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Chemical and ecotoxicological characterization of ashes obtained from sewage sludge combustion in a fluidised-bed reactor

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Abstract

In 1999, the DEECA/INETI and the UBiA/FCT/UNL started a researching project on the partition of heavy metals during the combustion of stabilised sewage sludge (Biogran®), in a fluidised-bed reactor, and on the quality of the bottom ashes and fly ashes produced. This project was entitled Bimetal and was funded by the Portuguese Foundation for Science and Technology. In this paper only the results on the combustion of Biogran® are reported. The combustion process was performed in two different trials, in which different amounts of sewage sludge and time of combustion were applied. Several ash samples were collected from the bed (bottom ashes) and from two cyclones (first cyclone and second cyclone ashes). Sewage sludge, bed material (sand) and ash samples were submitted to the leaching process defined in the European leaching standard EN 12457-2. The eluates were characterized for a set of inorganic chemical species. The ecotoxicological levels of the eluates were determined for two biological indicators (*Vibrio fischeri* and *Daphnia magna*). The results were compared with the limit values of the CEMWE French Regulation. The samples were also ranked according to an index based on the chemical characterization of the eluates. It was observed an increase of the concentration of metals along the combustion system. The ashes trapped in the second cyclone, for both combustion trials, showed the highest concentration of metals in the eluates. Chemically, the ashes of the second cyclone were the most different ones. In the ecotoxicological point of view, the ecotoxicity levels of the eluates of the ashes, for both combustion cycles, did not follow the same pattern as observed for the chemical characterization. The ashes of the first cyclone showed the highest ecotoxicity levels for *V. fischeri* and *D. magna*. This difference on chemical and ecotoxicological results proves the need for performing both chemical and ecotoxicological characterizations of the sub-products of such type of thermal processes.

Keywords: Sewage sludge; Incineration; Fluidised-bed reactor; Bottom and fly ashes; Ecotoxicological level

1. Introduction

One of the possible recycling options for many types of wastes is their use as a source of energy through combustion, contributing to reduce the use of natural fossil fuels [1–3]. In thermal processes, however, ashes are produced and their deposition/use demands a careful evaluation on the risk to the environment [4–10].

Due to its high content in organic matter, sewage sludge has been used in co-combustion processes for energy production [11]. It is foreseen a strong increase on the combustion of this type of wastes, due to the limitation imposed by the "Landfill Directive" [12] regarding to the disposal of organic wastes in landfills.

According to Lopes [13], the European statistics on sludge production in the EU Member States indicated a production of 7.6 to 8.9 million tonnes (dry matter), in 2000. This amount would rise to 10 million tonnes in 2005. US production was about 7 million tonnes in 1990, and the amount produced in Japan was similar. These are very significant amounts of sewage sludge, for which treatment and recycling are of major importance. Sewage sludge is produced in wastewater treatment plants with high moisture content, requiring a pre-drying process. They may be converted into a combustible derived from wastes

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(CDW), whose handling is easier, due to its greater homogeneity. There are already commercial CDW products, which are produced from sewage sludge, such as Biogran®. This material is produced through the anaerobic digestion of wastewater treatment sludge. The digested sludge is screened and centrifuged to a level of 30% solids (dry mass). The resulting solid material is then submitted to a thermal drying process of at least 400 °C, during about 30 min. The final material is of 95% dry matter with particles measuring between 2 and 4 mm [14].

This dry CDW is of major interest from the energetic point of view since it has a low calorific value (LCV) ranging from 10 to 15 MJ/kg. The energy for drying is partially obtained from the combustible gas produced during digestion.

2. Bimetal project

In 1999, the Portuguese Foundation for Science and Technology, from the Ministry of Higher Education and Technology, had funded the project entitled "Behaviour of Heavy Metals on the Thermal Treatment of Residues", under the acronym Bimetal. This project had the participation of two partners: Department of Energetic Engineering and Environmental Control (DEECA) of the National Institute of Engineering, Technology and Innovation (INETI) and Environmental Biotechnology Researching Unit (UBiA), from the Faculty of Science and Technology (FCT), of the New University of Lisbon (UNL). The main goal of this project was to study the behaviour of heavy metals during the co-combustion of coal and the commercial CDW Biogran®, in a fluidised-bed reactor. DEECA/INETI team performed four incineration assays: two mono-combustion assays of Biogran®, one co-combustion assay of Biogran® and coal and, finally, one mono-combustion assay of coal. In this paper, only the results of the mono-combustion assay of Biogran® are shown [15].

