Sources of heavy metals in nature are numerous. The heavy metals are released not only from industrial activities, but also from current household activities. Although most of the waste abandoned in nature is solid, under the influence of atmospheric agents and microorganisms, heavy metals pass into soluble form when reaching surface waters.

Soils, surface sediments, and aquatic environments are dynamic open systems characterized as mixtures of metastable solids. We can say that these systems never achieve a thermodynamic equilibrium, and we can expect to find more forms of an element present in that system. Thus, the presence of toxic elements and their chemical stability in these systems are given by the total amount of the most reactive forms of toxic elements and the reaction dynamics. Ideally, soil treatment technologies should facilitate the complete transformation of toxic elements from pre-existing forms into geochemically stable forms, but as we know, for reasons involving kinetic reactions, this will not happen. Fortunately, reducing the chemical reactivity of these toxic elements can be achieved by eliminating the most reactive forms [1].

According to the Center for Disease Control (CDC), heavy metals poisoning is the most common and the most devastating disease caused by the environment on young children. Pb levels in blood between 10-15 mg/dL can significantly reduce IQ and learning ability.

Lead is toxic to both humans and animals, and in certain concentrations it becomes a serious problem for public health around the world. Negative effects to health are caused by the accumulation of lead in the body, especially in young children. The effects on young people whose body is growing are more severe. Therefore, considerable effort is currently being made to treat lead wastes directly at source. Different treatment methods are used, including: chemical precipitation, coagulation, adsorption, ion exchange, chelation, osmosis and membrane processes to remove lead from soil or wastewater [2-10].

The pollutants must be immobilized in such a way to avoid solubilization and pollution of surface water. Chemical immobilization is the most efficient method for retaining heavy metal cations, which are dangerous to humans and the environment. This process is based on the exchange of alkaline or alkaline earth cations with heavy metal cations. The phenomenon involves the formation of new chemical bonds and the deformation of the original structures.

Many researchers have focused their research work to study and to develop new efficient and cost-effective adsorbents. Hydroxyapatite (Ca_{10}(PO_4)_{6}(OH)_2) is an ideal material specifically in medical applications for its excellent properties, such as the ability to adsorb a variety of chemical species and its biocompatibility [11]. Hydroxyapatite (HAP) is the main inorganic component of vertebrate's hard tissues such as bones and teeth with potential in trapping and retention of toxic heavy metals in ground water and soil [12]. It is known that Pb^{2+} in solution exchanges rapidly with Ca, causing morphological changes in the surface region. It has been proposed that the adsorption of lead to form Pb_{10-x}Ca_x(PO_4)_{6}(OH)_2 is rapidly followed by formation of the very stable and structurally different pyromorphite phase Pb_{6-x}Ca_x(PO_4)_{6}(OH)_2.

The development of new synthesis materials with the ability to retain heavy metal ions has been heavily interested especially in recent years due to increasing consumption of resources. As a result, new methods of synthesizing natural materials such as hydroxyapatite have been developed to limit the depletion of natural reserves and to respect one of the main principles of green chemistry and consequently sustainable development [13-17].

Performance to retain heavy metals from aqueous synthetic solutions is majorly influenced by material characteristics such as: composition, size (morphology), crystalinity and also by conditions for testing (process variables) like concentration of heavy metal ions in solution, pH of the solution and the time until equilibrium conditions. Adsorbents with high porosity imply a high specific surface area for adsorption, and thus a high adsorption capacity [18-22].

Knowing that the reactivity and retention capacity of the heavy metal ions is closely related to the particularities (composition, microstructure, morphology, etc.) of the adsorbent material, especially the electrical charge of the surface, the size and the specific surface thereof, three
types of HAP ceramic microspheres have been synthesised according to ceramic precursor characteristics (ceramic powders calcined at 650 °C and 800 °C), the amount of pore forming material (porogen in the proportion of 30 to 40% by weight, relative to the amount of HAP); and of the ratio of Na: HAP alginate solution (ratio ALG/HAP = 4) were used. The ceramic microspheres developed by the immiscible liquid technique were finally calcined at 1150 °C for 2 h.

