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Romanian bentonite and fly ash characterization and their use in heavy metal “in-situ” immobilization in polluted soils

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Abstract. This article presents the characterization of the Romanian bentonite and fly ash, using different techniques: FAAS, XRD, FT-IR, SEM and EDAX and their evaluation as sorbents for heavy metals immobilization in polluted soils coming from mining and metallurgical activities. The applicability of bentonite and fly ash for Pb (II) and Zn (II) immobilization was studied using aqueous solutions of these metals. The influence of the pH and contact time were studied. The results shown that the Romanian bentonite and fly ash could be used for Pb (II) and Zn (II) immobilization in polluted soils from brownfields.

1 Introduction

Heavy metals, such as lead, copper, zinc, nickel, cadmium, chromium are present in soil as natural components, but their presence in environment has increased due to the human activities. The heavy metals are released into the environment through various activities such as mining, energy and fuel production, electroplating, wastewater treatment [1]. The zinc is essential for life and for a healthy body and it is a common micronutrient in trace amounts [2]. In excess, zinc can be harmful and causes zinc toxicity. A long-time exposure to Zn(II) is harmful for human health. The free zinc ions in solution are highly toxic to plants, invertebrates and human. The lead is extremely toxic and it has adverse effects as it accumulates in the body. All lead compounds are cumulative poisons. In body, lead affects in special the neuronal system.

To reduce the risks associated to heavy metals presence in environment various treatment techniques are used, like: ion exchange, biodegradation, oxidation, solvent extraction and adsorption. The adsorption technique remains widely preferred due to its simplicity of design and operation, cost effectiveness, high efficiency and flexibility [3]. This method is usually used for waste water treatment, but the treatment of polluted soils with heavy metals is also based on the adsorption process. Different natural materials (clay, zeolite) or by-products (fly ash) are used for heavy metal immobilization in soil.

The fly ash is a by-product from electric power plant which utilizes lignite coal as fuel [4, 5]. The fly ash is removed from the emission control devices and it is transported and deposited in open dump where is accumulated in a large amount. For this reason, its disposal creates serious environment problems. The worldwide studies identify possibilities for fly ash use, such as: road construction, construction materials, cement industry, soil amendment and adsorbent material for the adsorption of heavy metals from waste waters [4, 6]. The major constituents of fly ash are silica, alumina, and iron oxide.

The clay minerals have a small grain size and a specific mineralogical structure which results in specific properties. The most important of these properties are the large specific surface area and the resulting ability to adsorb cations [7]. Therefore, clay minerals are used in a large variety of environmental applications. Clay minerals are composed from fine-grained aluminosilicates.

The aim of this paper is to assess the capacity of bentonite (natural clay) and fly ash to adsorb Pb(II) and Zn(II) ions from aqueous solutions. For this reason, the physical, chemical and mineralogical composition of bentonite and fly ash was determined. Batch adsorption experiments were performed to investigate the effect of pH and contact time on the adsorption of Pb(II) and Zn(II) ions onto these materials.

2 Materials and methods

The fly ash samples were obtained from power plant Govora, Romania. This power plant use lignite from Berbesti-Alunu coals mine. The fly ash was capture from the dry emission control system. In accordance with SR EN 450-1” Fly ash for concrete - Part 1, Definition, conditions and standards” these categories of fly ash, can be used as admixture type II for concrete, binder and cement slurry.

The bentonite was obtained from Orasul Nou (Maramures county) natural deposit. This bentonite is less commercialized.

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2.1 Characterization

The chemical composition of the fly ash and bentonite was determined by inductive coupled plasma optical emission spectrometer (ICP-OES) SPECTROFLAME – ICP model P, Germany and Flame Adsorption Atomic Spectroscopy (FAAS).

The mineralogical composition of the bentonite and fly ash was determined by the X-ray diffraction analysis for the qualitative evaluation of the common and predominant phases within the ash, using a BRUCKER D8 ADVANCE diffractometer and software package DIFRAC^{plus} BASIC Released 2006 (Brucker) and ICDD PDF-2 database release 2006.