Each combustion assay produced three samples of ashes: a bottom ash and two fly ashes captured in two cyclones. The combustion plant and the conditions of each assay are shown in Section 4.

UBiA/FCT/UNL team was responsible for the chemical and ecotoxicological characterization of the ashes produced in each combustion assay. This characterization was done according to the following aspects: (1) the quantification of the bulk content of ashes for a set of metals; (2) the quantification of metals and the determination of the ecotoxicological levels of the eluates produced according to the European Standard EN 12457-2 [16].

3. Conceptual methodology for chemical and ecotoxicological characterization of ashes

The evaluation of the ecotoxic properties (Hazardous property H14, according to the Council Directive 91/689/EEC [17]) of bottom and fly ashes were based on the criterion and evaluation methods for waste ecotoxicity (CEMWE) [18]. The original CEMWE methodology was adapted according to the discussion previously shown in Lapa et al. [5] and Barbosa [15]. The adopted criterion is shown in Fig. 1.

The release of pollutants is determined by placing the material in contact with deionised water, at a constant liquid/solid (L/S) ratio of 10 L/kg, for a batch cycle of 24 h. An assessment of the ecotoxic properties is then performed on the basis of the chemical and ecotoxicological characterization of the eluates (Fig. 1). The results obtained are compared with the CEMWE [18] limit values (Table 1). The material is then classified as ecotoxic or non-ecotoxic, according to both chemical and ecotoxicological characterizations.

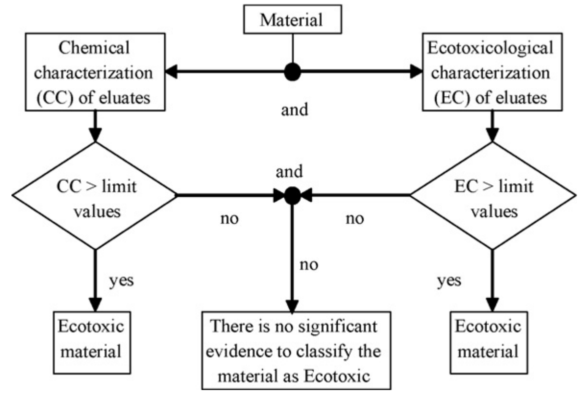

Fig. 1. Criterion applied to assess the ecotoxic properties of bottom and fly ashes (modified from French Ministry of Environment [18]).

4. Material and methods

4.1. Material incinerated

The Biogran® is a granular product obtained from thermally treated sewage sludge, which is produced by Wessex Water Company through the use of Biodriers manufactured by Swiss Combi Technology. The Biodriers are installed in urban wastewater treatment plants, in the region of Bristol (UK), that are managed by Wessex Water Company.

Through the thermal treatment, dewatered sewage sludge becomes a dry and pasteurized granulate suitable for a wide variety of uses, in which is included the energy production. Dry-

Table 1
Chemical and ecotoxicological limit values defined in CEMWE [18]

Characterization	Parameter	CEMWE limit
Chemical[a]	Free cyanide	0.1 mg/L
	Phenolic compounds	0.1 mg/L
	As	0.05 mg/L
	Cd	0.2 mg/L
	Cr	0.5 mg/L
	Cr(VI)	0.1 mg/L
	Cu	0.5 mg/L
	Pb	0.5 mg/L
	Hg	0.05 mg/L
	Ni	0.5 mg/L
	Sn	2 mg/L
	Zn	2 mg/L
Ecotoxicological[b]	*Vibrio fischeri* (EC_{50}-30 min)	10% (v/v)
	Daphnia magna (EC_{50}-48 h)	10% (v/v)

[a] Maximum admissible concentration, in the eluates, of non-ecotoxic materials.

[b] Minimum admissible dilution, of the eluates, for non-ecotoxic materials.

