymers, *Fuel*, 89 (2010) 1911–1918.

[67] Han, B., Chen, Y., Wu, Y., Hua, D., Chen, Z., Feng, W., Yang, M., Xie, Q., Co-pyrolysis behaviors and kinetics of plastics–biomass blends through thermogravimetric analysis, *Journal of Thermal Analysis and Calorimetry*, In press, 2013, doi: 10.1007/s10973-013-3228-7.

[68] Berrueco, C., Ceamanos, J., Esperanza E., Mastral, J.F., Experimental study of co-pyrolysis of polyethylene/sawdust mixtures, *Thermal Science*, 8 (2004), 2, 65-80.

[69] Cao, Q., Jin, L., Bao, W., Lv, Y., Investigations into the characteristics of oils produced from co-pyrolysis of biomass and tire, *Fuel Processing Technology*, 90 (2009) 337–342.

[70] Miranda, M., *Reciclagem Termoquímica de Resíduos de Plásticos e de Pneus por Pirólise*, PhD thesis submitted to Universidade de Aveiro, Aveiro, Portugal, 2009.

[71] Paradela, F., *Estudo da pirólise de misturas de resíduos de plásticos, pneus e biomassa*, PhD thesis submitted to Universidade Nova de Lisboa, Lisboa, Portugal, 2012.

[72] FItzer, E., Kochling, K.H., Boehm, H.P., Marsh, H., Recommended Terminology for the description of carbon as a solid, *Pure and Applied Chemistry*, 67:3 (1995) 473-506.

[73] Antal Jr, M.J., Grønli, M., The Art, Science, and Technology of Charcoal Production*, Industrial and Engineering Chemistry Research*, 42 (2003) 1619-1640.

[74] Yang, H., Yan, R., Chen, H., Lee, D.H., Zheng, C., Characteristics of hemicellulose, cellulose and lignin pyrolysis, *Fuel*, 86 (2007) 1781–1788.

[75] Raveendran, K., Ganesh A., Khilar, K.C., Pyrolysis characteristics of biomass and biomass components, *Fuel,* 75, 8 (1996) 987-998.

[76] Ball, R., McIntosh, A.C., Brindley, J., The role of char-forming processes in the thermal decomposition of cellulose, *Physical Chemistry Chemical Physics*, 1 (1999) 5035-5043.

[77] Shen, D.K., Gu, S., Bridgwater, A.V., The thermal performance of the polysaccharides extracted from hardwood: Cellulose and hemicellulose, *Carbohydrate Polymers,* 82 (2010) 39–45.

[78] Patwardhan, P.R., Brown, R.C., Shanks, B.H., Product Distribution from the Fast Pyrolysis of Hemicellulose, *ChemSusChem*, 4 (2011) 636 – 643.

[79] Hosoya, T., Kawamoto, H., Saka, S., Solid/liquid- and vapor-phase interactions between cellulose- and lignin-derived pyrolysis products, *Journal of Analytical and Applied Pyrolysis*, 85 (2009) 237–246.

[80] Hosoya, T., Kawamoto, H., Saka, S., Secondary reactions of lignin-derived primary tar components, *Journal of Analytical and Applied Pyrolysis,* 83 (2008) 78–87.

[81] Guerrero, M., Ruiz, M.P., Millera, A, Alzueta, M.U., Bilbao, R., Characterisation of Biomass Chars Formed under Different Devolatilization Conditions: Differences between Rice Husk and Eucalyptus, *Energy & Fuels,* 22 (2008) 1275–1284.

[82] Apaydın-Varol, E., Pütün, A.E., Preparation and characterisation of pyrolytic chars from different biomass samples, *Journal of Analytical and Applied Pyrolysis,* 98 (2012) 29–3.

[83] Beyler, C. L., Hirschler, M., Thermal decomposition of polymers, in: DiNenno, P.J. (Ed.), Handbook of Fire Protection Engineering, 3rd edition, National Fire Protection Association, USA, 2002, pp. 1-110 – 1-131.

[84] Cozzani, V., Characterisation of Coke Formed in the Pyrolysis of Polyethylene, *Industrial and Engineering Chemistry Research,* 36 (1997) 5090-5095.

[85] Karaduman, A., Şimşek, E.H., Çiçek, B., Bilgesu, A.Y., Thermal degradation of polystyrene wastes in various solvents, *Journal of Analytical and Applied Pyrolysis*, 62 (2002) 273–280.

[86] Liu, Y., Qian, J., Wang, J., Pyrolysis of polystyrene waste in a fluidized-bed reactor to obtain styrene monomer and gasoline fraction, *Fuel Processing Technology*, 63 (2000) 45–55.

[87] Williams, P.T., Pyrolysis of waste tyres: A review, *Waste Management*, 33 (2013) 1714–1728.

[88] Shah, J., Jan, M.R., Mabood, F., Shahid, M., Conversion of Waste Tyres into Carbon Black and their Utilization as Adsorbent, *Journal of the Chinese Chemical Society*, 53 (2006) 1085-1089.