The optical microscopy analysis were performed using a Zeiss – Jena – Axio IMAGER Alm microscope.

The scanning electron microscopy (SEM-EDAX) was used to determine the morphological and quantitative characteristics of the materials.

The IR spectra of bentonite was obtained using a FT-IR ABB MB 3000 spectrometer.

The leaching tests of fly ash were conducted in accordance with the EN 12457-1 si EN 12457-2 standards.

2.2 Preparation of the heavy metal solutions

Stock solutions of Pb(II) and Zn(II) (containing 1000 mg metal/L) were prepared using lead nitrate ($Pb(NO_3)_2$ and zinc sulphate heptahydrate ($ZnSO_4 \cdot 7H_2O$) of analytical purity. The pH adjustments were performed using nitric acid, sulphuric acid or sodium hydroxide 0.1 M aqueous solutions.

2.3 Experimental

The batch adsorption experiments were carried out at room temperature ($22^0C \pm 3^0C$). One hundred milliliters of solution containing 100 mg/L of Pb(II) or Zn(II) were treated with the desired amount of adsorbent in 250 mL conical flasks. The mixtures were stirred for 0 – 240 min. At the end of each time period, the adsorbent was removed by filtration and the filtrate was analyzed for residual metal concentration by atomic absorption spectroscopy and FAAS.

The efficiency of the removal of Pb(II)and Zn(II) from solution was calculated using Eqn.1 [1, 8]

$$Removal\ efficiency\ \% = \frac{C_0 - C_f}{C_0}\ \text{x}\ 100 \qquad (1)$$

where: R is the removal efficiency (%), C_0 is the initial metal concentration (mg/L), C_f is the final metal concentration (mg/L).

3 Results and Discussions

3.1 Bentonite and fly ash characteristics

The oxidic composition of the bentonite and fly ash is presented in table 1.

Table 1. The oxides composition of the bentonite and fly ash, [weight %].

	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	Na_2O	K_2O	H_2O	LOI* (1000^0C)
Bentonite	68.49	10.77	1.19	1.23	1.80	4.38	0.80	11.37	-
Fly Ash	52.11	20.2	7.14	2.33	8.14	-	-	0.14	3.06

**LOI- Loss of Ignition*

The fly ash has a low content of CaO. It is siliceous type fly ash, with low loss of ignition.

The bentonite has a ratio of SiO_2/Al_2O_3 = 6.36, SiO_2/Fe_2O_3= 38.05 and MgO/Fe_2O_3= 0.69. In the fly ash, the amorphous phase is 61.5 wt% and crystalline phase is 38.5 wt%, according to results obtained from XRD analysis. The main crystalline phases are: 45 wt% quartz (SiO_2), 21 wt% anorthite (calcium aluminosilicate $Ca_{0.88}Al_{1.77}Si_{2.23}O_8$), 14 wt% anhydrite ($CaSO_4$), 9 wt% gehlenite ($Ca_2Al[AlSiO]_7$), 6 wt% hematite ($Fe_2O_3$) and 5 wt% magnetite ($Fe_3O_4$) (figure 1).

The main crystalline phases in bentonite are beidellite/montmorillonite (> 70 wt%), cristobalite, albite (potassian and calcian), quartz (figure 2).

The optical microscopy analysis for fly ash highlights very well the amorphous and crystalline phases. In these phases, the grains of hematite and magnetite appear. Figure 3 shows the photo with the amorphous phase and hematite grain. The bentonite optical analysis presents the micro-crystalline phase (clay minerals) and some albite and quartz (figure 4).

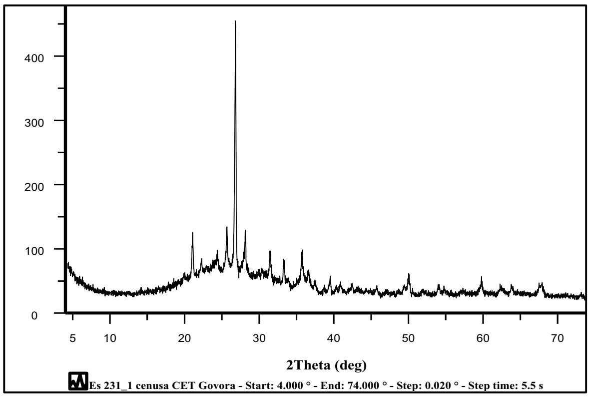


Fig. 1. Crystalline phases of fly ash determined by DRX.