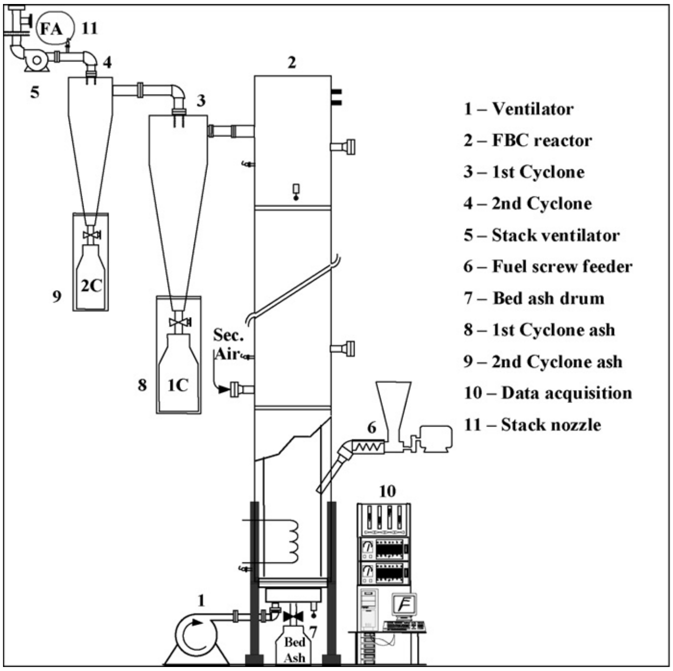

Fig. 2. Diagram of the fluidised-bed reactor, the cyclone systems and sampling points for fly and bottom ashes [13]).

ing reduces the volume of the sludge by 95% and the granular product has a moisture content of less than 10%.

The raw sludge recovered at the treatment works is thickened to between 6 and 8% solids content and then transferred to the anaerobic sludge digesters, which are preheated to 35 °C. The digested sludge, at 4–5% dry solids, is then fed into the Biodrier plant. The first stage in the production of granules is to strain the sludge through a fine screen and then centrifuge it to 30% solids. The resultant solution is then mixed with some of the recycled Biogran®, which takes the dry solids content to approximately 60%. This is then fed into the drying drum. The new granules are dried in the drum which is heated to 400 °C. This takes 30 min during which time the material gradually dries still further down to 95% dry matter and form granules of 2–4 mm ready for screening and entering the bagging hopper.

4.2. Combustion conditions

A sample of Biogran® was submitted to two combustion assays (“A” and “B”) using a pilot-scale fluidised-bed reactor (FBR) installed at INETI (Fig. 2). The system comprises the reactor and several auxiliary systems: fuel feed-in system; air fans for primary and secondary air injection and for exhaustion of gases, two heat exchangers and two cyclones for fly ash removal. The reactor has an internal square section with 0.3 m × 0.3 m and of 5 m height. The internal chamber is of refractory steel (AISI 310). The bottom of the reactor is settled over a wind box chamber with 0.3 m × 0.3 m and with 0.2 m height. The primary air is injected through the wind box and is distributed at the bottom of the reactor through an air distribution plate. 500 mm above the air distribution plate is located the fuel feed-in pipe. The feed-in system is constituted by a hopper and a worm controlled by an engine. The secondary air is injected 1100 mm above the air distribution plate. The heat exchangers are located at the bed region and at the top of the combustor. Both are used mainly for temperature control inside the combustor chamber. The FBR is computer controlled [19].

The average temperatures in the first and second cyclones were of 300 and 150 °C, respectively, during the average working conditions of both trials.

The fly ash removal is done through two cyclones connected in line. The flue gases are exhausted through a fan located in the bottom of a vertical stack. The bottom ashes are collected through the wind box and the fly ashes are collected in the bottom of the cyclones.

The combustion assays were carried out by DEECA/INETI team under the conditions defined in Table 2. Silica sand was used as the fluidisation agent in the bed.

For each combustion test condition (Table 2), the combustion trials were carried out for such an extent that the ashes (bottom and fly ashes) were collected only when the FBR was operated in the average conditions referred in Table 2. The ashes produced during the start-up and turn-off stages of the system were discarded.

During the operation of the FBR, for each combustion test condition, two samples of bottom ashes and fly ashes from the first and second cyclones were collected. All the results shown are average values of duplicate samples.

4.3. Samples analysed

Three sampling points were selected to collect the ashes (Fig. 2):

(a) Point 7 – drain out of bed ashes from the bottom of the combustor;
(b) Point 8 – drain out of ashes trapped in the first cyclone;
(c) Point 9 – drain out of ashes trapped in the second cyclone.

In each combustion assay, three types of ashes were collected at the sampling points identified above:

(a) Bottom ashes—samples A1 and B1;
(b) Fly ashes retained in the first cyclone—samples A2 and B2;

Table 2
Characterization of the combustion conditions to which Biogran® was submitted

Assay	Fuel	Mass of fuel (kg)	Mass of sand (kg)	Combustion temperature (°C)	Combustion duration (h:min)	Average flow of fuel (kg/h)
A	Biogran®	68.96	16.10	850	4:25	15.6
B	Biogran®	92.30	14.80	850	6:00	15.4

(c) Fly ashes retained in the second cyclone—samples A3 and B3.

