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Leaching behaviour and ecotoxicity evaluation of chars from the pyrolysis of forestry biomass and polymeric materials

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ABSTRACT

The main objective of this study was to assess the environmental risk of chars derived from the pyrolysis of mixtures of pine, plastics, and scrap tires, by studying their leaching potential and ecotoxicity. Relationships between chemical composition and ecotoxicity were established to identify contaminants responsible for toxicity. Since metallic contaminants were the focus of the present study, an EDTA washing step was applied to the chars to selectively remove metals that can be responsible for the observed toxicity. The results indicated that the introduction of biomass to the pyrolysis feedstock enhanced the acidity of chars and promote the mobilisation of inorganic compounds. Chars resulting from the pyrolysis of blends of pine and plastics did not produce ecotoxic eluates. A relationship between zinc concentrations in eluates and their ecotoxicity was found for chars obtained from mixtures with tires. A significant reduction in ecotoxicity was found when the chars were treated with EDTA, which was due to a significant reduction in zinc in chars after EDTA washing.

1. Introduction

The European Waste Framework Directive (EU, 2008) established the waste management hierarchy that should be respected and applied in the member states of the European community. Recycling and other hierarchical recovery activities such as the energy recovery from wastes are considered key parts of this classification. According to this directive, the thermochemical treatment of wastes without air supply, commonly known as pyrolysis, can be considered a recycling operation since waste materials are reprocessed into three types of products: chars, gases, and heavy compounds that condense as oils when cooled down (tars). The gaseous and liquid fractions can be used as a basic chemical feedstock in the petrochemical and refining industries (Vamvuka, 2011; Al-Salem et al., 2010; Quek and Balasubramanian, 2013). The char can be processed further to be used as adsorbent (González et al., 2009; Méndez-Liñán et al., 2010; Hale et al., 2013), for catalytic applications (Kastner et al., 2009; Zhang et al., 2011), for soil amendment (Uchimiya et al., 2010; Manyá, 2012), and as a metallurgical reducing agent (Griessacher et al., 2012; Kantarelis et al., 2010) among other uses. Alternatively, pyrolysis can also be considered an energy recovery operation, as the three products obtained can be used as fuels because of their calorific content (Vamvuka, 2011; Al-Salem et al., 2010).

The recycling attribute of pyrolysis is one step beyond incineration in the waste hierarchy and for this reason it should be preferred as a thermal treatment. In recent years, pyrolysis have received a great deal of attention from the scientific community and started to be commercially applied (Vamvuka, 2011; Al-Salem et al., 2010; Bosmans et al., 2013) because it can provide the same advantages of incineration (waste reduction by volume and weight) with additional advantages such as reduced gas emissions in volume and toxicity (Zaman, 2010). Therefore, it is expected that waste treatment by pyrolysis will grow in importance in the near future, being anticipated that large amounts of pyrolytic chars will be available as by-products or as main products. It is then important to study the properties, composition, and risk assessment of chars, in order to avoid risks to environmental compartments and to exploit the potential value of these pyrolysis products. In particular, applications of these materials involving contact with or potential exposition to water, require the knowledge of their leaching behaviour and ecotoxicological properties.

Chars are essentially carbon materials that retain the mineral matter initially present in the wastes and may contain significant amounts of pyrolytic tars. Therefore, the release of toxic compounds from chars is a possibility that might restrict their applications, which demands the evaluation of contaminant mobility through leaching tests.

Combining chemical analyses with ecotoxicological tests as an integrated strategy to characterise a given sample has the

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advantage of providing more complete information about its global toxic effects (Blasco and Pico, 2009). This strategy was applied for the first time to the characterisation of pyrolysis chars by Bernardo et al. (2009, 2010); the results underlined the need for relating chemical and ecotoxicological parameters in the hazard assessment of these carbon-based materials. Nevertheless, only very recently, a study of the ecotoxicological assessment of biochars by using both chemical and biological analyses was presented (Oleszczuk et al., 2013).

Given the aforementioned, the main objective of the present work was to provide a contribution to the environmental risk assessment of chars obtained in the pyrolysis of feedstocks with pine biomass, plastic wastes, and scrap tires. To achieve this goal, the potential release of contaminants from the chars was evaluated through the application of leaching tests and the ecotoxic levels of the obtained eluates were determined by combining chemical and ecotoxicological analyses. Possible relations within chemical and ecotoxicological data were made to identify contaminants responsible for the ecotoxicity levels. Metallic contaminants and their contribution to the ecotoxicity levels of the chars are the foci. 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.

2. Materials and methods

2.1. Raw materials—plastic wastes, used tires, and pine forestry biomass

The feedstock submitted to the pyrolysis experiments was composed by different mixtures of three materials: plastic wastes, used tires, and pine residues.

The plastics used were polyethylene (PE), polypropylene (PP), and polystyrene (PS) provided by a recycling company in the form of pellets with a diameter of approximately 2–5 mm. The scrap tires were provided by a recycling company in strips approximately 2 cm in length and 1–2 mm in diameter after the removal of metal components.

Pinus pinaster or maritime pine was selected as the biomass feedstock because it is the predominant specie in the Portuguese forest. This biomass was in the form of shredded pieces similar to the pieces of scrap tires and it was obtained from a sawmill.

Table 1 is a presentation of the elemental and proximate analysis of the raw materials used. Tire rubber and plastics were mainly composed by carbon and hydrogen, which was expected given their hydrocarbon character with very low heteroatom content. However, tire rubber presents significant sulphur content as the vulcanisation process of tire rubber is performed with sulphur.