[89] Miguel, G.S., Fowler, G.D., Sollars, C.J., Pyrolysis of Tire Rubber: Porosity and Adsorption Characteristics of the Pyrolytic Chars, *Industrial and Engineering Chemistry Research,* 37 (1998) 2430-2435.

[90] Quek, A., Balasubramanian, R., Preparation and characterisation of low energy post-pyrolysis oxygenated tire char, *Chemical Engineering Journal*, 170 (2011) 194–201.

[91] Chattopadhyay, J., Kim, C., Kim, R., Pak, D., Thermogravimetric characteristics and kinetic study of biomass co-pyrolysis with plastics, *Korean Journal of Chemical Engineering*, 25(5) (2008) 1047-1053.

[92] Lahijani, P., Zainal, Z.A., Mohamed, A.R., Mohammadi, M., Co-gasification of tire and biomass for enhancement of tire-char reactivity in CO2 gasification process, *Bioresource Technology,* 138 (2013) 124–130.

[93] Agirre, I., Griessacher, T., Rösler, G., Antrekowitsch, J., Production of charcoal as an alternative reducing agent from agricultural residues using a semi-continuous semi-pilot scale pyrolysis screw reactor, *Fuel Processing Technology,* 106 (2013) 114–121.

[94] Suopajärvi, H., Pongrácz, E., Fabritius, T., The potential of using biomass-based reducing agents in the blast furnace: A review of thermochemical conversion technologies and assessments related to sustainability, *Renewable and Sustainable Energy Reviews*, 25 (2013) 511–528.

[95] Kastner, J. R., Miller, J., Kolar, P., Das, K.C., Catalytic ozonation of ammonia using biomass char and wood fly ash, *Chemosphere*, 75 (2009) 739–744.

[96] El-Rub, Z.A., Bramer, E.A., Brem, G., Experimental comparison of biomass chars with other catalysts for tar reduction, *Fuel*, 87 (2008) 2243–2252.

[97] Meyer, S., Glaser, B., Quicker, P., Technical, Economical, and Climate-Related Aspects of Biochar Production Technologies: A Literature Review, *Environmental Science Technology*, 45 (2011) 9473–9483.

[98] Li, M., Liu, Q., Guo, L., Zhang, Y., Lou, Z., Wang, Y., Qian, G., Cu(II) removal from aqueous solution by Spartina alterniflora derived biochar, *Bioresource Technology,* 141 (2013) 83–88.

[99] Meng, J., Wang, L., Liu, X., Wu, J., Brookes, P.C., Xu, J., Physicochemical properties of biochar produced from aerobically composted swine manure and its potential use as an environmental amendment, *Bioresource Technology*, 142 (2013) 641–646.

[100] Deveci, H., Kar, Y., Adsorption of hexavalent chromium from aqueous solutions by bio-chars obtained during biomass pyrolysis, *Journal of Industrial and Engineering Chemistry*, 19 (2013) 190–196.

[101] Lian, F., Song, Z., Liu, Z., Zhu, L., Xing, B., Mechanistic understanding of tetracycline sorption on waste tire powder and its chars as affected by Cu2+ and pH, *Environmental Pollution*, 178 (2013) 264-270.

[102] Ahmad, M., Lee, S.S., Rajapaksha, A.U., Vithanage, M., Zhang, M., Cho, J.S., Lee, S., Ok, Y.S., Trichloroethylene adsorption by pine needle biochars produced at various pyrolysis temperatures, *Bioresource Technology,* 143 (2013) 615-622.

[103] Monsalvo, V.M., Mohedano, A.F., Rodriguez, J.J., Adsorption of 4-chlorophenol by inexpensive sewage sludge-based adsorbents, *Chemical Engineering Research and Design,* 90 (2012) 1807–1814.

[104] Agrafioti, E., Bouras, G., Kalderis, D., Diamadopoulos, E., Biochar production by sewage sludge pyrolysis, *Journal of Analytical and Applied Pyrolysis*, 101 (2013) 72–78.

[105] Sun, C., Snape, C.E., Liu, H., Development of Low Cost Functional Adsorbents for Control of Mercury (Hg) Emissions from Coal Combustion, *Energy Fuels*, 27(7) (2013) 3875–3882.

[106] Liu, Z., Zhang, F., Wu, J., Characterisation and application of chars produced from pinewood pyrolysis and hydrothermal treatment, *Fuel*, 89 (2010) 510–514.

[107] Zhou, Z., Shi, D., Qiu, Y., Sheng, G. D., Sorptive domains of pine chars as probed by benzene and nitrobenzene, *Environmental Pollution*, 158 (2010) 201–206.

[108] Mohan, D., Pittman Jr, C.U., Bricka, M., Smith, F., Yanceyd, B., Mohammad, J., Steele, P.H., Alexandre-Franco, M.F., Gómez-Serrano, V., Gong, H., Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production, *Journal of Colloid and Interface Science*, 310 (2007) 57–73.

[109] Chen, B., Zhou D., Zhu, L., Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures, *Environmental Science and Technology*, 42 (2008) 5137–5143.

[110] Nguyen, T.H., Cho, H., Poster, D.L., Ball, W.P., Evidence for a pore-filling mechanism in the adsorption of aromatic hydrocarbons to a natural wood char, *Environmental Science and Technology*, 41 (2007) 1212-1217.

