

DOI: <http://doi.org/10.21698/simi.2017.0009>

NEW ADSORBENT MATERIALS ON THE BASE OF ASH AND LIME FOR LEAD REMOVAL

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Abstract

The development of new materials, with imposing properties - for environmental protection, represents a challenge for contemporary society. In this paper, we propose obtaining of new adsorbent materials from thermo plant ash and lime. The use of ash presents the advantage, because this waste is in great quantities, and it is a way for its capitalization. The new materials offer new scientific and technological perspectives due to the specific interesting physical properties of these materials. The utilization of adsorbents based on ash/lime, for waste water depletion, represents an alternative with ecological and economic implications. The authors present in this study the results of experimental researches on the adsorbents prepared in the laboratory using fly ash produced at CET Holboca Iasi and lime from Bicaz. The experimental conditions of obtaining new adsorbents were established and the characterization of synthesized materials was realized. Raw and synthesized materials were characterized by: SEM/EDAX (Quanta 3D - AL99/D8229), XRD (X'Pert PRO MRD X-ray diffractometer), BET (Quanta-chrome Instruments) and FT-IR analysis (DIGILAB FTS 2000). Experimental results demonstrated that the new materials can be successfully used for removal of lead from waste water. The removal rate was over 97%, after 60 minutes, and adsorption capacities were obtained of 21.25 mg/g. The resulted product is easy to separate and can be used as building material. On the other hand, the product is not polluted for the environment.

Keywords: *adsorbent, ash, lead, lime, synthesis*

Introduction

The contemporary development is strongly connected to energy production. Because the power plants based on coal fuel greatly affect the environment, the improvement of producing processes of energy by diminishing the ecological impact is welcome. In the last years the remove of the polluting agents, from the waters, is placed on the priority place. Heavy metal ions may cause health risks to humans, the ecosystems, and this has been a great motivation for increasing of researches for reducing of its content. From heavy metal, removal of lead is important, because of its toxicity and its attendance in the wastewater. Lead is a well-known, highly toxic metal considered as a priority pollutant (Mondal 2009). It is an industrial pollutant, which enters the ecosystem through soil, air and water (Golbad 2017; Harja 2013). Different industries, such as battery manufacturing, metal plating and finishing, tetraethyl lead manufacturing, ceramic, glass, etc., are the major sources of lead pollution (Arbabi 2015). According to the World Health Organization (WHO) and Environmental

Protection Agency (EPA), the maximum permissible limit (MPL) of lead is 0.05 mg/L in drinking water and in wastewater (Abdel-Hakim 2003). In wastewaters, lead-ion concentrations may approach 180–450 mg/L, concentration very high in correlation with standards, consequently lead concentration from wastewaters must be reduced before discharging to effluent. The removal of lead ions from water may be used many processes like ion exchange, adsorption, biosorption, precipitation, coagulation/electro-coagulation, cementation, osmosis, electro-dialysis, etc. (Arbabi 2015; Golbad 2017; Remsi 2012; Wan Ngah 2010).

In order to remove lead ions, current methods, require the use of reagents for precipitation or coagulation. On the other hand ion exchangers are expensive. Treatment processes of Pb(II) removal from wastewater through adsorption on different low cost adsorbents were recently studied (Adebisi 2017; Arbabi, 2015; Nascimento 2009, Buema 2013; Harja 2013). Several natural or synthetic materials, such as natural/synthetic zeolites (Kotova 2017), fly ash (Harja 2016; Noli 2015), clays, carbonates, phosphate rocks, alkaline agents, carbon (Adebisi 2017), hydroxyapatite, etc. (Zarghami 2015) have been recently tested as to their ability to immobilize metals. Many researches are dedicated fly ashes and modified ashes as adsorbents for wastewater or air (Harja 2010). If the adsorption capacities of fly ash for lead ions were demonstrated (Buema 2013), we proposed synthesis and testing of new adsorbent materials obtained from ash and lime. The lime was used for precipitate soluble metals into their insoluble hydroxide forms, but in admixture with ash, under the imposed conditions for modification, can be obtaining of very efficient adsorbents. Analyzing the ash composition resulted from power plants, it was observed that it contains CaO and MgO, and by mixing with lime, in controlled conditions, it can synthesize adsorbents for environmental applications. By using the ash for obtaining the new materials, the pollution reduction is obtained in two ways:

- Reduction of lead content from wastewaters;
 - Capitalization of the ash, it causes pollution of soil and air from thermo plant area.
- The synthesis consists in preliminary hydrated of the lime, mixed with ash and mechanical agitation in imposing conditions. Solid/liquid ratio was varied between 1/2 ... 1/5, temperature between 20-50°C, and the curing time between 1-4 hours. The synthesized materials were characterized, and tested for adsorption of lead ions.

