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Biomass fly ashes as low-cost chemical agents for Pb removal from synthetic and industrial wastewaters

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ABSTRACT

The main aim of this work was to study the removal efficiency of Pb from synthetic and industrial wastewaters by using biomass fly ashes. The biomass fly ashes were produced in a biomass boiler of a pulp and paper industry. Three concentrations of Pb^{2+} were tested in the synthetic wastewater (1, 10 and 1000 mg Pb/L). Moreover, two different wastewaters were collected in an industrial wastewater treatment plant (IWWTP) of an industry of lead-acid batteries: (i) wastewater of the equalization tank, and (ii) IWWTP effluent. All the wastewaters were submitted to coagulation–flocculation tests with a wide range of biomass fly ashes dosage (expressed as Solid/Liquid – S/L – ratios). All supernatants were characterized for chemical and ecotoxicological parameters. The use of biomass fly ashes has reduced significantly the Pb concentration in the synthetic wastewater and in the wastewaters collected in the IWWTP. For example, the definitive coagulation–flocculation assays performed over the IWWTP effluent presented a very low concentration of Pb (0.35 mg/L) for the S/L ratio of 1.23 g/L. Globally, the ecotoxicological characterization of the supernatants resulting from the coagulation–flocculation assays of all wastewaters has indicated an overall reduction on the ecotoxicity of the crude wastewaters, due to the removal of Pb.

Introduction

The most common sources of lead in the environment are Pb-based pigments in paints, Pb-containing pesticides, discarded batteries, shooting ranges or waterfowl hunting sites and plumbing installations or repair sites [1]. Despite some efforts on the reduction of the use of lead in some industrial activities and in some manufactured products, there are still some industries that use lead as raw material. Since lead is a heavy metal which is toxic to humans and to other living beings it is extremely important to remove this pollutant from wastewater [2–5].

The precipitation of metals from wastewaters involves the conversion of the soluble metal salt to insoluble salts [6,7]. The precipitate formed can then be removed from the treated wastewater by sedimentation and/or filtration. This process usually needs a pH adjustment, followed by the addition of a chemical coagulant [8–12]. Typically, metals precipitate from the solution as hydroxides, sulfides or carbonates. Depending on the type of the process used, it may be produced a sludge with so high concentrations of metals that can be submitted to metal recovery [13,14]. The classical wastewater treatment systems use ferric-chloride, ferric-sulfate and aluminum sulfate as coagulation reagents, but due to their high cost, the industrial sector has begun to search for efficient and low cost chemical agents.

In this framework, several studies have been performed related to wastewater treatment using fly ashes produced from the combustion of several fuels [6,10,12,15–19]. However, these studies were not focused neither on the treatment of wastewaters produced by industries of lead-acid batteries nor on the use of biomass fly ashes from forestry residues as chemical agents for metal removal.

Coal fly ashes have a high potential in the treatment of wastewater because of their chemical composition. This type of fly ashes has high contents of alumina, silica, ferric oxide, calcium oxide, magnesium oxide and carbon, which can participate on the removal of several elements [6,7]. Moreover, the physical properties of coal fly ashes, such as porosity, particle size distribution and surface area, make them also attractive for the treatment of wastewaters. The alkaline nature of fly ashes is also a useful property which make them a good neutralizing agent of acid wastewaters [8,9].

Al Zboon et al. [12] have produced a geopolymer from coal fly ashes and used it for the removal of Pb^{2+} from an aqueous

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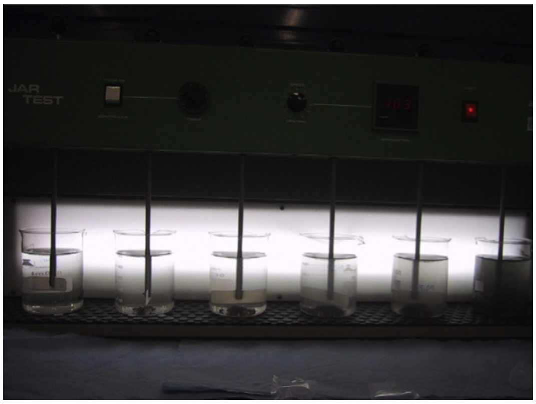

Fig. 1. Preparation of a coagulation–flocculation test with synthetic wastewater and using forestry fly ashes as removal agent of pollutants.

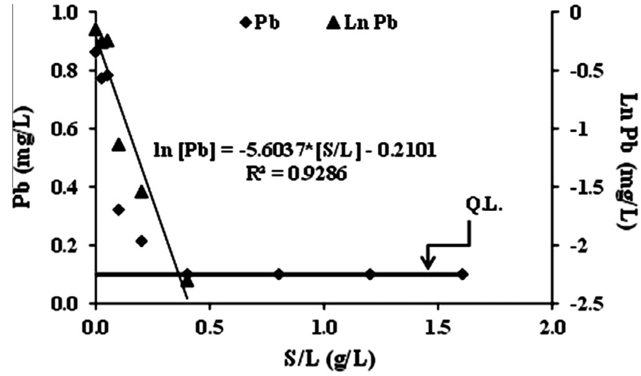

Fig. 2. Pb concentration and Ln (Pb) in the supernatants of the synthetic wastewater (1 mg Pb/L) as a function of the S/L ratio of biomass fly ashes used in the coagulation–flocculation assay.

wastewater. The authors have tested the effect of various parameters on lead adsorption, including geopolymer dosage, initial concentration, contact time, pH and temperature. Despite of the good results that were obtained, the assays performed were not applied to a real wastewater sample, but only to a synthetic one.

Gupta and Torres [15] have evaluated the removal of heavy metals and the changes on the toxicity of an effluent of a municipal wastewater treatment plant by using coal fly ashes. After the treatment with fly ashes, a reduction in toxicity and in the concentrations of Cu, Pb, PO_4^{3-}, and NO_3^- was registered.