[111] Wang, Y., Wang, L., Fang, G., Herath, H.M.S.K., Wang, Y., Cang, L., Xie, Z., Zhou, D., Enhanced PCBs sorption on biochars as affected by environmental factors: Humic acid and metal cations, *Environmental Pollution*, 172 (2013) 86-93.

[112] Mohan, D., Sharma, R., Singh, V.K., Steele, P., Pittman Jr, C.U., Fluoride Removal from Water using Bio-Char, a Green Waste, Low-Cost Adsorbent: Equilibrium Uptake and Sorption Dynamics, *Industrial and Engineering Chemistry Research,* 51 (2012) 900–914.

[113] Chen, Z., Chen, B., Chiou, C.T., Fast and Slow Rates of Naphthalene Sorption to Biochars Produced at Different Temperatures, *Environmental Science and Technology*, 46 (2012) 11104−11111.

[114] BaoLiang, C., DanDan, Z., LiZhong, Z., XueYou, S., Sorption characteristics and mechanisms of organic contaminant to carbonaceous biosorbents in aqueous solution, *Science in China Series B: Chemistry*, 51 (2008) 464-472.

[115] Helleur, R., Popovic, N., Ikura, M., Stanciulescu, M., Liu, D., Characterisation and potential applications of pyrolytic char from ablative pyrolysis of used tires, *Journal of Analytical and Applied Pyrolysis,* 58–59 (2001) 813–824.

[116] Mui, E.L.K., Cheung, W.H., McKay, G., Tyre char preparation from waste tyre rubber for dye removal from effluents, *Journal of Hazardous Materials,* 175 (2010) 151–158.

[117] Lian, F., Huang, F., Chen, W., Xing, B., Zhu, L., Sorption of apolar and polar organic contaminants by waste tire rubber and its chars in single- and bi-solute systems, *Environmental Pollution,* 159 (2011) 850-857.

[118] Troca-Torrado, C., Alexandre-Franco, M., Fernández-González, C., Alfaro-Domínguez, M., Gómez-Serrano, V., Development of adsorbents from used tire rubber. Their use in the adsorption of organic and inorganic solutes in aqueous solution, *Fuel Processing Technology,* 92 (2011) 206–212.

[119] Mastral, A.M., García, T., Callén, M.S., Navarro, M.V., Galbán, J., Removal of Naphthalene, Phenanthrene, and Pyrene by Sorbents from Hot Gas, *Environmental Science and Technology*, 35 (2001) 2395-2400.

[120] Alexandre-Franco, M., Fernández-González, C., Macías-García, A., Gómez-Serrano, V., Uptake of lead by carbonaceous adsorbents developed from tire rubber, *Adsorption,* 14 (2008) 591–600.

[121] Alexandre-Franco, M., Fernández-González, C., Alfaro-Domínguez, M., Gómez-Serrano, V., Adsorption of cadmium on carbonaceous adsorbents developed from used tire rubber, *Journal of Environmental Management*, 92 (2011) 2193-2200.

[122] Quek, A., Zhao, X., Balasubramanian, R., Mechanistic Insights into Copper Removal by Pyrolytic Tire Char through Equilibrium Studies, *Industrial and Engineering Chemistry Research,* 49 (2010) 4528–4534.

[123] van der Sloot, H.A., Comans, R.N.J., Meeussen, J.C.L., Dijkstra, J.J., Leaching methods for soil, sludge and treated biowaste, Final Report; Desk study no. 23; Project HORIZONTAL, Netherlands, 2004. Available online at: www.ecn.nl/horizontal

[124] Townsend, T., Jang, Y., Tolaymat, T., Leaching Tests for Evaluating Risk in Solid Waste Management Decision Making, Final report, Department of Environmental Engineering Sciences, University of Florida, USA, 2003.

[125] van der Sloot, H.A., Heasman, L., Quevauviller, P., Harmonization of leaching/extraction tests. Studies in Environmental Science, Volume 70, Elsevier Science, Amsterdam, Netherlands, 1997.

[126] United States Environmental Protection Agency (USEPA). Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods - Method 1311 Toxicity Characteristic Leaching Procedure, USA, 1992. Available online at: http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/1311.pdf

[127] Kosson, D.S., van der Sloot, H.A., Sanchez, F., Garrabrant, A.C., An Integrated Framework for Evaluating Leaching in Waste Management and Utilization of Secondary Materials, Environmental. Engineering Science, 19 (2002) 159–203.

[128] Ghosh, A., Mukiibi, M., Ela, W., TCLP underestimates leaching of arsenic from solid residuals under landfill conditions, *Environmental Science and Technology*, 38 (2004) 4677–4682.

[129] Hooper, K., Iskander, M., Sivia, G., Hussein, F., Hsu, J., Deguzman, M., Odion, Z., Ilejay, Z., Sy, F., Petreas, M., Simmons, B., Toxicity characteristic leaching procedure fails to extract oxoanion-forming elements that are extracted by municipal solid waste leachates, *Environmental Science and Technology*, 32 (1998) 3825–3830.