The scanning electron microscopy (SEM) was used to determine the morphological characteristics and surface texture of the bentonite and fly ash.

SEM images of the fly ash Govora are presented in figure 5 and the EDAX spectrum of the fly ash is presented in figure 6.

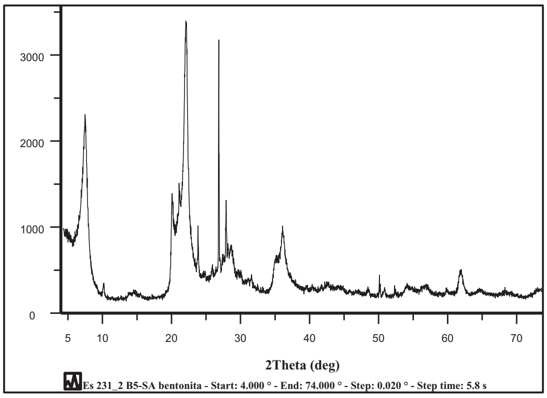


Fig. 2. Crystalline phases of the bentonite determined by DRX.

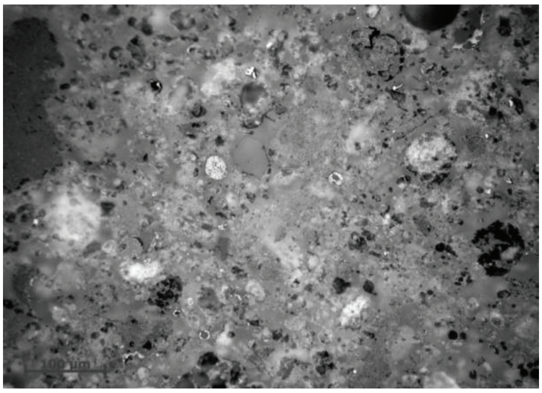


Fig. 3. The optical microscopy analysis of the fly ash.

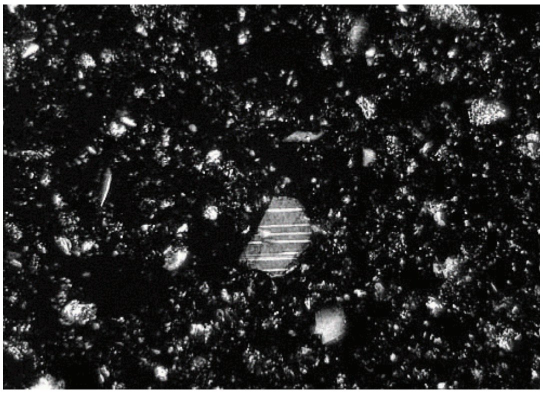


Fig. 4. The optical microscopy analysis of the bentonite.

The morphology of this ash is similar with the other ashes [9, 10, 12]. The fly ash is a fine powder, contains microspheres with diameter of 5-15 µm. The EDAX analysis shows the presence of carbon, magnesium and iron too, near the constituent elements of the minerals mentioned by DRX. The bentonite is formed from grains with submicron size (figure 7). These grains form aggregates with size of 1-10 µm.

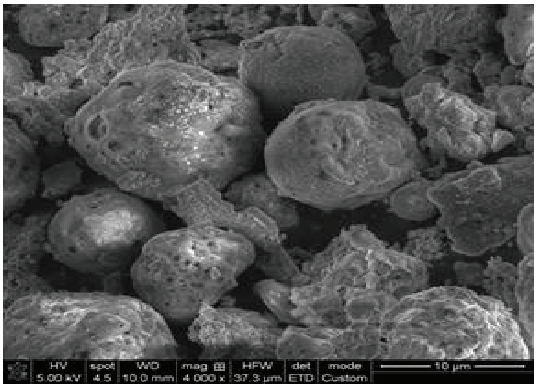


Fig. 5. SEM micrograph of the fly ash.