4.4. Chemical characterization of fuel, bottom ashes and fly ashes

4.4.1. Moisture content and bulk content of metals

The moisture content [20] was determined in bottom and fly ashes, in Biogran® and bed material (sand). All samples were submitted to an acid digestion, with 10 mL HNO_3 65% (v/v) for 0.25 g of sample. The acid digestion was carried out in closed vessels on a microwave digester (Milestone, Ethos 1600), for 20 min, with the following powers and times: 250 W (5 min); 350 W (5 min); 400 W (5 min); 250 W (5 min). The digestion conditions followed USEPA Method 3051A [21].

The digested samples were filtered over glass fibre filters (Schleicher & Schuell) and analysed for the following metals: As (hydride generation and quantification by atomic absorption spectrometry [22]), Hg (cold vapour flameless method [23]), Cd, Cu, Ni, Pb and Zn (quantification by flame AAS [24]), Al (quantification by flame AAS, after the reaction with 8-hydroxiquinolin and extraction with MIBK [25]), Fe (quantification by flame AAS [25]) and Cr (quantification by flame AAS—Method A [26]).

4.4.2. Leaching test

The samples of Biogran®, bottom and fly ashes were submitted to the leaching test described in the European standard EN 12457-2 [16]. The eluates were divided into sub-samples and each one was preserved according to the chemical species to be analysed [27]. For the ecotoxicological assays, the eluates were maintained at a temperature of $4 \pm 1\,^{\circ}C$.

4.4.3. Chemical characterization of eluates

The eluates were analysed for the following parameters: pH (electrometric method [28]), conductivity (electrometric method [29]), chemical oxygen demand (COD) (volumetric method [30]), phenol compounds (direct colorimetric method—Method A [31]), free cyanide (photometric method by using chloramine T and pyridine-barbituric acid [32]), total dissolved solids (TDS) (gravimetric method [25]), Cr(VI) (spectrophotometric method by using 1,5-diphenylcarbazide [33]), As (hydride generation and quantification by atomic absorption spectrometry [22]), Hg (cold vapour flameless method [23]), Cd, Cu, Ni, Pb and Zn (quantification by flame AAS [24]), Al (quantification by flame AAS, after the reaction with 8-hydroxiquinolin and extraction with MIBK [25]), Fe (quantification by flame AAS [25]) and Cr (quantification by flame AAS—Method A [26]).

4.4.4. Ecotoxicological characterization of leachates

The following ecotoxicological parameters were analysed in the eluates:

(a) Luminescence inhibition of the bacterium *Vibrio fischeri* (Azur Environmental Microtox® system [34]), in a 30 min batch culture.

Table 3
Metal bulk content of bed material (sand) and Biogran® used in the combustion tests “A” and “B” (dm: dry matter)

Parameter	Bed material (sand) (mg/kg dm)	Biogran® (mg/kg dm)
As	3.0	3.1
Cd	<2.7	<17.2
Cr	<12.1	78.9
Cu	<9.9	417
Hg	0.03	4.2
Ni	<15.2	<33.8
Pb	<24.2	277
Zn	9.2	1471
Fe	15.5	10,108
Al	185	13,817

(b) Mobility inhibition of the crustacean *Daphnia magna* (Microbiotests Company, Daphtoxkit F magna™), in a 48 h static test.

5. Results and discussion

5.1. Particle size distribution and bulk content

The ashes collected in both trials were very similar in what concerns the particle size distribution. The 75% (w/w) of the ashes retained in the first cyclone had a dimension ≤40 μm and 25% (w/w) had a dimension of 40–200 μm. The 80% (w/w) of the ashes trapped in the second cyclone had a dimension of ≤10 μm and 20% (w/w) had a dimension of 10–40 μm. In what concerns the bottom ashes, 55% (w/w) had a dimension ≤200 μm and 35% (w/w) had a dimension of 200–500 μm.

Table 3 shows the metal bulk content of the bed material (sand) and the fuel used in the combustion tests “A” and “B”. The concentrations of metals in the sand were much lower then the concentrations determined in the fuel. In the bed material it was possible to detect As, Hg, Zn, Fe and Al above the quantification limits. The sand was only submitted to a washing process with river water. Nevertheless, the concentrations of Hg, Zn, Fe and Al were several orders of magnitude lower in the sand than in the fuel (123-fold lower for Hg, 160-fold lower for Zn, 652-fold lower for Fe and 75-fold lower for Al).