Sodium alginate is soluble in water and forms a reticulated structure which can be cross-linked with divalent or polyvalent cations to form insoluble network. Calcium cations have been reported for cross-linking of acid groups of alginate. This method allowed formation of HAP granules with uniformly spherical shape through ionotropic gelation of sodium alginate in the presence of Ca²⁺ and also endowed the HAP granules with a porous structure.

The granular products obtained were the mass of adsorbents for dynamic adsorption tests. The selected adsorbents were encoded as follows: HAP-I; HAP-II and HAP-III. The obtained granular products consisted of the adsorbent mass and have been used for the dynamic adsorption tests for the removal of lead ions from synthetic aqueous solutions.

**Experimental part**

**Materials**

Hydroxyapatite nanoparticles previously developed by the authors have been used to prepare HAP ceramic microspheres [3], CaCl₂ - 2H₂O (0.1M) of analytical grade being purchased from Merck, Germany, Sodium Alginate (ACROS Organics origin) and Ethylcellulose Ethocel (Fluka origin) have been involved in HAP ceramic microspheres synthesis. Stock solutions of 1000 mg Pb(II)/L prepared from lead nitrate (Merck, Germany) have been diluted to prepare single heavy metals solution with established concentrations. Nitric acid HNO₃ 65% Suprapur®, sulfuric acid (Merck, Germany) have been used to adjust the solution’s pH without further purification.

**Preparation of HAP ceramic microspheres**

HAP’s ceramic granules (microspheres) were produced by immiscible liquids technique, in which the dispersion medium constitutes aqueous solutions of sodium alginate (1 ± 3% wt. /v), ACROS Organics, calcium chloride (CaCl₂ - 2H₂O) and Ethylcellulose (Fluka origin). This method allowed formation of HAP granules with uniformly spherical shape through ionotropic gelation of sodium alginate in the presence of Ca²⁺ and also endowed the HAP granules with a porous structure.

The granular products obtained were the mass of adsorbents for dynamic adsorption tests. The selected adsorbents were encoded as follows: HAP-I; HAP-II and HAP-III. The obtained granular products consisted of the adsorbent mass and have been used for the dynamic adsorption tests for the removal of lead ions from synthetic aqueous solutions.

### Table 1

| Adsorbant | Raw Materials | Method of HAP microspheres preparation | Temperature Precursor (°C) | Porogen material [%] | x HAP* |
|-----------|---------------|--------------------------------------|---------------------------|----------------------|--------|
| HAP-I     | Ceramic powder nano- HAP; Na-Alginate (sol. 20%), CaCl₂ - H₂O (0.1M) | Immiscible liquid technique: extrusion sol. HAP/Na Alg, in CaCl₂/H₂O solution for gelling; calcination: 1150 °C | 800 | 40 | x₄ |
| HAP-II    | Ceramic powder nano-HAP; Na-Alginate (sol. 20%), CaCl₂ - H₂O (0.1M) | Immiscible liquid technique: extrusion sol. HAP/Na Alg, in CaCl₂/H₂O solution for gelling; calcination: 1150 °C | 650 | 30 | x₄ |
| HAP-III   | Ceramic powder nano-HAP; Na-Alginate (sol. 20%), CaCl₂ - H₂O (0.1M) | Immiscible liquid technique: extrusion sol. HAP/Na Alg, in CaCl₂/H₂O solution for gelling; calcination: 1150 °C | 800 | 30 | x₄ |

* Na-Alginate/HAP ratio, the Ethocel—Fluka origin was used as pore-forming material.
Germany), which ensures the possibility of microstructural examination by the SEM method. For electronic microscopy analysis, the samples were subjected to a special 6 min cleaning preparation process in a plasma jet in a FISCHONE Plasma Cleaner. Density porosity determination was performed by gravimetric and dimensional measurements. Also, hydrostatic determinations were made (based on Archimedes’ law).