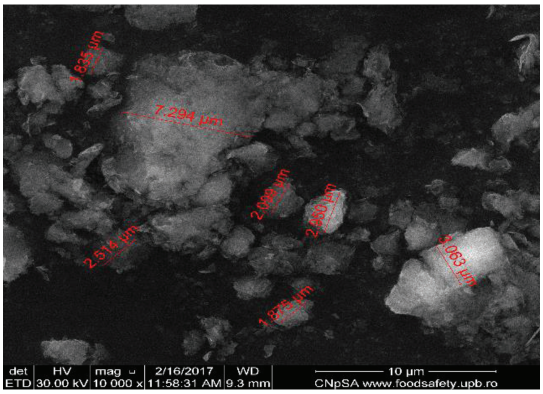


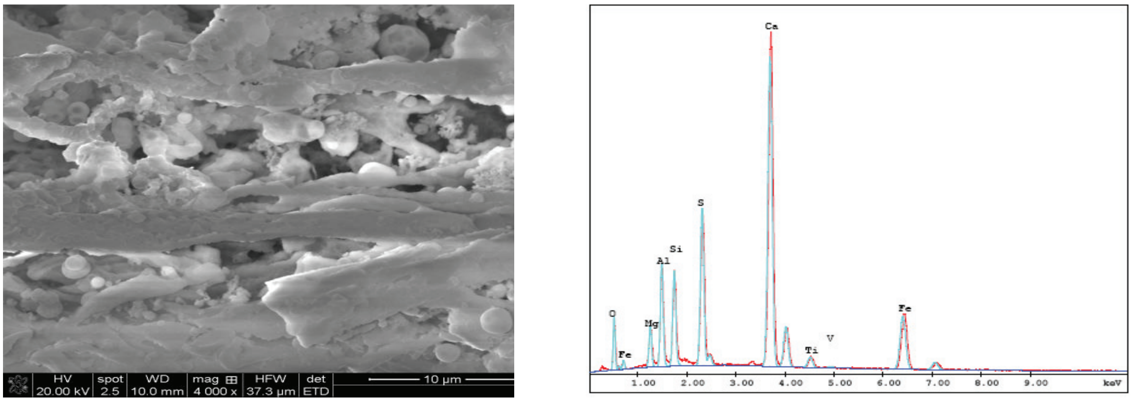
Fig. 6. SEM micrograph of the bentonite.

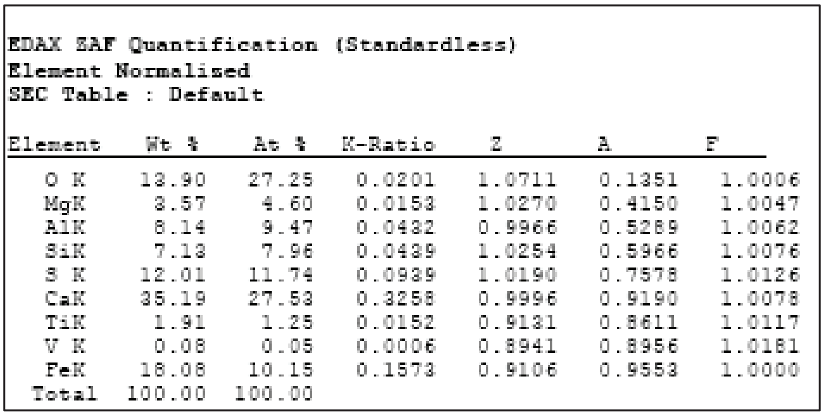
The EDAX analyses shown (figures 7, 8) the silicon and aluminium as main elements which form the crystalline framework together with oxygen. The other elements (Na, Mg, K, Ca and Fe) could isomorphic substitute silicon in tetrahedral layer. Fe and Mg could substitute Al in octahedral layer. The negative charges will be compensated by Na, K, Ca, Fe and Mg.