The fuel used in both combustion tests has shown high concentrations of Al and Fe, and significant concentrations of Zn. The metals As, Cr, Cu, Hg and Pb were also detected in concentrations above the quantification limits.

In Tables 4 and 5, it is shown the concentration of metals analysed in the acid extracts obtained for the bulk content quantification of bottom ashes and fly ashes. From the set of metals determined, Al and Fe were the metals with the major contribution in all ashes produced in the combustion tests “A” and “B”. Zn was present as a minor constituent of all ashes. Pb and Cu were also minor constituents in the ashes of the second cyclone, and were vestigial metals in the bottom ashes and fly ashes trapped in the first cyclone. All the other metals were present in vestigial concentrations for all ashes.

The evolution of the mass percentage of metals along the FBR also demonstrates that there was a tendency for an accumulation

Table 4
Metal bulk content of the bottom, first cyclone and the second cyclone ashes, produced in the combustion assay "A" (dm: dry matter)

Parameter	Bottom ash (A1) (mg/kg dm)	First cyclone ash (A2) (mg/kg dm)	Second cyclone ash (A3) (mg/kg dm)
As	<0.75	2.6	9.5
Cd	<7.5	11.4	28.5
Cr	134	435	719
Cu	450	799	1396
Hg	4.2	3.0	5.1
Ni	48.5	168	291
Pb	372	596	1115
Zn	1208	2340	13,245
Fe	11,131	9591	36,433
Al	20,976	33,051	57,462

Table 5
Metal bulk content of the bottom, first cyclone and the second cyclone ashes, produced in the combustion assay "B" (dm: dry matter)

Parameter	Bottom ash (B1) (mg/kg dm)	First cyclone ash (B2) (mg/kg dm)	Second cyclone ash (B3) (mg/kg dm)
As	6.1	13.9	12.9
Cd	<14.9	<14.7	19.6
Cr	128	337	307
Cu	435	866	1027
Hg	8.47	8.93	8.32
Ni	67.0	238	178
Pb	178	674	1587
Zn	1434	2655	3039
Fe	11,240	18,318	29,006
Al	16,792	32,986	42,754

of metals in the fly ashes, especially those retained in the second cyclone, for both combustion tests. These results are similar to those observed by Ref. [35].

5.2. *Eluates*

5.2.1. *Chemical characterization*

Table 6 shows the results of the moisture content and the chemical characterization of the eluates produced by the application of the European leaching test EN 12457-2 [16] on the bed material, Biogran®, and bottom and fly ashes of the combustion tests "A" and "B". The Biogran® was characterized by the highest moisture content, TDS, COD, phenolic compounds and free cyanides. It is also important to stress the high pH values of the ashes produced in the combustion tests, particularly the bottom ashes (A1 and B1), and the fly ashes collected in the first cyclone (A2 and B2). These high pH values can be attributed to the oxides produced during the combustion process.

The eluates produced by the ashes collected in the second cyclone (A3 and B3) showed lower pH values than the other ashes, which can be related with the presence of acidic condensates from the flue gases.

The thermo-chemical conversion of the organic compounds in CO_2 allowed the reduction of COD of the Biogran®. Nevertheless, the oxidation process was not fully completed, since it was possible to quantify COD in the eluates of all ashes.

In what is concerning the phenolic compounds and free cyanides, it was observed an important decrease on the release of these compounds when comparing the Biogran® to the ashes produced. This is also due to the thermo-chemical conversion of these compounds to the gas phase during the combustion trials.

It was observed an increasing of the TDS, and consequently of the conductivity, in the ashes retained along the system. This can be due to the retention of particles with higher salt content (chlorides and sulphates) in the second cyclone of the FBR system.

Table 7 shows the results of the metal content of the eluates produced by the application of the European leaching test EN 12457-2 [16] on the bed material, Biogran®, and bottom and fly ashes of the combustion tests A and B.

The fuel Biogran® was the material that showed the highest number of metals detected above the quantification limits of the analytical methods, namely, Cr, Cu, Ni, Zn, Fe and Cr(VI). However, comparing the concentrations of these metals in the eluates with the concentrations determined through the acid digestion (Table 3), it is possible to conclude that the soluble fraction of these metals was very low.

