STUDY OF THE POTENTIAL ECOLOGICAL RISK OF HEAVY METALS IN THE RESIDUE FROM THERMAL CONVERSION OF A SEWAGE SLUDGE

A. Ronda, V. Ferreira, J. Salinero, P. Haro, D. Fuentes-Cano, S. Nilsson, A. Gómez-Barea*
Bioenergy Group, Chemical and Environmental Engineering Department, Universidad de Sevilla
Camino de los Descubrimientos s/n. 41092 Seville (Spain)
agomezbarea@us.es

ABSTRACT: The thermal conversion of the sewage sludge by pyrolysis, gasification and combustion can be an attractive alternative because it reduces the volume of the residue and improve its properties for safe disposal. However, the high content of some heavy metals in sewage sludge has to be carefully considered to come up with rational and sustainable disposal methods. Therefore, the study of the heavy metals distribution in the final residue after the thermal conversion of the sewage sludge is a key topic in order to implement clean methods to valorize sewage sludge. Tests were performed in a horizontal fixed-bed reactor using both nitrogen (pyrolysis) and air (combustion) atmospheres at different temperatures for tests of 20 min duration. At the end of each test, the final residue was collected, and the concentration of main heavy metals was measured by ICP. The results were analyzed through various indexes to establish the enrichment of the species in different ash stream and to assess the potential ecological risk of heavy metals. Finally, obtained value were compared with existing works and standards to assess potential the application of proper management methods.
Keywords: combustion, gasification, heavy metals, potential ecological risk, pyrolysis, sewage sludge

1 INTRODUCTION

The management of waste has taken on great importance in the society in recent years. Inside it, the valorization of municipal solid waste, as the sewage sludge, is an important issue, moreover, since July 2002, European landfills are not authorized to receive this waste to which no pretreatments have been applied and must be reserved for the storage of ultimate waste [1]. Therefore, replacement solutions must be suggested for these wastes.

Thermal treatments have been proposed by several authors [2-6] as a valid option for reducing the amount of waste to be landfilled and simultaneously, for recovering the energy content them.

However, the thermal treatment of sewage sludge produces an ash waste in its turn, which is considered as ultimate waste. They usually are non-combustible materials rich in heavy metals [1].

Therefore, the potential ecological risk of these metals in the final residue has been analyzed before the final disposal, storage or valorization.

In this study, experiments with a sewage sludge were performed in a fixed-bed reactor, in order to collect the total final amount of residue, under different conditions relevant for pyrolysis, gasification and combustion. Final solid was analyzed and heavy metals concentration were determined through various indexes to establish the enrichment of the species and to assess the potential ecological risk of heavy metals. Results were compared with existing works and standards to assess potential the application of proper management methods.

2 MATERIAL AND METHODS

2.1 Sewage Sludge

The samples used in this study were dried sewage sludge obtained from an urban municipal wastewater treatment plan in Spain, in the form of granulated with a particle size in the range of 1-2 mm. It presented a low moisture content (12.57 %) due to the previous dried step, moreover, it had a high VM/FC ratio (8.6), indicating that it presented good properties as fuel. The initial concentrations of heavy metal in the feed SS were measured by Inductively Coupled Plasm (ICP) instrument after dissolved by HNO_3:$HClO_4$:HF (3:1:1 v/v/v solution) and results are presented in Table I (as the average value of three analyses performed over the same sample).

Concentration of heavy metals (HM) were in the same range that other sewage sludge types [7-11], although they were related with the source.

Table I: Initial concentrations of heavy metal in the feed SS.

Element	Concentration, mg/kg	Element	Concentration, mg/kg
Al	8258.1	Na	3050.2
As	4.6	Ni	106.8
Be	<0.3	P	27421.6
Ca	24470.4	Pb	48.7345
Cd	1.9615	Sb	13.7
Co	5.10	Se	<1.0
Cu	384.1	Si	464.5
Cr	73.4602	Sn	284.8
Fe	17859.9	Ti	1088.7
K	4511.6	Tl	<1.3
Mg	5629.7	V	59.8
Mn	206.0	Zn	304.4

2.2 Experimental set-up and procedure

Combustion and pyrolysis runs were carried out in a fixed bed reactor, which consisted in a stainless steel (24.5 mm internal diameter and 630 mm of length) where the material was put inside. Tests were performing at different temperatures and atmospheres during 20 min. Finally, the sample remaining was collected, weighed and the concentration of main heavy metals were measured by ICP. Several index factor were calculated to determine the potential ecological risk of the final solids.