[130] Mantis, I., Voutsa, D., Samara, C., Assessment of the environmental hazard from municipal and industrial wastewater treatment sludge by employing chemical and biological methods, *Ecotoxicology and Environmental Safety*, 62 (2005) 397–407.

[131] Roskam, G.D., Comans, R.N.J., Availability and leaching of polycyclic aromatic hydrocarbons: Controlling processes and comparison of testing methods, *Waste Management*, 29 (2009) 136–142.

[132] Leonard, S.A., Stegemann, J.A., Roy, A., Characterisation of acid tars, *Journal of Hazardous Materials*, 175 (2010) 382–392.

[133] Tiruta-Barna, L., Fantozzi-Merle, C., de Brauer, C., Barna, R., Leaching behaviour of low level organic pollutants contained in cement-based materials: Experimental methodology and modelling approach, *Journal of Hazardous Materials B*, 138 (2006) 331–342.

[134] Sakai, S., Urano, S., Takatsuki, H., Leaching behavior of PCBs and PCDDs/DFs from some waste materials, *Waste Management*, 20 (2000) 241-247.

[135] Roussat, N., Méhu, J., Abdelghafour, M., Brula, P., Leaching behaviour of hazardous demolition waste, *Waste Management*, 28 (2008) 2032–2040.

[136] Schultz, E., Vaajasaari, K., Joutti, A., Ahtiainen, J., Toxicity of Industrial Wastes and Waste Leaching Test Eluates Containing Organic Compounds, *Ecotoxicology and Environmental Safety*, 52, 248-255 (2002).

[137] Vaajasaari, K., Kulovaara, M., Joutti, A., Schultz, E., Soljamo, K., Hazardous properties of paint residues from the furniture industry, *Journal of Hazardous Materials*, 106 (2004) 71–79.

[138] Kim, Y., Osako, M., Sakai, S., Leaching characteristics of polybrominated diphenyl ethers (PBDEs) from flame-retardant plastics, *Chemosphere*, 65 (2006) 506–513.

[139] Hjelmar, O., Broholm, K., Larsson, L.B., Wahlstrøm, M., Development of tests for characterizing the leaching of organic compounds from contaminated soils and waste products, NT Technical Report 464, NT Project 1394-97, DHI Water & Environment, Denmark, 2000.

[140] Comans, R.N.J., Development of standard leaching tests for organic pollutants in soils, sediments and granular waste materials, progress report of the project under the Programme Standards, Measurements and Testing of the European Commission, Contract nº SMT4-CT97-2160, Netherlands Energy Research Foundation (ECN), Netherlands, 2001.

[141] Hansen, J.B., Gamst, J., Laine-Ylijoki, J., Wahlström, M., Larsson, L., Hjelmar, O., A framework for using leaching test for non-volatile organic compounds, NT Technical Report 585, Nordic Innovation Centre project number: 04050, Oslo, Norway, 2005.

[142] ISO/TS 21268 – 2. Soil Quality – Leaching Procedure for Subsequent Chemical and Ecotoxicological Testing of Soil and Soil Materials. International Organization for Standardization. Geneva, Switzerland, 2007.

[143] Miguel, G.S., Fowler, G.D., Sollars, C.J., The leaching of inorganic species from activated carbons produced from waste tyre rubber, *Water Research*, 36 (2002) 1939–1946.

[144] Agrafiota, E., Bouras, G., Kalderis, D., Diamadopoulos, E., Biochar production by sewage sludge pyrolysis, *Journal of Analytical and Applied Pyrolysis*, 101 (2013) 72–78.

[145] Galhetas, M., Lopes, H., Freire, M., Abelha, P., Pinto, F., Gulyurtlu, I., Characterisation, leachability and valorization through combustion of residual chars from gasification of coals with pine, *Waste Management*, 32 (2012) 769–779.

[146] Griffith, S.M., Banowetz, G.M., Gady, D., Chemical characterisation of chars developed from thermochemical treatment of Kentucky bluegrass seed screenings, *Chemosphere*, 92 (10) (2013) 1275-1279.

[147] Fuente-Cuesta, A., Lopez-Anton, M.A., Diaz-Somoano, M., van Zomeren, A., Cieplik, M., Martínez-Tarazona, M.R., Leaching of Major and Trace Elements From Paper-Plastic Gasification Chars: An Experimental and Modelling Study, *Journal of Hazardous Materials*, 244– 245 (2013) 70– 76.

[148] Li, C., Suzukib, K., Resources, properties and utilization of tar, *Resources, Conservation and Recycling*, 54 (2010) 905–915.

[149] Council Directive 91/689/CEE of 12 December 1991 on hazardous waste.

[150] United States Environmental Protection Agency (USEPA). Environmental databases, ECOTOX database. Available online at: http://cfpub.epa.gov/ecotox/

[151] European Standard 14735:2005. Characterisation of waste – Preparation of waste samples for ecotoxicity tests, European Committee for Standardization, Brussels, Belgium, 2005.

[152] Pandard, P., Devillers, J., Charissou, A., Poulsen, V., Jourdain, M., Férard, J., Grand, C., Bispo, A., Selecting a battery of bioassays for ecotoxicological characterisation of wastes, *Science of the Total Environment*, 363 (2006) 114–125.