In what concerns the ashes produced in both combustion tests, the release of metals through the European leaching test was very low for all metals and for all bottom and fly ashes analysed. Only the cases of Fe and Al must be stressed, because an increase on the mobility from the ashes was detected, when compared to the fuel Biogran®. For both these metals, the soluble fraction was higher for bottom ashes produced in both combustion tests.

Table 6
Moisture content and chemical characterization of the eluates of the bed material, Biogran®, bottom and fly ashes

Combustion test	Sample	Moisture content (%)	pH	Conductivity (μS/cm)	TDS (mg/kg dm)	COD (mg/kg dm)	Phenolic compounds (mg/kg dm)	Free cyanides (mg/kg dm)
n.a.	Bed material (sand)	0.03	8.9	3.8	11,542	<97	0.70	<0.10
n.a.	Biogran®	8.1	7.5	1288	50,847	56,514	11.8	1.2
	A1	0.20	10.1	501	5335	284	<0.50	<0.10
A	A2	0.64	11.2	890	7535	111	<0.50	0.17
	A3	0.91	8.4	1015	9938	162	1.4	<0.10
	B1	0.25	10.1	720	8110	110	<0.50	<0.10
B	B2	0.77	11.3	972	9652	111	<0.50	0.14
	B3	1.0	8.0	1382	15,750	168	<0.50	<0.10

n.a.: not applicable; dm: dry matter.

Table 7
Concentrations of metals in the eluates of the bed material, Biogran®, bottom and fly ashes

Combustion test	Sample	As (mg/kg dm)	Cd (mg/kg dm)	Cr (mg/kg dm)	Cr(VI) (mg/kg dm)	Cu (mg/kg dm)	Hg (mg/kg dm)	Ni (mg/kg dm)	Pb (mg/kg dm)	Zn (mg/kg dm)	Fe (mg/kg dm)	Al (mg/kg dm)
n.a.	Bed material (sand)	0.44	<0.32	<0.50	<0.50	<0.41	<0.012	<0.63	<1.0	<0.13	<0.60	<3.4
n.a.	Biogran®	<0.04	<0.35	1.5	1.0	4.1	<0.013	2.9	<1.1	2.4	3.9	<3.7
	A1	0.17	<0.32	<0.50	<0.50	<0.41	<0.010	<0.63	<1.0	<0.13	0.82	26.1
A	A2	<0.03	<0.32	1.6	1.1	<0.41	<0.010	<0.63	<1.0	0.16	<0.60	18.2
	A3	<0.03	<0.32	5.3	4.2	<0.41	<0.010	<0.64	<1.0	<0.13	<0.61	7.1
	B1	<0.03	<0.32	<0.50	<0.50	<0.41	<0.012	<0.63	<1.0	1.4	12.4	57.0
B	B2	<0.03	<0.32	<0.50	<0.51	<0.41	<0.012	<0.64	<1.0	<0.13	<0.61	29.0
	B3	0.52	<0.32	0.91	0.75	<0.41	<0.012	<0.64	<1.0	<0.13	<0.61	<3.4

n.a.: not applicable; dm: dry matter.

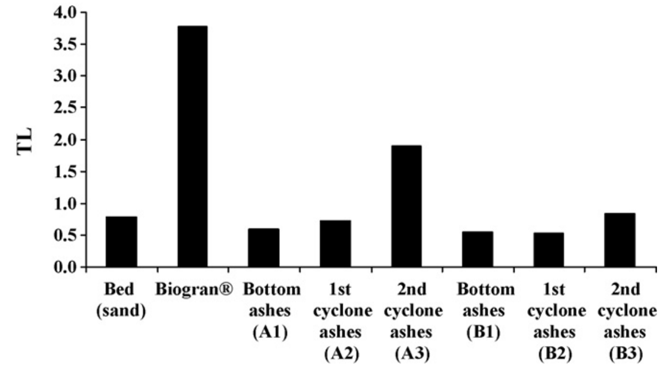

Fig. 3. Toxicity levels (TL) of bed material, fuel, bottom ashes, first cyclone and second cyclone ashes.

5.2.2. Ranking of bed material, fuel and ash samples according to a chemical index

All materials were ranked according to a chemical index based on the chemical composition of eluates and the limit values defined in CEMWE [18]. This chemical index is based on the following steps:

(a) Calculation of the toxicity equivalents (TE): The TE was calculated by the conversion of each CEMWE [14] limit value from mg/L to μmol/L. Then, it was calculated the ratios between the parameter with the highest hazardousness, i.e., the parameter with the lowest limit value (in μmol/L), and the limit value of other chemical parameters.
(b) Calculation the relative toxicity (RT): The RT for each chemical parameter is obtained through the product of the TE by the concentration determined in the eluates.
(c) Calculation the toxicity level (TL): The TL is calculated for each sample as the sum of all RT calculated for each chemical parameter.