- Enrichment factor (EF): It is defined as the concentration of each heavy metal in the collected ash (C_{ash}^{i}) divided by the concentration of each heavy metal in feed fuel (C_{fuel}^{i}), multiplied by the percentage of ashes in the fuel solid [9].

$$EF^i = \frac{C_{ash}{}^i}{C_{fuel}{}^i} \cdot \frac{\%\, Ash_{final\ solid}}{100} \qquad (1)$$

- Geo-accumulation index (I_{geo}): It is defined by the following equation proposed by Müller [12], where $B_n{}^i$ is the background value of each metal, where the reference in the upper continental crust (UCC) was considered according to Rodríguez-Oroz et al., [13]. The factor 1.5 minimized the effect of minor natural variations of an element and small fluctuations resulting from human activities [13,14].

$$I_{geo} = log_2\left(\frac{C_{ash}{}^i}{1.5 \cdot B_n{}^i}\right) \qquad (2)$$

- Potential ecological risk (RI): It is based on the concentration, number, toxicity and sensitivity of heavy metals [15], where $T_r{}^i$ is the heavy metal toxic response factor. These values, for each heavy metal, were: Cd= 30; As= 10; Ni=6; Co=Cu=Pb=5; Cr=2 and Mn=Ti=Zn=1 [16].

$$RI = \sum_i^n T_r{}^i \cdot \frac{C_{ash}{}^i}{C_{fuel}{}^i} \qquad (3)$$

3 RESULTS AND DISCUSSIONS

The final sample was collected, and the concentrations of heavy metal were measured by ICP. Results for pyrolysis and combustion tests are shown in Table II and III respectively.

From obtained data, proposed index factor was determined and compared to those from literature. The proposal classification for geo-accumulation index (I_{geo}) and potential ecological risk (RI) according other authors is showed in Table IV.

The chemical behavior of heavy metals is extremely complex in the environment since they often directly or indirectly enter into the people’s living environment [17].

Therefore, it is necessary to focus on the risk of heavy metals in the final residue of a thermal process, mainly, when the content of heavy metals in the feed sample is high. The total concentration of an element in sample provides insight into potential environmental hazards [13].

Table II: Concentrations of HM in the final sample after pyrolysis tests.

Element	Pyrolysis		
	500 ºC	700 ºC	900 ºC
Al	33734.94	44512.20	41633.27
As	<d.l	<d.l	<d.l
Be	<d.l	<d.l	<d.l
Ca	136596.39	178846.15	165230.46
Cd	2.01	3.28	3.01
Co	8.03	10.32	9.52
Cu	1556.22	1969.98	1953.91
Fe	62951.81	81848.03	75901.80
K	19026.10	23452.16	19639.28
Mg	22389.56	26969.98	24649.30
Mn	953.82	1125.70	1102.20
Na	7078.31	9005.63	8116.23
Ni	451.81	656.66	601.20
P	27359.44	42307.69	40881.76
Pb	94.88	110.69	56.11
Sb	0.00	0.00	0.00
Se	<d.l	<d.l	<d.l
Si	46385.54	37945.59	37024.05
Sn	0.00	0.00	0.00
Ti	3815.26	4502.81	4358.72
Tl	<d.l	<d.l	<d.l
V	9.54	13.13	12.53
Zn	2961.85	4737.34	1402.81

Table III: Concentrations of HM in the final sample after combustion tests.

Element	Combustion		
	500 ºC	700 ºC	900 ºC
Al	72403.26	74047.62	69858.49
As	<d.l	<d.l	<d.l
Be	<d.l	<d.l	<d.l
Ca	297556.01	303761.90	278632.08
Cd	6.62	6.19	6.60
Co	18.33	14.76	16.51
Cu	3411.41	3428.57	3349.06
Fe	121079.43	128761.90	125235.85
K	39103.87	42476.19	34952.83
Mg	44857.43	44714.29	40283.02
Mn	1680.24	1666.67	1650.94
Na	15987.78	15285.71	14764.15
Ni	1069.25	1000.00	990.57
P	64867.62	64285.71	68443.40
Pb	173.12	162.86	183.49
Sb	0.00	0.00	0.00
Se	<d.l	<d.l	<d.l
Si	96995.93	61809.52	50330.19
Sn	0.00	0.00	0.00
Ti	5855.40	5476.19	5377.36
Tl	<d.l	<d.l	<d.l
V	20.37	20.95	21.23
Zn	8197.56	8333.33	7216.98

Table IV: Proposal classification for geo-accumulation index (I_{geo}) and potential ecological risk (RI) according literature ranges [13,14].

Range	Classification
$I_{geo}\leq 0$	Uncontaminated
$0<I_{geo}\leq 1$	Uncontaminated to moderately contaminated
$1<I_{geo}\leq 2$	Moderately contaminated
$2<I_{geo}\leq 3$	Moderately to heavily contaminated
$3<I_{geo}\leq 4$	Heavily contaminated
$4<I_{geo}\leq 5$	Heavily to extremely contaminated
$I_{geo}>5$	Extremely contaminated
RI<150	Low
150<RI<300	Moderate
300<RI<600	Considerate
RI>600	High

The objective of this paper is to investigate the heavy metal content in the final solid and to evaluate their potential hazard using three index. Obtained results for the Enrichment Factor (EF) in pyrolysis and combustion tests are presented in Figure I and II, respectively and results for obtained geo-accumulation index are showed in Figure III.