Materials and Methods

For adsorbent synthesis it was used lime from Bicaz and ash from power plant Holboca Iași. The lime and the ash were characterized from the chemical, mineralogical and technological properties. Morphology of particles was determined by SEM with Vega Tescan - Analytical Scanning Electron Microscope.

Chemical and mineralogical characterization were realized by:

- Microanalysis by SEM/EDX - with a QUANTA 3D series AL99/D8229.
- FT-IR analysis with spectrometer DIGILAB FTS 2000.
- Multi-Parameter Consort C831 (pH, mV, C, Conductivity), measures of pH 0-14.00, electrical conductance 0 - 200 mS.

Samples of 50 g were prepared, by introducing in the reaction vessel of lime, at working temperature, for hydration, after this was introduced ash, with imposed ratio. After hydration of lime, the slurry was agitated 1-4 hours, the synthesis conditions are presented in Table 1. The samples were filtered, dried and analyzed.

Table 1. Adsorbent samples and working conditions

Sample	Time (h)	Temperature (°C)	Lime/ash ratio
LA1	1	50	1/3
LA2	2	50	1/3
LA3	4	50	1/3
LA4	1	50	1/3
LA5	2	50	3/1
LA6	4	50	3/1

Adsorption experiments

For adsorption experiment was prepared a stock solution, with 0.1 mol Pb(II)/L by dissolving Pb(NO₃)₂ in distilled water. In this work, the ratio adsorbent/solution was 1:100. All chemicals used to prepare reagent solutions were of analytical grade. Before starting the experiment the solution was contacted with adsorbent, the pH of the solution was adjusted to the required value. The pH was adjusted by 0.1 M HCl and/or 0.1 M NaOH to cover a range from 2 to 12. After pH stabilization, in the adsorption column was introduced required stock solution. When the absorption was realized, the adsorbent particles were filtrated and the residual concentration of lead was determined. The atomic spectroscopy type Buck Scientific for heavy metals determined were used for lead content determined.

Results and Discussion

The principal component of lime is calcium oxide. Near this the lime contains a series of impurities from the raw material. The chemical composition of lime, in oxide components is presented in Table 2. The ash, used in this study, has the oxidic components presented in Table 2 (Harja, 2010, 2015, 2013; 2010; 2012a&b).

Table 2. Chemical composition of ash and lime used for preparing the adsorbent

Component	Ash	Lime
SiO ₂	47.9	4.04
Al ₂ O ₃	34.94	0.56
Fe ₂ O ₃	4.82	0.34
CaO	2.86	87.4
MgO	1.42	3.65
K ₂ O	1.11	1.41
Na ₂ O	0.54	0.18
LOI	2.9	4.45

FTIR spectra are presented in Fig. 1, for lime and ash, resulted was in concordance with literature (Harja 2016).

From Fig. 1 it can observe that the principal component of lime is calcium oxide, but there are also some peaks which corresponds to the impurities from the coal, peak from 3641.6 cm⁻¹ corresponds to water, that means the lime was hydrated. The ash samples have components such as: hematite, quartz, kaolin, illit, rutil, montmorilonit, carbon (Noli 2016a, 2016b; Buema 2013), which is found in argillaceous material, ballast coal respectively.