[153] Wilke, B.-M., Riepert, F., Koch, C., Kühne, T., Ecotoxicological characterisation of hazardous wastes, *Ecotoxicology and Environmental Safety*, 70 (2008) 283–293.

[154] Pablos, M.V., Fernández, C., Babín, M., Navas, J.M., Carbonell, G., Martini, F., García-Hortigüela, P., Tarazona, J.V., Use of a novel battery of bioassays for the biological characterisation of hazardous wastes, *Ecotoxicology and Environmental Safety*, 72 (2009) 1594–1600.

[155] Rojíčková-Padrtová, R., Maršálek, B., Holoubek, I., Evaluation of alternative and standards toxicity assays for screening of environmental samples: selection of an optimal test battery, *Chemosphere*, 37 (3) (1998) 495-507.

[156] ISO 17616:2008. Soil quality -- Guidance on the choice and evaluation of bioassays for ecotoxicological characterisation of soils and soil materials, International Organization for Standardization. Geneva, Switzerland, 2008.

[157] Regulation (EC) Nº 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006.

[158] Council Regulation (EC) Nº 440/2008 of 30 May 2008 laying down test methods pursuant to Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH).

[159] Regulation (EC) Nº 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC.

[160] CEN/TR 16110:2010. Characterisation of waste - Guidance on the use of ecotoxicity tests applied to waste, European Committee for Standardization, Brussels, Belgium, 2010.

[161] Ministere de l'Amenagement du Territoire et de l'Environnement, Criteria and Evaluation Methods of the Ecotoxicity of Waste, Directorate for Prevention Pollutions and Risk Control, Products and Wastes Division, Waste Management and Treatment Office, Paris, France, 1998.

[162] Oleszczuk, P., Jośko, I., Kuśmierz, M., Biochar properties regarding to contaminants content and ecotoxicological assessment, *Journal of Hazardous Materials*, 260 (2013) 375– 382.

[163] Directive 2004/42/CE of the European Parliament and of the Council of 21 April 2004 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain paints and varnishes and vehicle refinishing products and amending Directive 1999/13/EC.

[164] World Health Organization (WHO), Indoor air quality: organic pollutants. Report on a WHO Meeting, Berlin, 23-27 August 1987. EURO Reports and Studies 111. Copenhagen, World Health Organization Regional Office for Europe, 1989.

[165] Annual Book of ASTM Standards, vol. 05.06. ASTM D121 – Standard Terminology of Coal and Coke, American Society for Testing and Materials, USA, 2000 edition.

[166] United States Environmental Protection Agency (USEPA), SW-846 Test Methods for Evaluating Solid Wastes-Physical/Chemical Methods, Method 3052 - Microwave Assisted Acid Digestion of Siliceous and Organically based Matrices, USA, 1996.

[167] Gao, N., Li, A., Quan, C., Du, L., Duan, Y., TG–FTIR and Py–GC/MS analysis on pyrolysis and combustion of pine sawdust, *Journal of Analytical and Applied Pyrolysis*, 100 (2013) 26–32.

[168] Grammelis, P., Basinas, P., Malliopoulou, A., Sakellaropoulos, G., Pyrolysis kinetics and combustion characteristics of waste recovered fuels, *Fuel*, 88 (2009) 195–205.

[169] Peterson, J.D., Vyazovkin, S., Wight, C.A., Kinetics of the Thermal and Thermo-Oxidative Degradation of Polystyrene, Polyethylene and Poly(propylene), *Macromolecular Chemistry and Physics*, 202 (2001) 775–784.

[170] Juma, M., Koreňová, Z., Markoš, J., Annus, J., Jelemenský, Ľ., Pyrolysis and combustion of scrap tire, *Petroleum & Coal*, 48 (1) (2006) 15-26.

[171] Tang, Y., Ma, X., Lai, Z., Zhou, D., Chen, Y., Thermogravimetric characteristics and combustion emissions of rubbers and polyvinyl chloride in N2/O2 and CO2/O2 atmospheres, *Fuel*, 104 (2013) 508–514.

[172] Coran, A.Y., Vulcanization, in: Mark, J.E., Erman, B., Eirich F.R. (Eds.), The Science and Technology of Rubber, Elsevier Academic Press, USA, 2005, pp. 321-364.

[173] Mouri, H., Fillers, in: De, S.K., White, J.R. (Eds.), Rubber Technologist's Handbook, Rapra Technology Limited, UK, 2001, pp. 131-165.

[174] Zweifel, H., Maier, R.D., Schiller, M., Plastics Additives Handbook, 6th edition, Hanser Publications, USA, 2009.

[175] Paradela, F., Estudo da pirólise de misturas de resíduos plásticos e de biomassa, Thesis submitted to Faculdade de Ciências e Tecnologia-Universidade Nova de Lisboa for the Master degree in Energy and Bioenergy, Lisboa, Portugal, 2007.

[176] Paradela, F., Pinto, F., Ramos, A.M., Gulyurtlu, I., Cabrita, I., Study of the slow batch pyrolysis of mixtures of plastics, tyres and forestry biomass wastes, *Journal of Analytical and Applied Pyrolysis*, 85 (2009) 392–398.