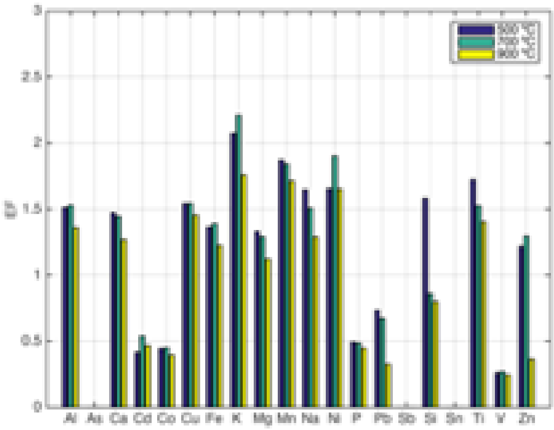

Figure 1: ER of the studied elements in the final solid residue after pyrolysis tests at different temperatures.

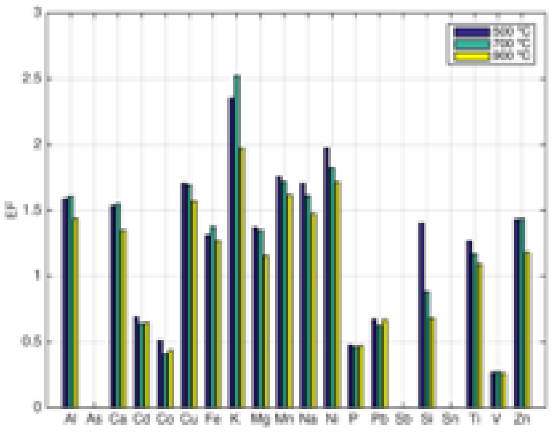

Figure 2: ER of the studied elements in the final solid residue after combustion tests at different temperatures.

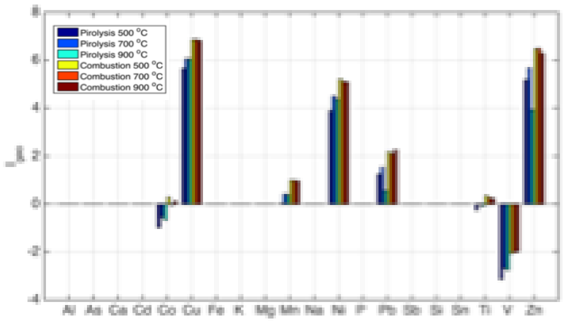

Figure 3: Geo-accumulation index of the studied elements in the final solid residue after pyrolysis and combustion tests at different temperatures.

Finally, the potential ecological riks of final solid residues was obtained based on the concentration of mian heavy metals, and results are showed in Table V.

Table V: Value of the potential risk for six final residue samples.

Operational Conditions		RI
Atmosphere	Temperature, ºC	
N_2	500	81.5072
	700	120.9601
	900	107.1748
Air	500	214.4353
	700	202.6016
	900	208.4037

It was concluded that the values of these indexes in combustion were slightly higher than those obtained for pyrolysis, because of the elevated metal concentration in the combustion residue, since higher amount of mass is lost in combustion compared to pyrolysis. Moreover, EF decreased with the temperature, being more significant during combsution tests, where mass loss was also more significant. The RI values of the residues showed a low contamination index for pyrolysis tests, whereas the calculated RI was moderate for combustion, in all cases, being witthin the range of values reported in literature.

Besides, the Cd, Cu and Ni contributed more significantly to RIs, representing the 73.8, 77.4 and 81.5 % of the total RI for pyrolysis at 500, 700 and 900 ◦C, respectively; and 79.9, 80.3 and 80.0 % of the total RI for combustion tests, respectively. Finally, the calculated geo-accumulation index that most metals in the final residue (with the exception of Cu, Ni and Zn) were categorized as uncontaminated or moderately contaminated.

Finally, in addition, the utilization of ash has been the focus of many studies, which will significantly reduce the volume of ash disposed at landfills [18]. Thus, suggested uses for ash includes the application of ash as agricultural fertilizers, as a fuel due to the presence of high unburned carbon content, as biosorbent material, or as an additive in construction materials.

4 CONCLUSIONS

For all tests, the concentration of most elements in the solid residue were higher than in the raw sewage sludge, mainly due to the mass loss of organic compounds during thermal conversion.

The EF decreased with the temperature and increased with the oxygen amount, where mass loss was also more significant. The potential ecological risk of heavy metals were slightly higher after a combustion process, due to the elevated metal concentration in the combustion residue, since higher amount of mass is lost in combustion compared to pyrolysis.

However, the concentrations of heavy metals in the final residue were below the limit imposed by European legislation, demonstrating the environmental and technical feasibility of ash generated during thermal treatment of sewage sludge.

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