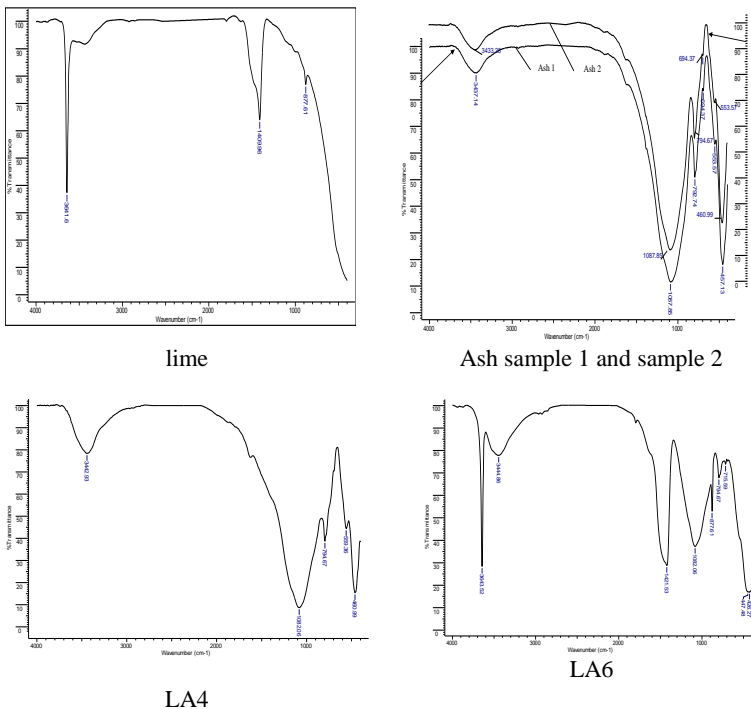


Figure 1. FTIR spectra for raw and synthesized materials

The adsorbents were analyzed; FTIR spectra of LA2 and LA4 are presented. In the case of LA4 and LA6 it can be observed peaks, corresponding to zeolitic/geopolimeric materials (Harja 2016; Harja 2009a; Noli 2015).

SEM analysis was done for all samples, for selected samples: LA2, LA4 and LA6 are presented in Fig. 2. By modification the new particles grow on the surface of oldest ash particles, obtaining a higher surface of adsorbent (Harja 2009b). SEM images to 10 and 5 μm respectively, allow the observed differences between the surface morphology of new materials function of modification conditions. The increase of temperature and curing time determined increasing of surface area.

By increasing the time of reaction, the adhesion of lime particles to the ash is better, for the same ratio lime-ash. Lime hydration has as effect the increasing of specific surface and a very good adhesion to ash particles.

Adsorption studies. For adsorption studies the, on the base of results obtaining from characterization, the LA6 adsorbent was selected. The adsorption capacity (q , mg/g) and the removal rate (R%) were calculated by means of the following relationships:

$$\text{Adsorption capacity } (q, \text{ mg/g}) = (C^0 - C) \times V / m \quad (1)$$

$$\text{Removal rate } (R \%) = [(C^0 - C) / C^0] \times 100 \quad (2)$$

where C^0 and C , are initial and respectively, final concentrations of the lead ion in solution mg/L, V – volume, L, m – mass of adsorbent, g.