The thermal analysis (DSC) shows three peaks (endotherm effects) situated at 96,5^{0}C, 178^{0}C and 673^{0}C. At 96,5^{0}C and 178^{0}C the adsorbed water is eliminated. The peak from 673^{0}C is characteristic for bentonite (which has montmorillonite as main component) aluminium – iron – magnesium. Generally, the MgO/Fe_2O_3 ratio in bentonite is less than 0.9. The studied bentonite has the MgO/Fe_2O_3 ratio equal with 0.69.

The pH_{pzc} of bentonite was below 2. This shows that Si and Al were isomorphic substituted in the crystalline framework and the negative charges have permanent character and don't depend on pH.

The FT-IR study (figure 9) of bentonite shows the characteristic peaks at 3632 cm^{-1} assigned for stretching vibration of OH^- groups and characteristic for montmorillonite.





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EDAX ZAF Quantification (Standardless)
Element Normalised
SEC Table : Default

Element    Wt %     At %    K-Ratio      Z          A          F

   O K    13.90    27.25    0.0201    1.0711    0.1351    1.0006
   MgK     3.57     4.60    0.0153    1.0270    0.4150    1.0047
   AlK     8.14     9.47    0.0432    0.9966    0.5289    1.0062
   SiK     7.13     7.96    0.0439    1.0254    0.5966    1.0076
   S K    12.01    11.74    0.0939    1.0190    0.7578    1.0126
   CaK    35.19    27.53    0.3258    0.9996    0.9190    1.0078
   TiK     1.91     1.25    0.0152    0.9131    0.8611    1.0117
   V K     0.08     0.05    0.0006    0.8941    0.8956    1.0181
   FeK    18.08    10.15    0.1573    0.9106    0.9553    1.0000
  Total  100.00   100.00
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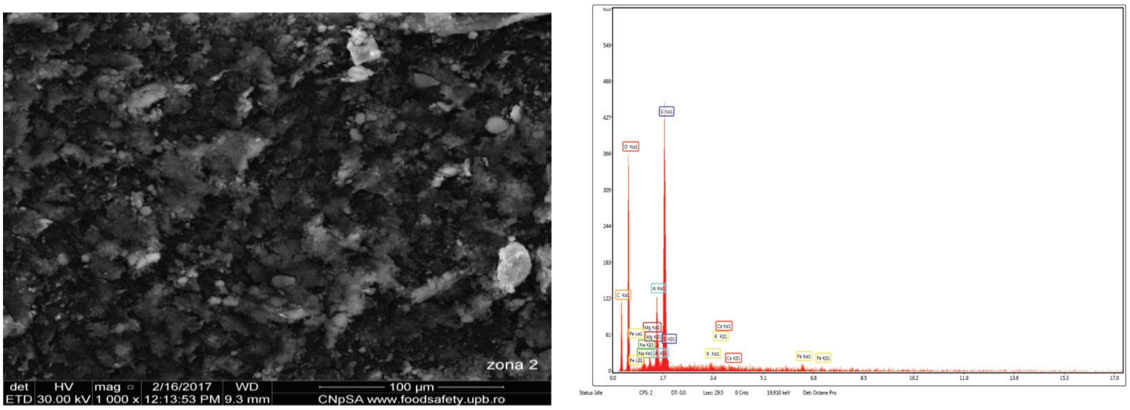
Fig. 7. EDAX of fly ash.



Element	Weight, %	Atomic, %	Error, %	Net Int.	K Ratio	Z	A	F
O K	59.11	71.4	9.91	57.79	0.2032	1.0336	0.3326	1
Na K	3.91	3.29	24.14	4.63	0.0085	0.947	0.2273	1.0059
Mg K	1.33	1.06	32.12	3.14	0.0043	0.9654	0.3288	1.0107
Al K	7.43	5.32	12.02	25.45	0.0325	0.9316	0.463	1.0143
Si K	26.42	18.18	7.65	106.19	0.1321	0.9539	0.5226	1.003
K K	0.6	0.29	63.65	2.69	0.0044	0.8918	0.8191	1.0196
Ca K	0.33	0.16	64.72	1.39	0.0027	0.9095	0.8745	1.025
Fe K	0.87	0.3	61.56	2.7	0.0081	0.8194	1.0105	1.1142

Fig. 8. EDAX of bentonite.