The high nitrogen content of PS should also be underlined being most likely associated to an additive of this plastic.

Table 1
Elemental and proximate analysis of plastics, used tires and pine biomass. Analyses performed in the materials as received.

	Tire	Pine	PE	PP	PS
LHV (MJ/kg daf)	n.d.	n.d.	43.3	35.1	37.4
HHV (MJ/kg daf)	38.5	20.2	46.4	37.6	39.0
Proximate analysis					
Fixed carbon[a] (per cent w/w)	33.5	13.6	0.1	0.1	0.2
Volatiles (per cent w/w)	61.6	74.5	99.8	82.6	99.5
Ash (per cent w/w)	2.9	0.3	0.1	17.2	0.0
Moisture (per cent w/w)	2.0	11.6	0.0	0.1	0.3
Elemental analysis					
C (per cent daf)	86.1	50.6	84.8	70.5	86.1
H (per cent daf)	7.2	6.4	14.5	11.6	7.4
S (per cent daf)	1.5	0.2	0.3	<0.1	<0.1
N (per cent daf)	0.2	0.2	0.3	0.5	6.1
Cl (per cent daf)	–	0.07	–	–	–
O (per cent daf)	0.1	42.5[a]	–	–	–

LHV – low heating value; HHV – high heating value; daf – dry ash free; n.d. – not determined.

[a] Estimated by difference.

The high ash content of PP (17.2 per cent) is related to its origin. PP wastes were obtained from automobile fenders containing calcium as the major metal (Bernardo et al., 2009) because of the use of calcium carbonate as inorganic filler in PP for automotive applications (Moritomi et al., 2010).

2.2. Pyrolysis experiments

Pyrolysis experiments were carried out in stirred batch reactors of 1 and 5 l (Parr Instruments), built in Hastelloy C276, a nickel—molybdenum–chromium alloy, which were purged and pressurised to 0.41 MPa with nitrogen. Heating rates of approximately 5 °C/min were used until the desired reaction temperature of 420 °C was reached. This temperature was maintained for 15 min. At the end of this period, the reactor vessel was cooled to room temperature. Given the low heating rate and the cooling period, the total residence time of the materials inside the reactor vessel was approximately 90 min. When the temperature inside the reactor reached near room temperature, the reactor was depressurised and the volume of the gaseous fraction was measured using a gas metre (the volume of nitrogen was discounted). The gaseous compounds were then collected in a sampling bag for density determination; afterwards the gases mass yield was obtained.

More information about the pyrolysis installation and experiments can be found in the previous works (Miranda et al., 2010; Paradela et al., 2009a, 2009b).

Three different mixtures of the raw materials were subjected to pyrolysis:

1) Mixture 1–30 per cent (w/w) pine biomass + 30 per cent (w/w) used tire rubber + 40 per cent (w/w) plastics;
2) Mixture 2–50 per cent (w/w) pine + 50 per cent (w/w) plastics;
3) Mixture 3–50 per cent (w/w) used tire rubber + 50 per cent (w/w) plastics.

Plastics were the common raw material in the three feedstocks with the objective to improve the quantity and quality of the pyrolysis liquid fraction through the H-donor effect of plastics. This was the main objective of the previous studies (Miranda et al., 2010; Paradela et al., 2009a, 2009b).

In the three experiments, plastics were a mixture of 56 per cent (w/w) PE, 27 per cent (w/w) PP, and 17 per cent (w/w) PS, simulating the average composition of the plastic fractions present in the Portuguese municipal solid wastes (MSW).

2.3. Char samples

The chars obtained from the pyrolysis of mixtures 1, 2, and 3 were named as chars 1, 2, and 3, respectively.

Given the batch operation of the pyrolysis process, the resulting solids were a carbonized pasty residue covered with oils and tars. The high concentrations of pyrolytic liquids in the chars are of concern given their composition rich in aromatic, oxygenated, and aliphatic hydrocarbons, some of them of high toxicity and a particularly high environmental mobility. Moreover, the physical characteristics of the chars (viscous, pasty, and very smelly) make them difficult to handle. Thus, it is crucial to remove and recover these liquids, because of the environmental risks they pose and because both of these oils and tars are potential sources of valuable chemicals.

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 Soxhlet method. This strategy has previously proved to be efficient for the decontamination of pyrolysis chars, allowing the removal of several organic compounds from different classes (Bernardo et al., 2012). 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 °C for 24 h in a vacuum oven.

The chars were then submitted to a thermal analysis that consisted of measuring the progressive weight loss associated with the combustion of samples in a muffle furnace, under an air atmosphere, from room temperature up to 750 °C with increments of 50 °C, remaining 10 min. at each temperature stage. This thermal analysis allows defining the composition of the chars in terms of the volatility of their components. It was considered that volatile compounds were those volatilised up to 250 °C; the weight loss registered between 250 °C and 350 °C was attributed to semi-volatile compounds, while the weight decrease observed from 350 °C to 600 °C was assigned to the volatilization and combustion of heavy compounds denominated as fixed residue; the residue non-combusted above 600 °C that presented a stable weight was considered to be the ashes.

The chars were also submitted to an elemental analysis performed with a LECO elemental analyser by combustion technique. Carbon, hydrogen, and nitrogen were determined according to the ASTM D5373 standard and sulphur determination followed the ASTM D4239 standard (ASTM, 2002).

2.4. Metal content of chars

The metal content of chars was estimated according to the following procedure: the chars were submitted to a previous digestion in porcelain crucibles performed with hydrogen peroxide 30 per cent (v/v) in a heated bath at a