[177] United States Environmental Protection Agency (USEPA), SW-846 Test Methods for Evaluating Solid Wastes-Physical/Chemical Methods, Method 3015A - Microwave Assisted Acid Digestion of Aqueous Samples and Extracts, USA, 2007.

[178] ISO 11348 – 3, Water quality – determination of the inhibitory effect of water samples on the light emission of *Vibrio fischeri* (luminescent bacteria test) – Part 3: method using freeze/dried bacteria, International Organization for Standardization, Geneva, Switzerland, 2003.

[179] Lapa, N., Barbosa, R., Morais, J., Mendes, B., Méhu, J., Oliveira, J.F.S., Ecotoxicological assessment of leachates from MSWI bottom ashes, *Waste Management*, 22 (2002) 583–593.

[180] Council Decision of 19 December 2002 (2003/33/EC) establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC.

[181] European Standard EN 12457-2:2002. Characterisation of waste – Leaching - Compliance test for leaching of granular waste materials and sludges – Part 2: one stage batch test at a liquid to solid ratio of 10 L/kg for materials with particle size below 4 mm (without or with size reduction), European Committee for Standardization, Brussels, Belgium, 2002.

[182] Kistler, R.C., Widmer, F., Brunner, P.H., Behavior of chromium, nickel, copper, zinc, cadmium, mercury, and lead during the pyrolysis of sewage sludge, *Environmental Science and Technology*, 21 (1987) 704-708.

[183] Costa, P., Produção de hidrocarbonetos líquidos e gasosos por pirólise de resíduos plásticos, Thesis submitted to Faculdade de Ciências e Tecnologia-Universidade Nova de Lisboa for the doctoral degree in Chemical Engineering, Lisboa, Portugal, 2006.

[184] Ren, S., Frymier, P.D., Toxicity of metals and organic chemicals evaluated with bioluminescence assays, *Chemosphere*, 58 (2005) 543–550.

[185] Mansfield, C.T., Barman, B.N., Thomas, J.V., Mehrotra, A.K., Philp, R.P., Petroleum and Coal-review, *Analytical Chemistry*, 69 (1997) 59R-93R.

[186] Brown, D.G., Gupta, L., Kim, T., Moo-Young, H.K.. Coleman, A.J., Comparative assessment of coal tars obtained from 10 former manufactured gas plant sites in the Eastern United States, *Chemosphere*, 65 (2006) 1562–1569.

[187] Benhabib, K., Faure, P., Sardin, M., Simonnot, M., Characteristics of a solid coal tar sampled from a contaminated soil and of the organics transferred into water, *Fuel*, 89 (2010) 352–359.

[188] Guillén, M.D., Domínguez, A., Iglesias, M.J., Blanco, C.G., Semiquantitative gas chromatographic analysis of the volatile fraction in several extracts obtained by treatment of coal tar pitches with different organic solvents, *Fuel*, 74 (1995) 233-240.

[189] López, D., Acelas, N., Mondragón, F., Average structural analysis of tar obtained from pyrolysis of wood, *Bioresource Technology*, 101 (2010) 2458–2465.

[190] Ku, C.S., Mun, S.P., Characterisation of Pyrolysis Tar Derived from Lignocellulosic Biomass, *Journal of Industrial and Engineering Chemistry*, 12 (2006) 853-861.

[191] Milne, T.A., Abatzaglou, N., Evans, R.J., Biomass Gasifier "Tars": Their Nature, Formation, and Conversion, National Renewable Energy Laboratory, U.S. Department of Energy, USA, 1998. Available online at: http://www.ps-survival.com/PS/Gasifiers/Biomass_Gasifier_Tars_Their_Nature_Formation_And_Conversion_1998.pdf

[192] United States Environmental Protection Agency (USEPA), SW-846 Test Methods for Evaluating Solid Wastes. Physical/Chemical Methods. Method 3611B – Alumina column cleanup and separation of petroleum wastes, USA, 1996.

[193] Hartnik, T., Norli, H.R., Eggen, T., Breedveld, G.D., Bioassay-directed identification of toxic organic compounds in creosote-contaminated groundwater, *Chemosphere*, 66 (2007) 435–443.

[194] Reineke, N., Bester, K., Hühnerfuss, H., Jastorff, B., Weigel, S., Bioassay-directed chemical analysis of River Elbe surface water including large volume extractions and high performance fractionation, *Chemosphere*, 47 (2002) 717–723.

[195] Galassi, S., Guzzella, L., Croce, V., Screening organic micropollutants in surface waters by SPE extraction and ecotoxicological testing, *Chemosphere*, 54 (2004) 1619–1624.

[196] Marvin, C.H., Hewitt, L.M., Analytical methods in bioassay-directed investigations of mutagenicity of air particulate material-review, *Mutation Research*, 636 (2007) 4–35.

[197] Płaza, G., Nałęcz-Jawecki, G., Ulfig, K., Brigmon, R.L., The application of bioassays as indicators of petroleum-contaminated soil remediation, *Chemosphere*, 59 (2005) 289–296.