The size of a droplet formed depends on the size of the needle opening; a needle having ~2 mm internal diameter was found to be suitable for preparing the spheres. Needles having larger openings produced larger sized spheres. It was found that dropping the suspension from a height greater than 4.0-6.0 cm resulted in spheres which were flat in shape, while dropping the suspension from a height of less than 4.0 cm produced irregularly shaped spheres. A height of 4.0-6.0 cm produced reasonably spherical and acceptable spheres.

**Fixed-bed column experiments**

To fulfill all of the proposed objectives, experimental studies were carried out in continuous mode in which lead solutions of the concentration of 100.53 mg/L were used. The experimental plant used is shown in figure 1. The length of the glass column was 30 cm with a 1.5 cm internal diameter.

The impact of bed height on the adsorption of Pb(II) onto HAP beads was assessed at four different bed heights (1, 2, 3 and 4 cm). To study the impact of flow rate on the adsorption of Pb(II) onto HAP beads, experiments were carried out at three different flow rates: 10, 15 and 22.5 mL/min. The column studies were performed in duplicate for all three HAP samples and mean values are used for data analysis.

The concentration of lead ions in the initial solutions and in the purified solutions was determined by atomic absorption spectrophotometry using a ContraAA 300 atomic absorption spectrophotometer.

**Results and discussions**

**HAP ceramic microspheres characterization**

The X-ray diffractograms of all three HAP samples are depicted in figure 2. The crystalline phases have been determined by comparing with the registered standard JCPDS (Joint Committee on Powder Diffraction File) database (HAP: 09-0432) with the obtained powder diffraction files. As it can be seen from figure 2, in the case of all HAP microsphere samples, all the diffraction peaks can be indexed as hydroxyapatite indicating that HAP is the single phase obtained. The characteristic peaks of HAP appears in figure 2 at $2\theta \approx 19.8^\circ$, 22.9°, 25.9°, 31.8°, 32.8°, 34.1°, 39.9°, 42.7°, 46.7°, 48.2° and 49.6° [20].

By processing the diffractograms it was possible to calculate and evaluate the average crystallite size and respectively the degree of crystallinity of the adsorbent material shown in table 2.
The data obtained revealed that the microstructural test adsorbents are comprised of 64 ... 114 nm agglomerates with a high crystallinity degree of 90-92%.

Figure 3 shows the IR spectra for the three types of adsorbents (ceramic microspheres HAP) calcined at 1150 °C. The characteristic peaks of the HAP compound are well represented for all ionic species, PO$_4$$^{3-}$ (1089-964 cm$^{-1}$ and 631 cm$^{-1}$), -OH (3571-3573 cm$^{-1}$) and peaks characteristic of adsorbed water (3300-3530 cm$^{-1}$) [23].

Microstructural measurements (SEM) have allowed the dimensional assessment of adsorbents (HAP microspheres), micro/macroporous level and degree of interconnection. The influence of the addition of porous material on the porosity level, an essential condition in the adsorption process of heavy metals in their aqueous solutions, was followed.

The granular products developed (HAP ceramic microspheres) and calcined at 1150°C are consisting of porogenic addition (30-40% by weight, reported to the amount of HAP), and the NaALG: HAP with value of 4.

Figure 4 shows the microstructure of the samples with 40% gr. addition of porogen (the maximum amount introduced) and the ratio of Na-ALG: HAP with value of 4.

Maximum amount of organic material generates, after calcinations, a large porosity constituted by micro and macropores, with the size of 100 ÷ 500 nm and consequently smaller particle blocks of dimension order microns. The obtained microspheres have an average size of ~ 1.83 mm. The amount of porogen (40% by weight) and the ratio of Na-ALG: HAP equal with 4 allow us to obtain granules with a more rough surface, with a high microporosity relatively interconnected, with macropores of slightly smaller dimensions (average diameter in range 100 ... 500 nm). The average size of the microspheres is ~ 1.83 mm.

The high calcination temperature (1150°C) provides sufficient resistance to the adsorbent material, especially in dynamic tests. Micro and macroporosity give the adsorbent material capabilities increased adsorption through an increased transfer area (multiple active points).

SEM images of HAP-II sample obtained by the use of a lower amount of porogen material (30% by weight) and the ratio of Na-ALG: HAP equal with 4 are described in figure 5.