Cho et al. [17] have investigated the possibility of using coal fly ashes as chemical adsorbents. The authors have performed batch experiments to evaluate the removal of heavy metals from synthetic aqueous solutions by fly ashes. Adsorption studies were done at various pH values (3–10), at 25 °C, and for heavy metal concentrations (Zn, Pb, Cd and Cu) of 10–400 mg/L using fly ashes dosages of 10, 20 and 40 g/L. The authors have concluded that coal fly ashes may promote good removal efficiencies unless the wastewater is strongly acidic.

Alinnor [10] has evaluated the removal characteristics of Pb^{2+} and Cu^{2+} ions from aqueous solution by coal fly ashes under various conditions of contact time, pH and temperature (30–60 °C). The level of removal of these metals has generally increased with the increase in pH values. In what concerns the effect of temperature, the highest removal rate of those metals was achieved at 40 °C. According to this author, the main mechanisms involved in the removal of Pb^{2+} and Cu^{2+} from solution were adsorption at the surface of the coal fly ashes and precipitation.

Malakootian et al. [18] have evaluated the removal of heavy metals (Pb and Co) from an effluent produced by a paint industry. The effect of pH and dosages of wood ashes was tested. This effluent contained initial concentrations of Pb and Co of 5.4 mg Pb/L and 1.15 mg Co/L, respectively. The highest Pb removal efficiency was of 96.1%, at pH 2, with a contact time of 3 h and 100 g/L wood ashes. The highest Co removal efficiency was of 99.0%, at pH 2, with a contact time of 3 h and 100 g/L wood ashes.

Many other studies could be referred here. Nevertheless, to the author's knowledge, none of these studies was focused neither on the treatment of wastewaters from an industry of lead-acid batteries nor on the use of biomass fly ashes from forest residues as a chemical agent for Pb removal. In this framework, the main goal of this study was to assess the removal efficiency of Pb^{2+} from a synthetic wastewater containing initial concentrations of 1, 10 and 1000 mg Pb/L, and from two wastewaters of an industry of lead-acid batteries, by using biomass fly ashes from a biomass boiler of a pulp and paper industry.

Materials and methods

Origin and characterization of biomass fly ashes

The biomass fly ashes were produced in a Portuguese biomass boiler of a pulp and paper industry that produces electricity by burning eucalyptus and pine bark in a Bubbling Fluidized Bed Combustor (BFBC). The fly ashes were collected in the hopper of the electrostatic precipitator. The BFBC uses sand as fluidizing agent. The ashes were stored in air-tight polypropylene containers, at 4 ± 1 °C, in the absence of light. In a previous work, Barbosa et al. [20] have characterized this biomass fly ashes for (i) chemical composition through an acidic digestion (USEPA Method 3051A, 2007),

Table 1
Chemical characterization of the supernatants resulting from the coagulation–flocculation assays of the synthetic wastewater with an initial concentration of 1 mg Pb/L and different S/L ratios of the biomass fly ashes (n = 2; ±SD; n.a.: SD not applicable).

Parameter	Unit	S/L ratios (g/L)								
		0.00	0.03	0.05	0.10	0.20	0.40	0.80	1.20	1.61
pH	Sorensen	4.64 ± 0.62	4.95 ± 0.13	4.73 ± 0.38	6.73 ± 0.35	8.01 ± 1.42	10.32 ± 0.22	10.78 ± 0.16	11.00 ± 0.04	11.21 ± 0.07
Redox	mV	+255 ± 4	+270 ± 28	+288 ± 5	+205 ± 37	+206 ± 39	+127 ± 47	+80 ± 30	+81 ± 7	+54 ± 6
SO_4^{2-}	mg/L	<3.0(n.a.)	8.5 ± 0.7	4.5 ± 1.1	7.5 ± 1.2	5.0 ± 1.5	8.5 ± 2.1	15.5 ± 2.2	6.0 ± 0.1	9.0 ± 0.5
F^-	mg/L	<0.05(n.a.)	0.48 ± 0.04	0.48 ± 0.04	0.38 ± 0.11	0.68 ± 0.32	0.45(<0.01)	0.53 ± 0.04	0.53 ± 0.04	0.58 ± 0.32
Total hardness	mg $CaCO_3$/L	2.5 ± 0.7	3.5 ± 0.7	2.8 ± 0.4	5.3 ± 1.1	7.5 ± 1.4	13.3 ± 0.4	24.0 < 0.1	35.3 ± 1.1	37.8 ± 5.3
Calcic hardness	mg $CaCO_3$/L	0.5(<0.1)	0.75 ± 0.2	0.75 ± 0.2	3.8 ± 0.5	5.3 ± 0.4	11.5(<0.1)	21.5(<0.1)	32.0 ± 1.4	32.5 ± 8.5
Fe	mg/L	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)
Al	mg/L	<0.34(n.a)	<0.34(n.a.)	<0.34(n.a)	<0.34(n.a)	<0.34(n.a)	<0.34(n.a)	0.47 ± 0.07	0.92 ± 0.01	1.32 ± 0.19
Ca	mg/L	<0.015(n.a.)	<0.015(n.a.)	<0.015(n.a)	0.72 ± 0.03	0.77 ± 0.03	0.89 ± 0.03	4.46 ± 0.32	4.57 ± 0.20	4.75 ± 0.11
Sb	µg/L	<0.3(n.a.)	<0.3(n.a.)	<0.3(n.a.)	<0.3(n.a.)	<0.3(n.a.)	<0.3(n.a.)	<0.3(n.a.)	<0.3(n.a.)	0.35 ± 0.03
As	µg/L	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)