[198] Giltrap, M., Macken, A., McHugh, B., Hernan, R., O'Rourke, K., McGovern, E., Foley, B., Davoren, M., Bioassay-directed fractionation of marine sediment solvent extracts from the east coast of Ireland, *Chemosphere*, 76 (2009) 357–364.

[199] Marvin, C.H., McCarry, B.E., Lundrigan, J.A., Roberts, K., Bryant, D.W., Bioassay-directed fractionation of PAH of molecular mass 302 in coal tar-contaminated sediment, *Science of Total Environment*, 231 (1999) 135-144.

[200] United States Environmental Protection Agency (USEPA), SW-846 Test Methods for Evaluating Solid Wastes. Physical/Chemical Methods. Method 3540C – Soxhlet Extraction, USA, 1996.

[201] Azur Environmental Microtox® system, Microtox® Omni – user manual, Microbics Corporation, Carlsbad, CA, USA, 1992.

[202] Kaiser, K.L.E., Palabrica, V.S., Photobacterium phosphoreum toxicity data index, *Water Pollution Research Journal of Canada*, 26(3) (1991) 361-431.

[203] American Society for Testing and Materials Standards, ASTM D5373 – Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Laboratory Samples of Coal and Coke, USA, 2002.

[204] American Society for Testing and Materials Standards, ASTM D4239 – Standard Test Methods for Sulfur in the Analysis Sample of Coal and Coke Using High-Temperature Tube Furnace Combustion Methods, USA, 2002.

[205] Darmstadt, H., Roy, C., Kaliagljine, S., Characterisation of pyrolytic carbon blacks from commercial tire pyrolysis plants, *Carbon*, 33:10 (1995) 1449-1455.

[206] Lin, H., Chen, W., Yuan, C., Hung, C., Surface Functional Characteristics (C, O, S) of Waste Tire-Derived Carbon Black before and after Steam Activation, *Journal of the Air & Waste Management Association*, 58 (2008) 78–84.

[207] Mukherjee, A., Zimmerman, A.R., Harris, W., Surface chemistry variations among a series of laboratory-produced biochars. *Geoderma*, 163 (2011) 247–255.

[208] Lewis, A.E., Review of metal sulphide precipitation, *Hydrometallurgy*, 104 (2010) 222–234.

[209] Johnson, B.T., Microtox Acute Toxicity Test, in: Blaise, C., Férard, J.-F. (eds.), Small-scale Freshwater Toxicity Investigations, Vol. 1, Springer, Netherlands, 2005, pp. 69-105.

[210] Peters, R.W., Chelant extraction of heavy metals from contaminated soils. *Journal of Hazardous Materials*, 66 (1999) 151–210.

[211] Udovic, M., Lestan, D., EDTA and HCl leaching of calcareous and acidic soils polluted with potentially toxic metals: Remediation efficiency and soil impact, *Chemosphere*, 88 (2012) 718–724.

[212] Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy.

[213] Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy.

[214] Uchimiya, M., Lima, I.M., Klasson, K.T., Chang, S., Wartelle, L.H., Rodgers, J.E., Immobilization of Heavy Metal Ions (CuII, CdII, NiII, and PbII) by Broiler Litter-Derived Biochars in Water and Soil, *Journal of Agricultural and Food Chemistry*, 58 (2010) 5538–5544.

[215] Lu, H., Zhang, W., Yang, Y., Huang, X., Wang, S., Qiu, R., Relative distribution of Pb2+ sorption mechanisms by sludge-derived biochar, *Water Research*, 46 (2012) 854-862.

[216] Machida, M., Yamazaki, R., Aikawa, M., Tatsumoto, H., Role of minerals in carbonaceous adsorbents for removal of Pb(II) ions from aqueous solution, *Separation and Purification Technology*, 46 (2005) 88–94.

[217] Inyang, M., Gao, B., Yao, Y., Xue, Y., Zimmerman, A.R., Pullammanappallil, P., Cao, X., Removal of heavy metals from aqueous solution by biochars derived from anaerobically digested biomass, *Bioresource Technology*, 110 (2012) 50–56.

[218] Kołodyńska, D., Wnętrzak, R., Leahy, J.J., Hayes, M.H.B., Kwapiński, W., Hubicki, Z., Kinetic and adsorptive characterisation of biochar in metal ions removal, *Chemical Engineering Journal*, 197 (2012) 295–305.

[219] Cao, X., Ma, L., Gao, B., Harris, W., Dairy-Manure Derived Biochar Effectively Sorbs Lead and Atrazine, *Environmental Science and Technology*, 43 (2009) 3285–3291.

[220] Uchimiya, M., Bannon, D.I., Wartelle, L.H., Lima, I.M., Klasson, K.T., Lead Retention by Broiler Litter Biochars in Small Arms Range Soil: Impact of Pyrolysis Temperature, *Journal of Agricultural and Food Chemistry,* 60 (2012) 5035−5044.

[221] Quek, A., Balasubramanian, R., Low-Energy and Chemical-Free Activation of Pyrolytic Tire Char and Its Adsorption Characteristics, *Journal of the Air & Waste Management Association*, 59:6 (2009) 747-756.