Generally, the products obtained are better densified, on the one hand due to increased reactivity of the ceramic precursor, but also the use of a lower amount of porous material (30%). In this case, the microspheres have an average size of ~ 2mm, a small and non-communicating microporous structure, with large agglomerates of nanometric particles.

Figure 6 shows the micrographs (SEM) for less porous products (well densified - calcining temperature 1150 °C) in exchange, with mechanical strength and high stability. The amount of porogen is minimal (30%) and the ratio Na-ALG: HAP = 4.

The obtained microspheres have a relatively smooth surface, with small pore inclusions the size of 100 ÷ 350 nm, with an average size of ~ 2 mm.

The method used for determining density porosity is called Arthur (or Archimedes modified) and mainly consists of:

| Table 2 | THE PHYSICAL CHARACTERISTICS (MEAN CRYSTALLITE SIZE AND DEGREE OF CRYSTALLINITY) OF ADSORBENTS USED FOR ADSORPTION TESTS |
|---------|----------------------------------------------------------------------------------|
| HAP sample | Diameter [nm] | Xc (degree of crystallinity) |
| HAP-I    | 76.9         | 0.92                        |
| HAP-II   | 114.2        | 0.91                        |
| HAP-III  | 64.0         | 0.90                        |

Fig. 4. SEM image of HAP-I sample (at 101X magnification (a) and 50.00 K X magnification (b))

Fig. 5. SEM image of HAP-II sample (at 56 X magnification (a) and 20.00 K X magnification (b))

Fig. 6. SEM image of HAP-III sample (at 60 X magnification (a) and 20.10 K X magnification (b))
- weighing the initial sample, obtaining the mass $m_0$,
- placing the sample in the vacuum cleaner and rinse off for 15 min., after which the samples are immersed in xylene and kept for another 15 min.

3. opening the desiccators in order to remove the samples and weigh them twice as follows:
   - in air, thus having the mass $m_1$ (mass of the sample saturated in xylene and weighed in air)
   - in xylene (put in a spherical device and sink into xylene - the classic Archimedes method),
     now having a mass of $m_2$ (saturation mass in xylene and weighed in xylene).

The formulas used to determine the ceramic properties are:

- apparent density ($\rho_a$)
  \[ \rho_a = \frac{m_0 - m_2}{m_1 - m_2} \text{ [g/cm}^3\text{]} \]

- apparent porosity ($P_a$)
  \[ P_a = \frac{m_0 - m_1}{m_1 - m_2} \text{ [%]} \]

where: $\rho_x = $ xylene density at at the measuring temperature.

The values of density and porosity of samples developed are presented in table 3.

| HAP sample | $\rho_a$ [g/cm$^3$] | $P_a$ [%] |
|------------|---------------------|-----------|
| HAP-I      | 2.07                | 28.50     |
| HAP-II     | 2.34                | 26        |
| HAP-III    | 2.26                | 34.50     |

Thus, the increase in the amount porogen material from 30 to 40% results in an increase in porosity from 26% (compound HAP-II) to 28.50% (compound HAP-I), and also in decreasing of apparent density from 2.34 g/cm$^3$ to 2.07 g/cm$^3$ for microspheres calcination temperature of 1150 °C.

Thus, well-densified granular products with a reasonable porosity were prepared by using the amount of porogen in the range of 30 - 40% and the ratio Na-ALG:HAP at 4. The use of calcined precursors at 650°C (finer ceramic powder with higher specific surface area - more reactive ceramic powders) allows the production of granular products (microspheres) (HAP-II) although porous (30% porogenic addition) with superior mechanical strength.

The value of porosity recommend using of HAP microspheres in Pb(II) removal experiments.

Removal of Pb(II) in fixed-bed column
This study can be regarded as an attempt to evaluate the potential of HAP beads for the removal of Pb(II) from aqueous solutions using fixed-bed column studies. The surfaces of HAP beads are rough and porous having a high sorption capacity. Calcium ions from HAP structure can be replaced by Pb(II) from aqueous solutions.

