Novel biomass fly ash-based geopolymers for environmental applications

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Abstract: - Geopolymers are widely known as a promising and environmental friendlier alternative to Portland cement and for that reason numerous investigations have been focused on the development of geopolymers, most of them aiming to reach high mechanical properties for potential structural applications. However, these materials show a variety of other interesting properties, suggesting their use in innovative applications where their performance ability outperforms other common materials. Environmental applications ranging from thermal insulating, pH buffering and wastewater treatment are envisioned. In this study the feasibility of using biomass fly ash-based geopolymers as lead adsorbents was evaluated. The influence of heavy metal concentration in aqueous solutions, their pH, the adsorbent amount, and contact time on the lead removal efficiency by the geopolymers was investigated. Results show a lead uptake up to 35 mg/g which demonstrates the potential of these novel materials as lead adsorbents.

Key-Words: - Biomass fly ash; geopolymer; lead adsorption.

1 Introduction

The presence of lead in industrial wastewaters raises serious environmental concerns [1]. Firstly lead is known to be toxic for humans and plants [2], and secondly leakage from the wastewaters can cause groundwater contamination. Therefore their removal from wastewaters is of the foremost importance. Among the several methods that have been carried out for heavy metal removal (e.g. chemical precipitation, coagulation, ion exchange) adsorption has attracted increasing attention do to its simplicity, efficiency and low cost [3].

In recent years the annual production of biomass fly ash (FA) wastes has sharply increased, which is explained by the renewed interest in the production of electrical energy through the use of biomass [4]. The current management strategies (e.g. incorporation in cements and addition to forest soils) are unable to consume the massive production volumes of these wastes, with large quantities still disposed in landfills. In this context the possibility of converting this waste product into a useful and valuable material can mitigate its environmental impact. One approach to recycle these FA could be their incorporation as raw materials in the geopolymers production. Geopolymers are amorphous materials produced when aluminosilicate sources are dissolved at a very high pH. Their chemical structure, composed by negatively charged aluminosilicate framework where charge-balancing cations can be exchanged with cations in the solution [5], suggests the possibility of using them as adsorbents. Nevertheless this possibility has scarcely been investigated [5, 6].

The use of geopolymers for environmental applications has attracted increased attention over the past years. In fact previous investigation have demonstrated the potential of porous geopolymers for innovative applications, such as thermal insulation [7, 8], pH buffering [9] and heavy metal adsorption [10].

In this work, biomass FA-based geopolymers were produced and then evaluated as lead adsorbents. Adsorption of Pb^{2+} by these geopolymers is studied as a function of heavy metal concentration in aqueous solutions, their pH, the adsorbent weight, and contact time.

2 Experimental

2.1 Materials
Metakaolin (MK) was purchased under the name of Argical™ M1200S from Univar®, while FA from biomass combustion was collected at the electrostatic precipitator of a Portuguese industrial co-generation plant with bubbling fluidized combustor, that consumes a mixture of eucalyptus bark with minor amounts of other residual biomass from forestry operations as fuel.

For the alkaline activation, a mixture of sodium silicate solution (Quimialmel, Portugal) and NaOH (reagent grade, 97%, Sigma Aldrich) was used in a 2:1 proportion. The 10 M NaOH solution was prepared by dissolution of sodium hydroxide beads in distilled water.

The Pb^{2+} ion stock solutions were prepared by dissolving $Pb(NO_3)_2$ (analytic grade reagent) in distilled water.

2.2 Geopolymers preparation
Geopolymers were prepared using a mixture of 2/3 (weight basis) biomass FA and 1/3 MK as a source of aluminosilicate. The mixing was carried out following a procedure described elsewhere [7]. After mixing the slurry was transferred to plastic moulds and sealed with a plastic film. The samples were cured in controlled conditions (40 ℃ and 65% relative humidity) using a climatic chamber for 3 days. Afterwards, the specimens were demoulded and kept sealed in the same curing conditions until the 7th curing day. Upon curing the samples were crushed and sieved to control the particle size (d< 75 μm).

2.3 Lead adsorption test
Before the adsorption and considering the alkaline nature of the geopolymers [9] they were treated with a nitric acid solution (2 vol. %) for 60 min. This way, we tried to avoid metal precipitation. Then, the samples were washed with distilled water until the pH of the washing water was kept at 7.0 ± 0.5.

Lead adsorption tests were carried out in order to study the influence of Pb^{2+} initial concentration (C_0), geopolymer dosage, contact time and pH. Distinct geopolymer dosages (0.05-0.20 g) were added to 50 mL of a solution containing a specified Pb^{2+} concentration (10-120 ppm) with a specific pH (4 and 5) and shaken during a predetermined period of time (2-60 min) at room temperature. The Pb^{2+}

concentration was determined using an atomic absorption spectrometer (Avanta PV, GBC).