Table 2. Concentration of heavy metals in leachate [17].

Heavy metal	**Concentration limits**					
	Inert waste (RL)		**Non - hazardous waste (RL)**		**Leachate**	
	L/S=2 l/kg mg/kg	**L/S=10 l/kg mg/kg**	**L/S=2 l/kg mg/kg**	**L/S=10 l/kg mg/kg**	**L/S=2 l/kg mg/kg**	**L/S=10 l/kg mg/kg**
Cu	0.90	2.00	25	50	0.02	0.12
Ni	0.20	0.40	5.0	10	0.04	0.19
Zn	2.00	4.00	25.0	50	0.42	4.79
Pb	0.20	0.50	5.0	10	0.09	1.53
Cd	0.03	0.04	0.6	1	0.02	0.10

The peaks 3491, 3410 and 1639 cm^{-1} are assigned for stretching and deformation vibration of OH^- groups from adsorbed water in bentonite network; 918 cm^- for stretching vibration of OH^- from the Al_2OH; 795 cm^{-1} for Fe(II)Fe(III)OH group presence; peaks at 1043 and 627 cm^{-1} are attributed to the Si-O and Si-O-Al vibrations [13-16].

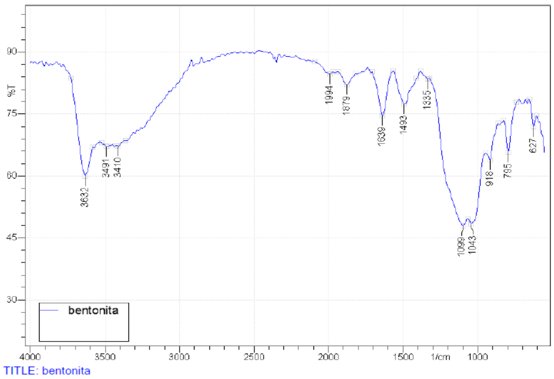


Fig. 9. The FT - IR spectra of bentonite.

The leaching test of the fly ash, presented in table 2, shows that the leachates contain heavy metals below the standards for non-hazardous waste in accordance with national legislation (RL) [17].

3.2 Adsorption tests

3.2.1 Effect of pH

The removal efficiency was studied at pH values between 2.5 and 7.0. The influence of pH on the removal efficiency of Pb(II) and Zn(II) onto bentonite (B) and fly ash (FA) is presented in figure 10. The Pb (II) removal efficiency on FA increases starting from pH = 2.5 until pH = 5.0, when the efficiency is maximum. The Zn (II) removal efficiency on FA was 95% at pH = 7.0. The Zn (II) removal efficiency is very low between pH = 2.7 - 3.6. This should be explained with the presence of silica in fly ash. The silica could uptake either positive or negative contaminants depending on the solution pH. The silicon, the central ion of silica, has electron affinity, giving the oxygen atoms bound to it low basicity. This enables the silica surface to act as a weak acid, which can react with water, forming silanol (SiOH) groups. As a result, at low pH the silica surface is positively charged and at high pH values is negatively charged [18, 19]. The other solid materials, for example iron oxide (another constituent of FA), develops positive or negative charges also. In accordance with this theory, at pH = 2.7 - 3.6, the number of sites with negative charge is very low and only a very small quantity of Zn(II) ions can be fixed with electrostatic interactions on the silica surface. Pb(II) ions can be fixed both on the silica and iron oxide surface.

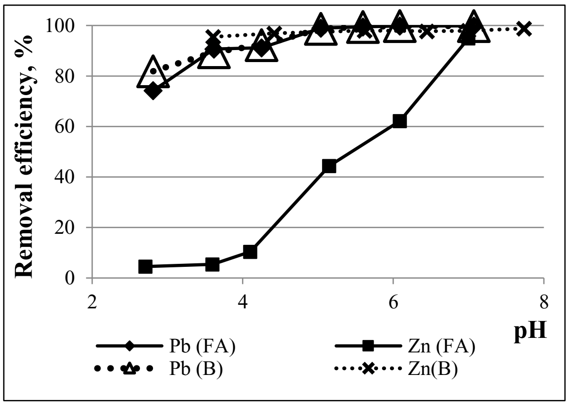


Fig. 10. Effect of pH on the Pb(II) and Zn(II) removal efficiency on bentonite (B) and fly ash(FA).