[222] Liu, Z., Zhang, F., Removal of lead from water using biochars prepared from hydrothermal liquefaction of biomass, *Journal of Hazardous Materials*, 167 (2009) 933–939.

[223] Inyang, M., Gao, B., Ding, W., Pullammanappallil, P., Zimmerman, A.R., Cao, X., Enhanced Lead Sorption by Biochar Derived from Anaerobically Digested Sugarcane Bagasse, Separation Science and Technology, 46 (2011) 1950–1956.

[224] Xue, Y., Gao, B., Yao, Y., Inyang, M., Zhang, M., Zimmerman, A.R., Ro, K.S., Hydrogen peroxide modification enhances the ability of biochar (hydrochar) produced from hydrothermal carbonization of peanut hull to remove aqueous heavy metals: Batch and column tests, *Chemical Engineering Journal,* 200–202 (2012) 673–680.

[225] Qiua, Y., Cheng, H., Xu, C., Sheng, G.D., Surface characteristics of crop-residue-derived black carbon and lead(II) adsorption, *Water Research*, 42 (2008) 567–574.

[226] Gutiérrez-Segura, E., Colín-Cruz, A., Fall, C., Solache-Ríos, M., Balderas-Hernández, P., Comparison of Cd–Pb adsorption on commercial activated carbon and carbonaceous material from pyrolysed sewage sludge in column system, *Environmental Technology*, 30:5 (2009) 455-461.

[227] Manchón-Vizuete, E., Macías-García, A., Gisbert, A.N., Fernández-González, C., Gómez-Serrano, V., Preparation of mesoporous and macroporous materials from rubber of tyre wastes, *Microporous and Mesoporous Materials*, 67 (2004) 35–41.

[228] American Society for Testing and Materials Standards, ASTM D3173-03 – Standard Test Method for Moisture in the Analysis Sample of Coal and Coke, USA, 2003.

[229] American Society for Testing and Materials Standards, ASTM D3174-02 – Standard Test Method for Ash in the Analysis Sample of Coal and Coke from Coal, USA, 2002.

[230] American Society for Testing and Materials Standards, ASTM D3175-02 - Standard Test Method for Volatile Matter in the Analysis Sample of Coal and Coke, USA, 2002.

[231] Bernardo, M., Lapa, N., Gonçalves, M., Mendes, B., Pinto, F., Fonseca, I., Lopes, H., Physico-chemical properties of chars obtained in the co-pyrolysis of waste mixtures, *Journal of Hazardous Materials*, 219–220 (2012) 196–202.

[232] Han, Y., Boateng, A.A., Qi, P.X., Lima, I.M., Chang, J., Heavy metal and phenol adsorptive properties of biochars from pyrolyzed switchgrass and woody biomass in correlation with surface properties, *Journal of Environmental Management*, 118 (2013) 196-204.

[233] Fu, P., Hu, S., Xiang, J., Sun, L., Su, S., Wang, J., Evaluation of the porous structure development of chars from pyrolysis of rice straw: Effects of pyrolysis temperature and heating rate, *Journal of Analytical and Applied Pyrolysis*, 98 (2012) 177–183.

[234] Sing, K.S.W., Everett, D.H., Haul, R.A.W., Moscou, L., Pierotti, R.A., Rouquerol, J., Siemieniewska, T., Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity, *Pure and Applied Chemistry*, 57 (1985) 603–619.

[235] Powell, K.J., Brown, P.L., Byrne, R.H., Gajda, T., Hefter, G., Leuz, A., Sjöberg, S., Wanner, H., Chemical speciation of environmentally significant metals with inorganic ligands. Part 3: The Pb^{2+} + OH^-, Cl^-, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-} systems (IUPAC Technical Report), *Pure and Applied Chemistry*, 81:12 (2009) 2425–2476.

[236] Zhang, K., Cheung, W.H., Valix, M., Roles of physical and chemical properties of activated carbon in the adsorption of lead ions, *Chemosphere*, 60 (2005) 1129–1140.

[237] Li, L., Quinlivan, P.A., Knappe, D.R.U., Effect of activated carbon surface chemistry and pore structure on the adsorption of organic contaminants from aqueous solution, *Carbon*, 40 (2002) 2085-2100.

[238] Kikuchi, Y., Qian, Q., Machida, M., Tatsumoto, H., Effect of ZnO loading to activated carbon on Pb(II) adsorption from aqueous solution, *Carbon*, 44 (2006) 195–202.

[239] Goel, J., Kadirvelu, K., Rajagopal, C., Garg, V.K., Removal of lead (II) by adsorption using treated granular activated carbon: Batch and column studies, *Journal of Hazardous Materials B*, 125 (2005) 211–220.

[240] Macías-García, A., Valenzuela-Calahorro, C., Espinosa-Mansilla, A., Bernalte-García, A., Gómez-Serrano, V., Adsorption of Pb2+ in aqueous solution by SO2-treated activated carbon, *Carbon*, 42 (2004) 1755–1764

[241] Wajima, T., Murakami, K., Kato, T., Sugawara, K., Heavy metal removal from aqueous solution using carbonaceous K_2S-impregnated adsorbent, *Journal of Environmental Sciences*, 21 (2009) 1730–1734.