The removal efficiency (E) was calculated using the following equation [11]:

$$E\ (\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

where C_e is the remaining equilibrium lead concentration (ppm).

The quantity of lead uptake by the geopolymer was determined according to the following equation [12]:

$$q = \frac{(C_0 - C_e)}{m} \times V \tag{2}$$

where q is the quantity of lead uptake by the geopolymer ($mg_{lead}/g_{geopolymer}$), V is the solution volume (L) and m is the mass of geopolymer (g).

2.4 Materials characterization
Scanning electron microscopy (SEM - Hitachi S4100 equipped with energy dispersion spectroscopy, EDS – Rontec) was used, at 25 kV, to investigate the microstructure of the geopolymers.

The mineralogical compositions of MK, FA and FA-based geopolymer (cured for 7 days) were assessed by X-ray powder diffraction (XRD). The XRD was conducted on a Rigaku Geigerflex D/max-Series instrument (Cu Kα radiation, 10–80°, 0.02° 2θ step-scan and 10 s/step), and phase identification by PANalytical X'Pert HighScore Plus software.

The chemical composition of FA and MK was obtained by using X-ray fluorescence (Philips X´Pert PRO MPD spectrometer).

The chemical analysis (for Pb) of the aqueous solutions obtained from the adsorption/desorption tests was performed by using the same atomic absorption spectrometer.

3 Results and Discussion

3.1 Geopolymers characterization
The XRD patterns of the FA, MK and the FA-based geopolymer are presented in Fig. 1. The diffraction peaks in the geopolymer coincide with those of the precursors; nevertheless the peaks' intensity decreases and some crystalline peaks were lost. The geopolymer pattern shows a broad hump between 20-40° (2θ), the centre being located around 30° (2θ) while in the MK at about 23° (2θ). This right shift is typically attributed to the formation of new amorphous phases, providing evidence of geopolymerization occurrence [13]. The chemical

composition shows that the most abundant oxides in the FA are CaO (36.72 wt.%), SiO_2 (25.34 wt.%), Al_2O_3 (6.05 wt.%), K_2O (5.84 wt.%), and Fe_2O_3 (4.15 wt.%). Not surprisingly the dominant elements in MK are SiO_2 (54.40 wt.%) and Al_2O_3 (39.40 wt.%).
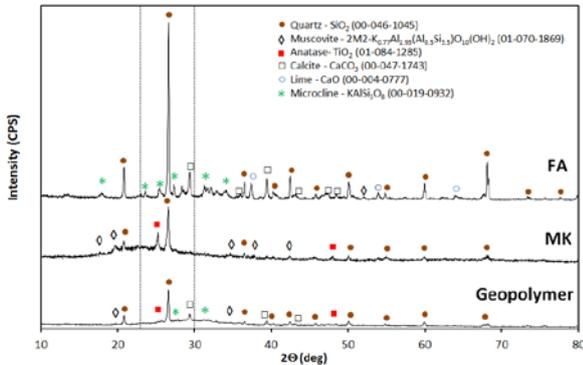

Fig. 1. XRD patterns of FA, MK and the synthesized geopolymer.

Fig. 2 presents the SEM micrographs and the corresponding EDS spectrum of the geopolymers before and after being treated with the acidic solution. As expected, the EDS spectrum of the produced geopolymers (Fig. 2c) shows significant sodium content, considerably higher than that evaluated in the raw materials [9]. However after the acidic treatment sodium was no longer observed, while the intensity of the calcium peaks decreased (see Fig. 2d). This fact suggests that the free alkalis remaining in the geopolymer structure were leached out during the pH neutralization step.
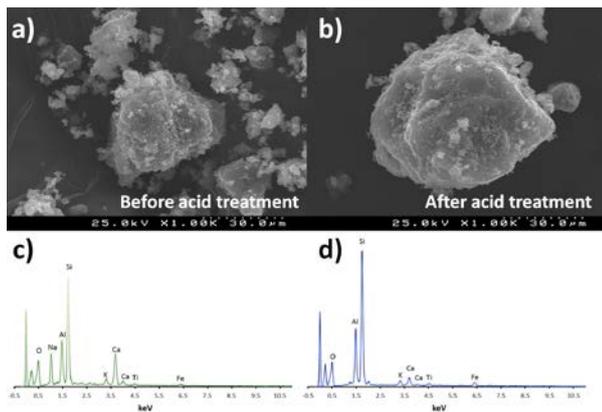

Fig. 2. SEM micrographs (a and b) and EDS spectrum (c and d) of the FA-based geopolymer before (a and c) and after (b and d) acid treatment.