The removal efficiency of Pb(II) and Zn(II) on bentonite is high (above 80%) even at low pH. The removal of these ions from aqueous solution using B doesn’t depend on pH. The pH_{pzc} of bentonite is below 2, that means the bentonite surface above pH=2 has negative charges. These negative charges result from isomorphic substitutions of Si in the tetrahedral layer and of Al in octahedral layer. The removal efficiency is maximum at pH = 5.5 for both Pb(II) and Zn(II).

3.2.2 Effect of contact time

The removal efficiency of heavy metal ions (Pb(II) and Zn(II)) from solution using bentonite and fly ash versus time is presented in figure 11.

The results indicated that the Pb(II) and Zn(II) ions uptake increase with contact time, until an equilibrium is reached. The equilibrium was reached within 60 minutes for Pb(FA) and in 30 minutes for Pb(B). For Zn(FA), the equilibrium was obtained at 180 minutes and for Zn(B) in 120 minutes. The adsorption capacity obtained for Pb(FA) was 19.9 mg/g at 60 minutes and for Zn(FA) was 5.31 mg/g at 180 minutes. The adsorption capacity of 5.31 mg/g for Zn(II) o FA is higher than the values found by other researchers for the adsorption of zinc onto fly ash [20, 21], but is very closed to q_e = 4.505 mg/g obtained by reference [22]. The adsorption capacity of 19.9 mg/g for Pb(FA) is closed to the value 18.8 mg/g obtained by authors [20].

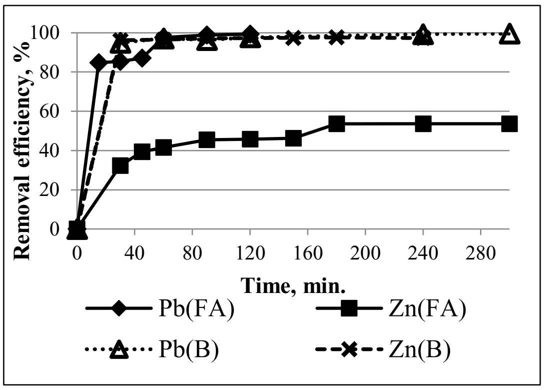


Fig. 11. Effect of contact time on the Pb(II) and Zn(II) removal efficiency on bentonite (B) and fly ash(FA).

The adsorption capacity obtained for Pb(B) was 8.96 mg/g at 30 minutes. The adsorption capacity obtained by different authors varies between 7.56 and 16.30 mg/g Pb(II) on bentonite, as function of the initial concentration of the solution and the type of bentonite used in process [23-25].

The adsorption capacity obtained for Zn(B) was 10.88 mg/g at 120 minutes. The adsorption capacity obtained by different authors varies between 3.24 and 11.84 mg/g [26-28] Zn(II) on bentonite, as function of the type of bentonite used in process.

The results showed that bentonite adsorb better Zn(II) and fly ash Pb(II).

4 Conclusions

This paper presented the chemical, structural and morphological characteristic of the bentonite and fly ash from Romania. These materials are suitable for uptake of Pb (II) and Zn(II) ions from aqueous solutions.

The removal capacity of fly ash increases with pH, when pH is between 2.5 and 5. and after that, remains constant. The removal capacity of bentonite doesn't depend on pH.

The adsorption capacity of fly ash towards Pb (II) ions is 19.9 mg/g and 5.31 mg/g for Zn(II).

The adsorption capacity of bentonite is 8.96 mg/g for Pb(II) and 10.88 mg/g for Zn(II).

The fly ash has a higher affinity for Pb(II) ions while bentonite for Zn(II).

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