58. Study for removal of heavy metals from sewage sludge by biomass fly ash

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Abstract Within sewage sludge treatment for their use as fertilizer it is common the problem associate with the presence of heavy metals. Some researchers have proved the utilization of coal fly ashes as heavy metals adsorbent (Ahmaruzzaman 2010). In addition, there are evidences of the hydraulic behavior of this kind of ashes -as well as the technical viability for their employment as addition in cement-based materials (Rajamma et al. 2009).
The object of the study is addressed within the European Union strategy about circular economy betting on the incorporation of wastes as resources in production cycle. It is demonstrate the potencial use of biomass fly ash as heavy metals low cost adsorbent.
Results from compositional and microstructural characterization of biomass fly ashes from a power plant placed in Extremadura and a comparative analysis of these properties according to the biomass origin are presented. Moreover, in this work, the influence of adsorbed metals in potential properties such as hydraulic and pozzolanic capacity among others, for their possible use as addition in cement-based materials were analyzed.

Keywords Fly ash; Sludge; Biomass; Adsorption; Metals

1 Introduction

Water treatment plants generate high amounts of sewage sludge, which need to be treated with the object of eliminate toxic compounds and pathogens present in this short of wastes. In many occasions, water treatment plants do not have means to carry out the already said treatment, therefore, the sludge is collected without any use.
European Union with the concept of circular economy promotes the recycling and reuse of this kind of wastes, among others. This is the case of sewage sludge being used as fertilizer or being incorporated in construction materials (Johnson et al. 2014).

The current issue in sewage sludge treatment is focused in the heavy metals elimination. Along these lines, some researches demonstrate the viability of the use of coal ash as heavy metal adsorbent (Ahmaruzzaman 2010).
On the other hand, with the employment of biomass to produce energy, wastes are also generated and to this point have been used as fertilizers and addition to concrete mixtures. The present research pretends demonstrating the potential use of biomass fly ash as adsorbent of heavy metals from sewage sludge. In this way, two different wastes, with origin in water treatment plants and energy production, are been valued, and two more industries, fertilizers and construction, are been benefited.
Furthermore, fly ash poses hydraulic and pozzolanic properties which fit to be incorporated to cement based materials.
The study described belongs to the LIFE14 project iCirBus-4Industries, carried out for different industries in the Extremadura region (Spain). This European project started in 2015 and its estimated end date is 2020, now the project is in laboratory research phase that will continue during 2017. The results of the study are preliminary and will be completed with the planned future works.

2 Experimental procedure

2.1 Material

Fly ashes were collected monthly for a year, from the electrostatic precipitator of a biomass power plant placed in Mérida (Spain). In this work, three samples have been chosen tending to the biomass employed in power plant, therefore, samples from forest biomass (F1) and samples from forest biomass with a certain percentage of woody agricultural residue (FAL1, FAL2), have been employed for sewage sludge treatment..

Within samples with the same origin and the same collection date, different samples are found depending on the collection method: direct collection or collection by blowing off the fly ash from the collection sleeves (Fig. 1). The second fly ash has been chosen for the analyses.
Before testing, samples were dried in a heater to constant mass in order to remove moisture.