3.2 Influence of Pb^{2+} concentration

The influence of the heavy metal initial concentration in the solution on the Pb^{2+} removal is illustrated in Fig. 3. A sixfold increase on the lead uptake was observed when the heavy metal concentration jumped from 10 ppm to 100 ppm, however the uptake decreases for higher concentrations. The latter suggests that above 100 ppm the geopolymer reached the saturation level. In agreement, the removal efficiency remains higher than 88% up to 100 ppm, while dropping for higher Pb^{2+} concentrations. This shows that the heavy metal removal is dependent on its concentration. Indeed the latter has been previously reported [14].

Fig. 4 presents the EDS of the FA-based geopolymer after adsorption tests for two heavy metal initial concentrations. Fig. 4a and 4b clearly show the presence of lead in the geopolymer, while it was absent before the test (see Fig. 2d). Furthermore the intensity of the lead peak increases when the initial concentration of heavy metal in solution rises, thus supporting the abovementioned remarks.
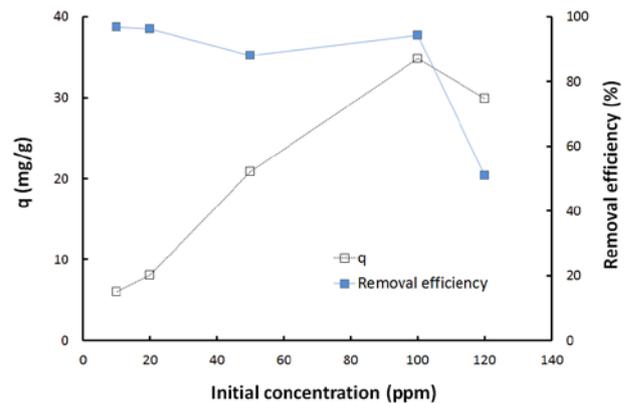

Fig. 3. Effect of initial concentration of Pb^{2+} on the removal efficiency of this heavy metal (geopolymer dosage: 0.10 g, pH = 5; contact time: 60 min).
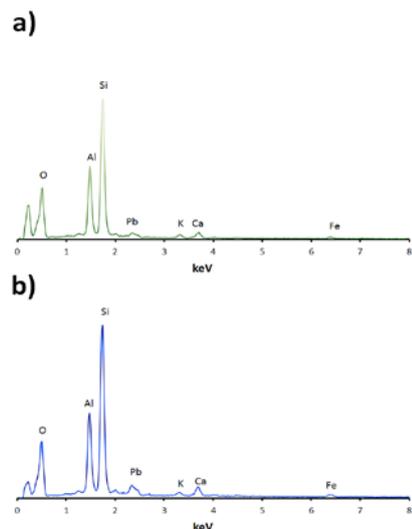

Fig. 4. EDS spectrum of the FA-based geopolymer after 10 min contact time in distinct Pb^{2+} concentration: a) 50 ppm and b)100 ppm.

3.3 Influence of adsorbent weight

The influence of the adsorbent content on the Pb^{2+} removal efficiency is shown in Fig. 5. As depicted the removal efficiency increases from around 30% to circa 100% as the weight rises from 0.05 g (1 g/L) to 0.15 g (3 g/L), which was attributed to the higher number of active sites available for adsorption. Minor fluctuations on the removal efficiency are observed above this content, which suggests that 0.15 g is the optimal amount for such experimental conditions. The low removal efficiency at low adsorbent content indicates that the number of available sites for Pb^{2+} adsorption is insufficient for removal all the Pb^{2+} ions from the solution [6].
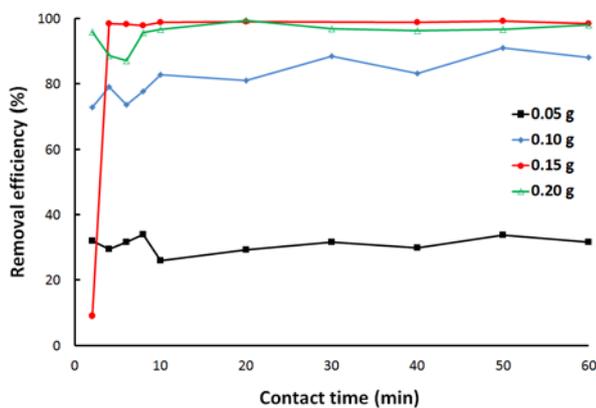

Fig. 5. Effect of geopolymer dosage on the lead removal efficiency ($[Pb^{2+}]$ = 50 ppm, pH = 5).

3.4 Influence of contact time

The influence of contact time of the Pb^{2+} uptake and removal efficiency was studied for contact times up to 60 min, for different C_0 at fixed geopolymer dosage (0.1 g) and pH (5). As expected the removal efficiency (see Fig. 6a) increases with contact time, in particular in the first 10-20 min. Nevertheless the lead adsorption occurs rapidly for all considered conditions, an equilibrium being reached after 30 min. The time dependence of heavy metals adsorption has been reported in other investigations [15, 16], still the equilibrium time here reported is significantly lower than that reported by Al-Zboon et al. (120 min) [15].