Fig. 3 shows the toxicity levels (TL) of the bed material, fuel, bottom ashes, and ashes trapped in the first and second cyclones. In the chemical point of view, the Biogran® showed the highest TL value, which was 4.8 times higher than the TL of the bed material. All the bottom and fly ashes trapped in the first cyclone, had TL values similar to the TL value of the bed material. The fly ashes A3 and B3 showed TL values higher than those determined for bed material, bottom ashes and fly ashes retained in the first cyclone, mainly due to the contamination with Cr.

5.2.3. Ecotoxicological characterization

The ecotoxicological levels of the eluates of bed material, fuel, and all the ashes produced in both combustion tests are shown in Table 8. The toxicity units (TU) were calculated by multiplying the inverse of the effective concentration (EC) for 100 ($TU = 100/EC_{50}$).

The bed material did not show any significant ecotoxicity level for both bio-indicators. A similar result was observed for the eluates of the ashes trapped in the second cyclone for both combustion tests (A3 and B3). The ecotoxicity levels of the bottom ashes (A1 and B1) were not significant for *V. fischeri*

Table 8
Ecotoxicological levels determined in the eluates of the bed material, the Biogran®, the bottom ashes, the first cyclone ashes and the second cyclone ashes

Assay	Material	*V. fischeri*		*D. magna*	
		EC_{50}-30 min (%, v/v)	Toxicity units (TU)	EC_{50}-48 h (%, v/v)	Toxicity units (TU)
n.a.	Sand	>99	<1.0	>95	<1.1
n.a.	Biogran®	88	1.1	16	6.3
A	Bottom ash (A1)	>99	<1.0	39	2.5
	First cyclone ash (A2)	24	4.1	10	10
	Second cyclone ash (A3)	>99	<1.0	>95	<1.1
B	Bottom ash (B1)	>99	<1.0	21	4.7
	First cyclone ash (B2)	23	4.4	15	6.8
	Second cyclone ash (B3)	>99	<1.0	>95	<1.1

n.a.: not applicable.

and were low for *D. magna*. The higher ecotoxicity levels were observed for Biogran® and for the ashes trapped in the first cyclone of both combustion tests.

It is also important to stress, for helping on the selection of bio-indicators to assess the ecotoxicity levels of this kind of materials, that *D. magna* bio-indicator showed ecotoxicity levels lower than those determined for *V. fischeri*. This means that *D. magna* bio-indicator seemed to be more sensitive for the type of materials tested in this work than the bio-indicator *V. fischeri*. A similar result was reported by Tsiridis et al. [7] on the characterization of eluates produced through the application of the leaching tests EN 12457-2 and TCLP on coal fly ashes.

The ecotoxicity levels determined in the eluates of all ashes seemed to be related to their pH values (Fig. 4). The higher sensitivity of *D. magna* may be explainable by its greater sensitivity to pH values, as is indicated by the significance of the correlation and by the higher slope of the linear regression fitted between the biological reaction of both organisms and the hydroxyl concentration of the eluates. This aspect of the relation between the biological response and the pH value of the media, in which the organisms are placed in, should be further studied as it was done in the near past by Lopes et al. [36], Seco et al. [37] and Skodras et al. [8]. The ecotoxic effects of the eluates on *V. fischeri*, found by Skodras et al. [8], were lower than those reported herein may be due to the pH correction that was done in the eluates by those authors.

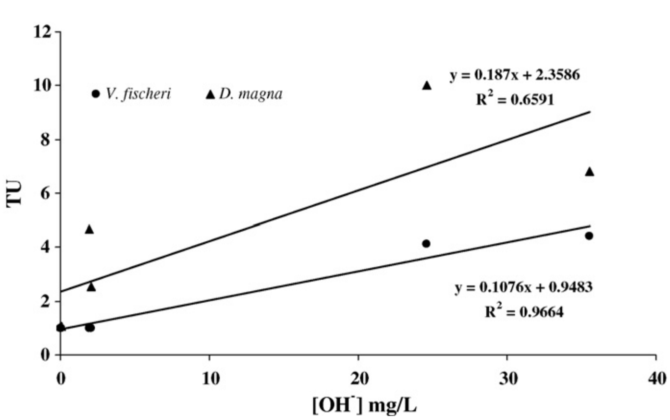

Fig. 4. Correlations between the biological responses of *D. magna* and *V. fischeri* and the pH value of the eluates, expressed by their hydroxyl concentration.