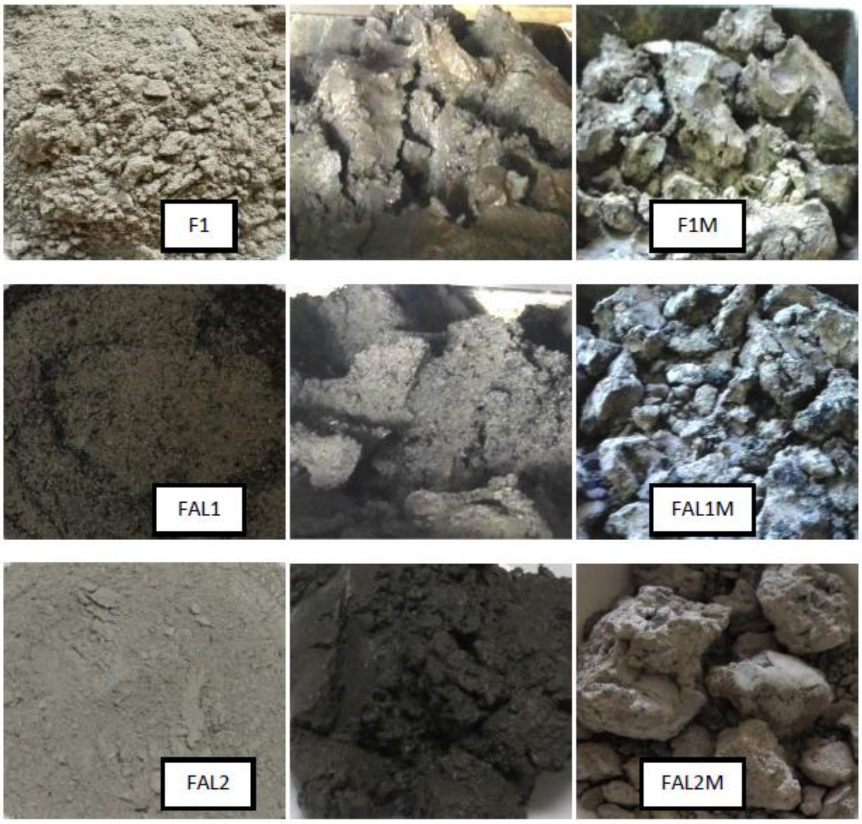

Fig. 1 F1, FAL1 and FAL2 before sewage sludge treatment, after treatment and dried at 40ºC

2.2 Sewage sludge treatment by means of biomass fly ash

Samples F1, FAL1 and FAL2 have been taken for the treatment of sewage sludge which origin is the water treatment plant placed in Lobón (Badajoz, Spain). All samples have followed the same procedure, immersion of a porous bag containing fly ash into sludge during three hours with slight agitation, and in a proportion of 1/10.

The laboratory methodology has been developed for that specific treatment; it has low energy consumption and could be extrapolated to a future prototype plant of sewage sludge treatment by fly ash. After treatment samples with high moisture are obtained (F1M, FAL1M, FAL2M) and analyzed with the aim to evaluate the possible heavy metals adsorption and its influence in initial fly ash microstructure. Cd, Cu, Ni, Pb, Zn, Hg and Cr were analyzed according to regulatory requirements included in the R.D. 506/2013 (Annex V). According to the R.D., depending on the amount of each metal three classes (A, B or C) of fertilizer are defined; with the sludge treatment is intended to achieve a Class A fertilizer, the one with a lower amount of heavy metals.

2.3 Microstructural characterization

Absolute density, specific surface and pore size distribution have been measured by mercury porosimetry and helium picnometry, employing suitable laboratory instrumental: Micrometrics Autopore IV 9500, Quantachrome stereopicnometer.

2.4 Compositional characterization

2.4.1 X-Ray fluorescence spectroscopy

XRF was used to determine the bulk chemical concentrations of major and trace elements present in the biomass fly ash. The chemical compositions expressed as oxides were determined with a spectrometer ARL ADVANT`XP+ with a Rhodium tube and chemical concentrations were obtained by UNIQUANT software and an international standard database.
In order to determine trace elements, measurements were acquired from pressed powder samples with a spectrometer Bruker S4 Pioneer with an X-ray tube with a rhodium anode under helium atmosphere at 200 mbar.

2.4.2 Fourier transformed infrared spectroscopy

Infrared spectrums were obtained in order to determine main functional surface groups as well as major compounds and minerals present in fly ash. Spectroscopy was carried out with a Thermoscientific Nicolet 6700 Fourier transform infrared (FTIR) spectrometer.

2.4.3 Thermogravimetric and derivated thermogravimetric analyses

Thermogravimetric analyses were performed on a SETARAM LABSYS EVO 1600 in order to determinate main chemical compounds present in fly ash from the steepest loss of mass observed at certain temperature. Helium was used as the purge gas at a pressure of 1600 mbar to avoid oxidation and combustion of unburned carbon and organic matter remained in samples.

3 Results and discussion

3.1 Microstructural characterization

In the collected data in table 1, can be observed that starting fly ash samples F1, FAL1 and FAL2 are predominantly macroporous. Macropores volumes (V_{macro}) are between 0.927-1.220 $cm^3\ g^{-1}$. A very low mesopore volume was calculated around 0.001-0005 $cm^{-3}g^{-1}$. Difference between total pore volume and mercury volume intruded (V_p-V_{Hg}) is related to a more or less developed microporosity and closed-pores.
After treatment of sewage sludge microstructural parameters were also determined on the fly ash samples containing adsorbed metals F1M, FAL1M and FAL2M. As observed in table 1 a decreasing of the evaluated parameters is produced on each fly ash. This may be explained due to the fact that when sewage sludge compounds, including metals, are adsorbed on the pore surface of fly ash, pore diameter may be reduced towards smaller sizes that lead to a lower pore volume (V_p) and specific surface (S_{Hg}). This effect is always observed over the three studied samples.
Different behaviour of pore volume as a function of their size is observed. On each sample macropore volume decreases after treatment of sewage sludge. This is due to that normally macropores are in the outer surface of sample, thus they can act as channels for transporting metals to the inner surface of fly ash which is composed by mesopores and micropores.