3.5 Influence of pH

Previous investigations have shown that the pH strongly affects the heavy metals removal [3,17]. At low pH the adsorption is hindered by the excess of H^+ ions, while high pH promotes the formation of lead hydroxides that might precipitate. In that sense

adsorption tests were performed at pH 4 and 5, at constant geopolymer weight and C_0. Fig. 7 shows that the lead uptake (q) drops from 20.88 mg/g to 7.05 mg/g (60 min contact time) when the pH decreases. This performance loss is probably associated with the increase on H^+ ions at lower pH values, which raises the competition with the Pb^{2+} for the adsorption sites. Indeed the low removal efficiency at pH = 4, around 40%, indicates that the H^+ ions are the prevalent species, while at higher pH (5) Pb^{2+} ions prevail and removal efficiency rises to nearly 90%.
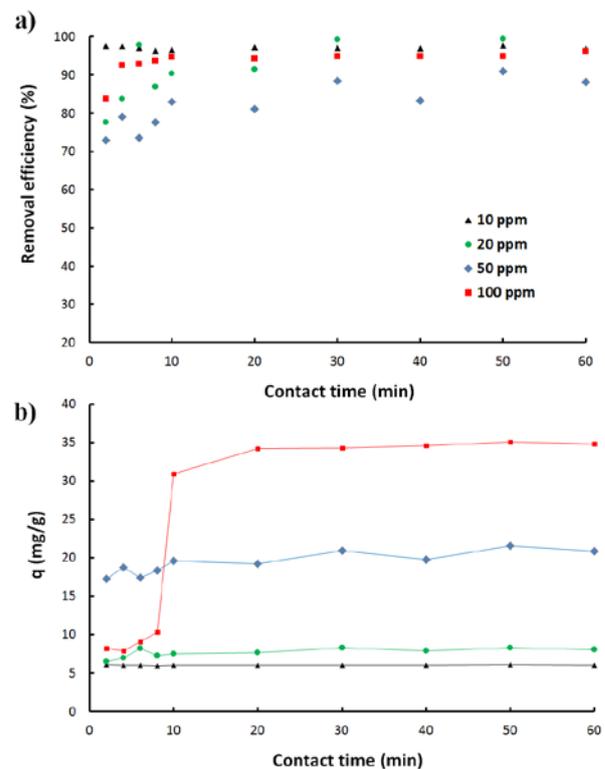

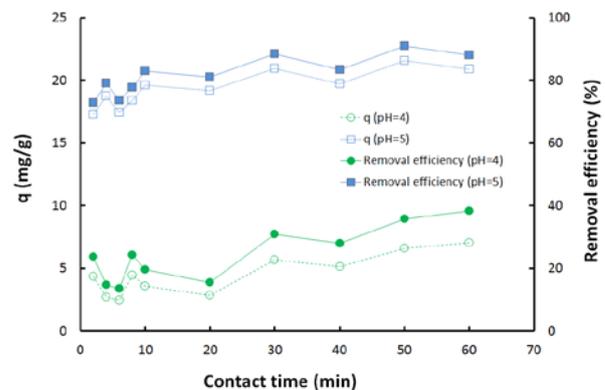Fig. 6. Influence of contact time on the Pb^{2+} removal efficiency (a) and lead uptake (b).

Fig. 7. Influence of pH on the Pb^{2+} uptake and removal efficiency ($[Pb^{2+}]$ = 50 ppm, geopolymer dosage: 0.10 g).

4 Conclusions

In the present work, biomass FA-based geopolymers were used as lead adsorbents from synthetic wastewaters. Results demonstrate that the initial concentration of Pb^{2+}, the adsorbent weight and the pH are the most influential factors affecting the removal efficiency, while the contact time is less relevant. In fact the adsorption by these innovative materials occurs rapidly, 20 min being the average equilibrium time among the investigated conditions. Results show a sixfold increase on the lead uptake when the heavy metal concentration rises from 10 ppm to 100 ppm, after which the uptake drops. As for the adsorbent dosage the highest efficiency was observed when using 0.15 g (3 g/L).

A decrease on pH (from 5 to 4) was found detrimental to lead removal, which was attributed to the higher competition between the H^+ and the Pb^{2+} ions.

The maximum geopolymers adsorption capacity here reported (35 mg/g) demonstrates the potential of these novel materials as lead adsorbents. Furthermore the incorporation of biomass fly ash in the geopolymers promotes waste valorization, while mitigating the environmental impact of these wastes.

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