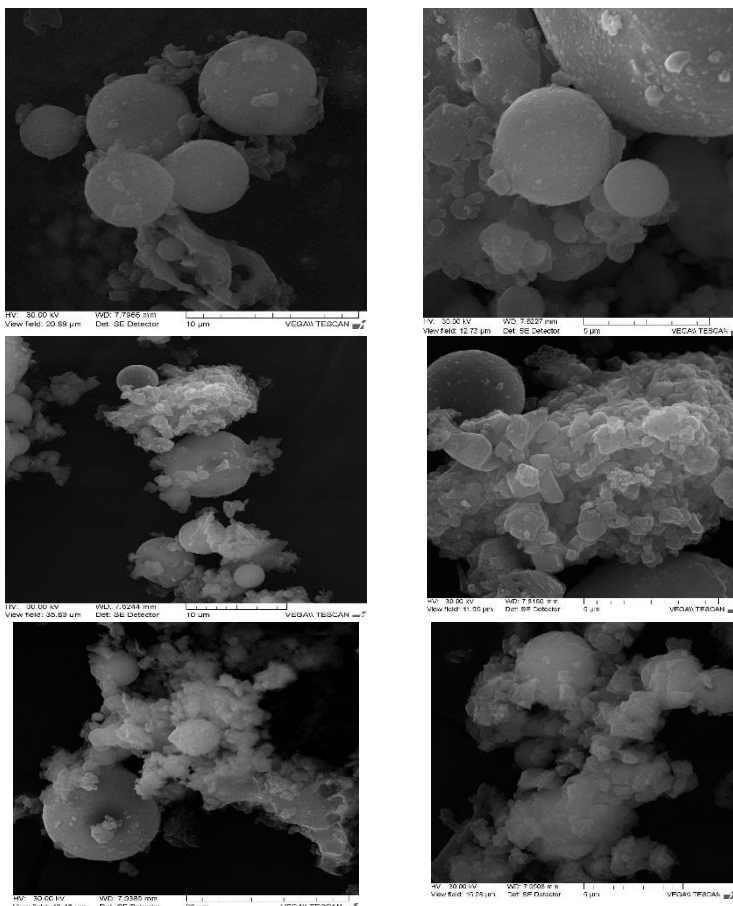


Figure 2. SEM analysis for samples LA2, LA4 and LA6

The pH of the solution plays a very important role in the removal of lead ions. The influence of the pH over adsorption capacities is presented in Fig. 3. The adsorption capacities of Pb^{2+} ions increased little from pH 4 to pH 6. After pH 7, we obtained a gradual increase in the Pb^{2+} ion removal up to pH 10, and then remaining almost constant up to pH 12. The obtained data show a very good adsorption capacity of Pb^{2+} ions, at a pH over 9, this was reason for use pH 9 in all other experiments. The adsorption capacity was 21 mg/g, and the removal rate was obtained over 97%.

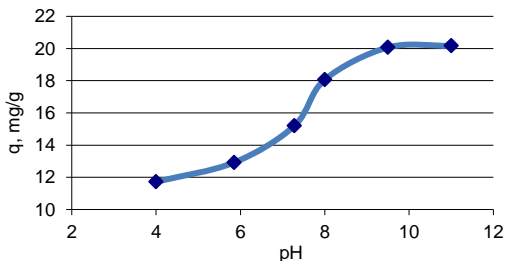


Figure 3. Influence of pH over adsorption capacity of Pb^{2+}

The effect of contact time on the lead removal (the initial pH 9, adsorbent dose 10 mg/L, initial concentration 65 mg/L, temperature 20°C) is depicted in Fig. 4.

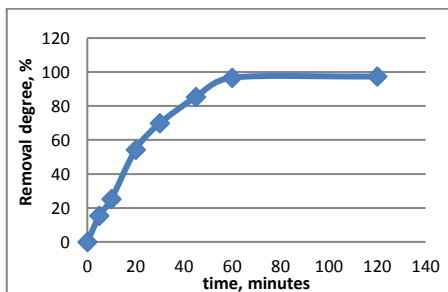


Figure 4. Influence of contact time over removal degree of Pb^{2+}

The amounts of the lead adsorbed on the LA 4 sample increased rapidly in the first 40 minutes changing them slightly over 60 minutes. The drastic increase of lead adsorption in the first 40 minutes may be due to the availability of numerous vacant sites, after this the adsorption sites become unavailable. The adsorption equilibrium time was prolonged from 40 min to 80 min on account of the slow pore diffusion of lead ions into the bulk of the adsorbent.

Conclusions

The objective of this study was to develop an effective adsorbent for the removal of lead ions from aqueous solution.

Adsorption of $Pb(II)$ ions through new adsorbent is an economically feasible technique for removing metal ions. In the first stage of the study, the characterization of the adsorbent was done. The researches have continued with the study of pH and contact time influence over the removal process. The highest degree of lead ions removal was obtained at pH over 9. In the case of pH about 9, the degree of uptake was about 97%.

The kinetics study of lead ions removal onto new adsorbent materials indicates a removal degree over 60% after 20 min, which increases to 97% after 60 min.

It can be concluded that the new adsorbent can be used for removal of lead ions from wastewater with 21 mg/g adsorption capacity and removal rate over 97%.

Capitalizations of ash as adsorbent represent a superior way to the recovery of this waste and, on the other hand the water, air and soil pollution can be reduced.

Acknowledgements

This work was performed with the support of Doctoral school – Faculty of Chemical Engineering and Environmental Protection, "Gheorghe Asachi" Technical University of Iasi.

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