5.2.4. Ecotoxicological classification

The concentrations shown in Tables 6 and 7 of the parameters defined in the French Regulation CEMWE [18] were converted to mg/L as a function of the L/S ratio used in the leaching test and the moisture content of each sample (data not shown). These concentrations were compared with the limit values indicated in CEMWE [14]. The bed material showed all concentrations below the CEMWE [18] limit values. The fuel Biogran® showed concentrations of free cyanide and phenolic compounds above the CEMWE [18] limit values. Therefore, in the chemical point of view, the bed material was classified as non-ecotoxic and the Biogran® as ecotoxic material.

In what concerns the bottom ashes, the concentrations for all chemical parameters were below the CEMWE [18] limit values, for both combustion tests. Therefore, all bottom ashes were classified as non-ecotoxic material.

In the combustion test “A”, the concentration of Cr(VI) in the eluate of the ashes of the first cyclone was above the limit value indicated in CEMWE [18]. In the combustion test “B”, all parameters showed concentrations in the eluate of the ashes of the first cyclone below the CEMWE [18] limit values. The fly ashes collected in the first cyclone were classified as ecotoxic material for the combustion test “A” and as non-ecotoxic for the combustion test “B”.

The fly ashes trapped in the second cyclone were classified as ecotoxic material for both combustion tests, due to the concentrations of Cr, Cr(VI) and phenolic compounds for the combustion test “A”, and of As for the combustion test “B”.

Taking into account the ecotoxicological levels determined for *V. fischeri* and *D. magna*, the comparison between the results indicated in Table 8 and the ecotoxicological limit values defined in the French Regulation CEMWE [18] (Table 1) allows to conclude that only the first cyclone ash produced in the combustion trial “A” (ash A2) can be classified as an ecotoxic material. This was due to the EC_{50}-48 h value determined for *D. magna* (10% v/v), which is equal to the minimum admissible dilution defined in CEMWE [18]. All the other ashes produced in both combustion trials and the Biogran® fuel were classified as non-ecotoxic for the two bio-indicators used.

According to the French Regulation CEMWE [18], the fuel used in the combustion trials (Biogran®), the ashes trapped in the first and second cyclones of the combustion test “A” and the ashes retained in the second cyclone during the combustion test “B” must be classified as ecotoxic materials. All the other materials (sand, bottom ashes of both combustion tests and ashes trapped in the first cyclone during the combustion trial “B”) showed no evidence of ecotoxicity.

6. Conclusions

In the chemical point of view, no differences were observed in the composition of the bottom ashes and fly ashes produced in both combustion trials (“A” and “B”). This means that the additional time of combustion and the additional amount of Biogran® incinerated in the combustion test B did not promote a modification on the metal composition of the ashes produced in this combustion trial.

Nevertheless, in each combustion test, the ashes trapped in the two cyclones showed a different chemical composition from the bottom ashes. This difference was much higher between the bottom ashes and the ashes trapped in the second cyclone, than between the bottom ashes and the ashes retained in the first cyclone. In fact, the concentrations of metals had increased along the combustion system, being much higher in the acid extracts and eluates of the ashes trapped in the second cyclone. The ranking of the ashes through the chemical index and their classification through the chemical component of the French Regulation CEMWE [18] have demonstrated the tendency for a higher release of metals in the ashes of the second cyclone.

This tendency for the increasing of the toxicity index from the bottom ashes to the ashes retained in the second cyclone was not confirmed through the ecotoxicological characterization of the eluates by using the bio-indicators *V. fischeri* and *D. magna*. The highest ecotoxicity levels for these bio-indicators were determined in the ashes of the first cyclone.

The difference observed in the ecotoxic levels determined through the chemical and the ecotoxicological analyses of the eluates can be attributed to the different chemical species in which the metals can be present in the different ashes retained in the combustion system or to the presence of other chemical species not analysed in this study. Further studies are needed in this subject of investigation.

Nevertheless, differences on the results of the chemical and ecotoxicological analyses of the eluates prove that the ecotoxicological analyses are complementary of the chemical analyses and indicate the need of these two characterizations to be performed simultaneously in the sub-products of the combustion processes.

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