Table 1 Microstructural parameters of fly ash before and after treatment of sewage sludge

Fly ash sample	**ρ apparent g cm^{-3}**	**Vp cm^3 g^{-1}**	**Vmacro cm^3 g^{-1}**	**V meso cm^3 g^{-1}**	**Vp-VHg cm^3 g^{-1}**	**SHg m^2 g^{-1}**	**Median diameter nm**
F1	0.614	1.238	1.141	0.002	0.095	3.126	7942
F1M	0.716	1.016	0.815	0.000	0.202	1.050	5616
FAL1	0.596	1.318	1.220	0.001	0.097	5.294	4141
FAL1M	0.907	0.701	0.663	0.009	0.029	3.119	13434
FAL2	0.744	0.957	0.927	0.005	0.026	3.524	9642
FAL2M	1.015	0.604	0.538	0.005	0.060	2.909	2470

Mesopore volume (V_{meso}) and estimated micropore and closed-pore volume not accessible by mercury intrusion but to helium (V_p-V_{Hg}) show an inverse relationship. In samples F1, F1M, FAL2 and FAL2M and FAL2M when macroporous volume decreases, mesoporous volume and V_p-V_{Hg} value increase. The opposite effect on FAL1 and FAL1M samples is produced. As mentioned above, this behaviour might be influenced by collapse of surface and shrinkage of fly ash pore structure due to occupied space of molecules and metals adsorbed. This may progressively transform macropores in mesoporous and mesoporous in micropores and finally micropores in closed or not accessible pores. In addition, apparent density values are in agreement with the latest results which are related to decreasing of pore size and voids. These results point out that a certain quantity of matter has been at least retained on the fly ash surface. In Fig. 2 pore size distribution obtained by mercury intrusion shows the size modification and of macropores and mesoporous after treatment as observed in data from table 1.

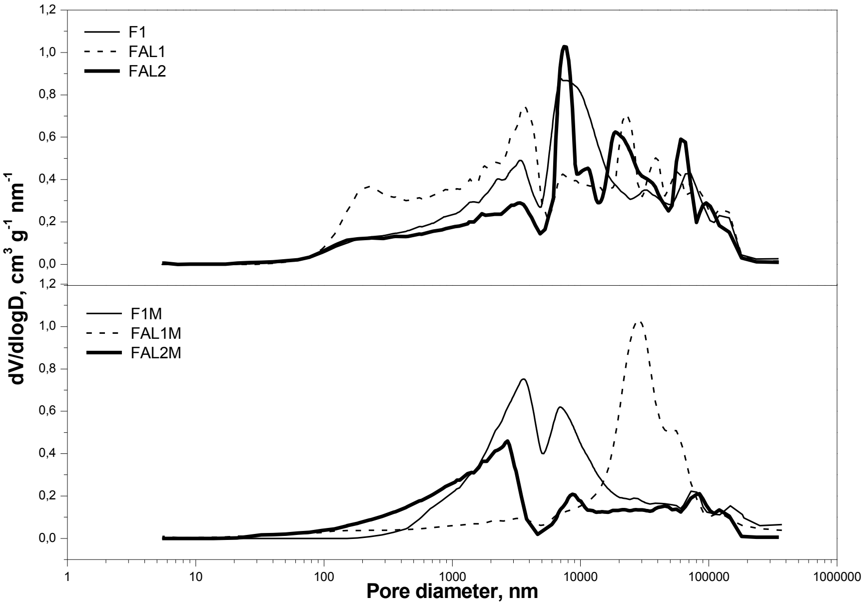

Fig. 2 Pore size distributions of fly ash samples before (up) and after (down) treatment

3.2.1 X-Ray fluorescence spectroscopy

Once that the modification of microstructural parameters after treatment have been verified, it could be confirmed an adsorption and retention of metals from sludge. When the sewage sludge is treated with fly ash, some metals are adsorbed on ash specific surface, and, as a result, the amount of those metals increase. In other cases the transference of elements happens inversely, the fly ash loses compounds by solubilization.

With the aim to prove the heavy metals adsorption capacity of biomass fly ash six samples have been analyzed by XRF analysis: three before treatment and the same samples after sewage sludge treatment.