Fig. 7. The breakthrough curves for Pb(II) removal from 100.53 mg/L aqueous solutions by HAP-I sample with different bed height (flow rate = 10 mL/min)

Fig. 8. The breakthrough curves for Pb(II) removal from 100.53 mg/L aqueous solutions by HAP-II sample with different bed height (flow rate = 10 mL/min)
seen from figures 7-9, for all three HAP samples the best results have been obtained by using a high bed height adsorbent. Differences observed for bed with height = 3 cm and one with height = 4 cm is not significant; consequently in the experiments performed for determination of influence of other parameters we used an adsorbent bed with 3 cm height.

The impact of flow rate on Pb(II) adsorption onto HAP beads was investigated by varying the flow rate at 10, 15, and 22.5 mL/min, while the initial Pb(II) concentration (100.53 mg/L), and bed height (3 cm) of the column were held constant. The plots of Ce/C0 ratio versus time at different flow rates are shown in figures 10-12.

Data presented in figures 10-12 revealed that the time required to reach the breakthrough (tB) decreases from 1440 to 950 minute with an increase in flow rate from 10 ml/min to 22.5 mL/min (for HAP-I), from 135 to 95 min with an increase in flow rate from 10 ml/min to 22.5 mL/min (for HAP-II, and from 240 to 160 min with increase in flow rate from 10 ml/min to 22.5 mL/min (for HAP-III). A decrease of adsorption capacity with increase in flow rate was also observed. The decreased adsorption at higher flow rate (22.5 mL/min) is probably due to limited retention time for Pb(II) to interact with the HAP beads and the limited diffusivity of solute into the sorption sites or pores of HAP beads.

On the whole, lower flow rate allows for sufficient contact time between Pb(II) and HAP beads to reach their equilibrium. The optimum flow rate for HAP beads in the fixed-bed columns was 10 mL/min. The results are in agreement with previous fixed-bed column studies [24].

All three HAP beads samples have been tested comparatively to assess the influence of the main characteristics onto sorption properties. The plots of Ce/C0 variation with time are given in figure 13.
Results presented in figure 13 reveal that the high value of the time required to reach the breakthrough ($t_B$) was registered for HAP-III, and the lower value was recorded for HAP-I. Thus, more volume of wastewater (2950 mL) can be treated by using fixed-bed HAP-III beads column with 3 cm bed height, 1.5 cm diameter, and 10 mL/min flow rate.

The total uptake capacity for all three HAP beads samples has been calculated and the following values have been obtained: 7.42 mg/g for HAP-I, 33.66 mg/g for HAP-II and 59.99 mg/g for HAP-III.

Consequently, of the three tested materials, HAP-III has the best properties to be used continuously for the treatment of lead-containing wastewater.

Conclusions

By correlating the data from the experimental study, the following conclusions can be drawn:
- all tested materials have lead retaining capacity from synthetic aqueous solutions;
- the retention capacity depends on the characteristics of the tested materials;
- breakthrough volume and breakthrough time depend on the characteristics of the tested materials;
- a larger volume of wastewater can be efficiently cleaned using HAP-III adsorbent material which is characterized by a higher porosity value and a higher density value;
- as regards the height of the adsorbent bed used, it has been found that an increase of bed height has as a result an increase in breakthrough volume and breakthrough time. There are no significant differences between the 3 cm bed height and the 4 cm bed height, as a consequence in the following tests an adsorbent bed of 3 cm in height and 1.5 cm in diameter was used;
- a lower value of the rate flow of the influent solution has as an effect the recording of a higher value of the breakthrough volume and breakthrough time;
- the retention capacity of materials studied in the continuous treatment system varies in the order of HAP-I < HAP-II < HAP-III. The highest retention capacity recorded for HAP-III is 59.99 mg/g, and the lowest value was recorded for HAP-I (7.42 mg/g). These values are according to the porosity values;
- adsorbent materials can be regenerated using dilute nitric acid solution;
- retention capacity, breakage volume, and breakthrough times recommend that HAP-III microspheres be used in lead-bed removal processes containing lead ions.

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