Related to the metals to be analyzed, they are determined quantitatively in each fly ash before and after treatment, as well as in initial sludge. In graphic below (Fig. 3) are presented the obtained results, noting that Ni and Cr are hardly retained in fly ash. With respect to Zn, Cu and Pb, for samples F1 and FAL2 the increase in final metal content is greater, indicating a higher retention. These data have been contrasted with de analyses performed in treated sludge (Fig. 4).

It is important to say that neither Cd nor Hg are detected in any fly ash sample.

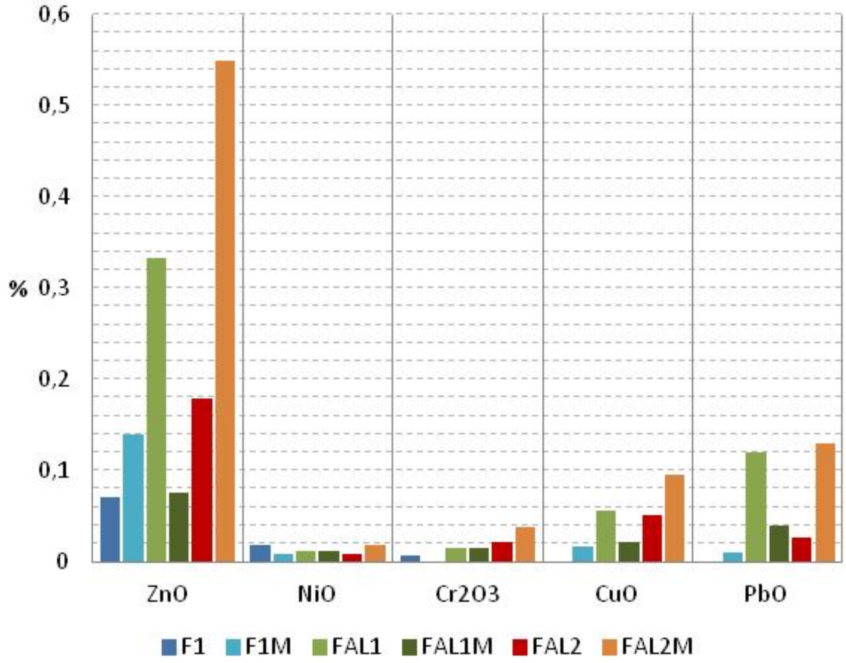

Fig. 3 Graphic of the different amount of heavy metals for the analyzed fly ash samples F1, F1M, FAL1, FAL1M, FAL2 and FAL2M

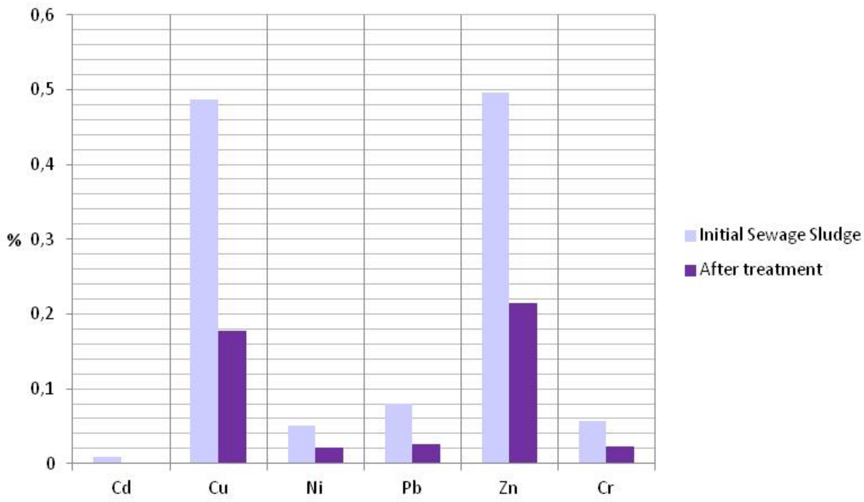

Fig. 4 Graphic of the decrease in heavy metals for sewage sludge

For two of the samples (F1M and FAL2M) it is demonstrated the adsorption of heavy metals, furthermore, for FAL2M the sewage sludge treated has been analyzed and the adsorption of heavy metals in fly ash corresponds to the decrease of this elements in sludge. For FAL1M there is no evidence of adsorption and, at microstructural level, it is observed a reduction of active specific surface.
The performed analyses will be repeated and the amount of sludge that could become part of the fly ash will be measured, in order to control the obtained results.

3.2.2 Fourier transformed infrared spectroscopy

FTIR spectrums on fly ash samples after treatment present almost identical composition when is compared to fly ash before (Fig. 5). It is observed a strong band around 998-1026 cm^{-1} that can be attributed to Si-O-Si asymmetric stretching vibrations from minerals as mullite, quartz and glass very typical compounds of fly ash. The overlaps bands at 776 and 802 cm^{-1} confirms presence of quartz. The little band appearing around 1100 cm^{-1} is associated with Al–O or Si-O asymmetric stretching vibrations what indicate presence of aluminosilicates. Sharp medium intensity peaks at 871 and 1412 cm^{-1} correspond to different vibrations of inorganic carbonates, mainly calcite, and 1786 cm^{-1} is due to water molecules adsorbed on the fly ash surface due to moisture content. Around 3623 cm^{-1} the little peak observed is according to presence of calcium hydroxide which is consistent with results obtained from thermal analysis.
After treatment is observed a broad band around 3300-3400 cm^{-1} only when fly ash have been treated. Normally, this band is associated to vibration of water molecules and hydroxyl functional groups of calcium silicate hydrate which is present similar to that ordinary hydraulic cement. This indicate that a residual hydraulic capacity in fly ash which is very useful for their incorporation as addition in fabrication of cement-based materials for construction.

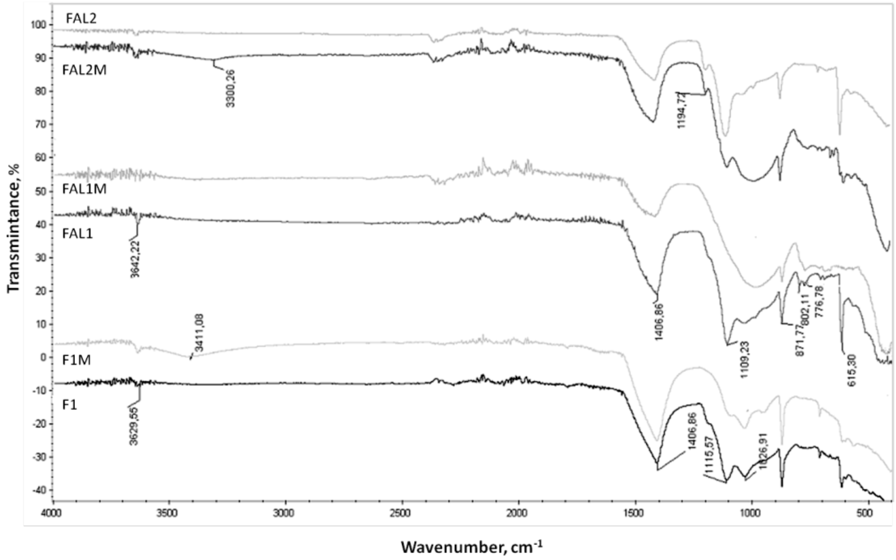

Fig. 5 FTIR spectrums on selected fly ash samples before and after sewage sludge treatment

3.2.3 Thermogravimetric and derivated thermogravimetric analyses

Thermal analysis gave further information about main chemical compounds. It was always observed that for all samples the weight loss takes place mainly in three distinct steps due to removing of water physically adsorbed, releasing of water molecules present in hydraulic compounds as calcium hydroxide ($Ca(OH)_2$) and emissions of large amounts of carbon dioxide from decomposition of inorganic carbonates as calcium carbonate ($CaCO_3$). Observed differences between treated and original samples may be due to two reasons: progressive hydration of free lime and ulterior carbonation by contact in wet sewage sludge during treatment; dilution effect due to more or less content of residual sludge on the fly ash, what might affect to percentages of determined compounds.

Table 2 Major compounds in fly determined by thermal analysis before and after treatment of sewage sludge

Sample	Moisture, %	Ca(OH)2, %	CaCO3, %
F1	1,30	3,83	15,24
F1M	2,95	14,34	37,17
FAL1	0,91	1,86	4,55
FAL1M	0,57	0,80	2,77
FAL2	0,77	5,59	16,20
FAL2M	1,49	4,06	12,90

4 Conclusions

- Biomass fly ashes present a microstructural behavior that gives them the capacity of using them as a potential heavy metal adsorbent.
- Biomass fly ash treated with sewage sludge and after the adsorption of heavy metals, keeps its hydraulic properties for its potential use as an addition for cement-based construction materials.
- The methodology employed is presented as a possible effective method, efficient and sustainable, for the reduction of pollutant metals from sewage sludge, answering to a current environmental problem related to wastes riskiness.
- The obtained results bring to light the possibility of incorporating two wastes, sludge and fly ash, as raw material to generate products like fertilizers or construction materials, this object is in line with the circular economy strategy.

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