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ADSORPTION OF La³⁺ AND Dy³⁺ IONS ON BIOHYDROXYAPATITE OBTAINED FROM PORK BONES GASIFIED WITH STEAM

Adsorption of La³⁺ and Dy³⁺ from their aqueous nitrate solutions on biohydroxyapatite (BHAP) originally prepared from raw pork bones by steam gasification of has been investigated for the La³⁺ and Dy³⁺ concentrations within the range of $1.44 \cdot 10^{-4}$ – $8.06 \cdot 10^{-3}$ mol/dm³ and $2.71 \cdot 10^{-5}$ – $5.68 \cdot 10^{-3}$ mol/dm³, respectively. It was found that saturation of the lanthanide uptake occurred at 0.0625 moles of Ln³⁺ per mole of BHAP. Two model isotherms, i.e., Langmuir ($q_e = q_m C^e / ((1/K_L) + C^e)$) and Freundlich ($\log q_e = \log K_F + (1/n) \log C^e$), were used to fit the adsorption data. The following isotherm parameters were found for La³⁺: $q_m = 0.1265$ mol/kg, $K_L = 2701$ dm³/mol, $n = 5.61$, $K_F = 0.283$ (mol/kg)·(dm³/mol)^{1/n} and for Dy³⁺: $q_m = 0.1223$ mol/kg, $K_L = 3635$ dm³/mol, $n = 5.82$, $K_F = 0.306$ (mol/kg)·(dm³/mol)^{1/n}. A better correlation was found for the Freundlich model. A relatively high value of the n parameter in the Freundlich equation suggests heterogeneous chemisorption of lanthanide ions.

1. INTRODUCTION

The potential uses of biohydroxyapatite (BHAP) from meat and bone meal incineration (MBM ashes) as a raw material for the phosphate industry, a stabilizing agent for the waste treatment by phosphatation, an immobilizer of heavy metals and a possible admixture for construction materials have been reviewed in literature [1–8]. In particu-

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lar, affinity of bone structures for f-metals, trivalent actinides and lanthanides was discussed from a point of view of medicine and chemistry [9, 10]. However, it should be noted that there are diverse approaches to describing lanthanides uptake from aqueous solutions. For example, in the paper [11] the process is discussed as the adsorption behavior whereas in [12] it is described as ion exchange. An approach presented in [11] refers to adsorption and kinetics as well as to the thermodynamic parameters (enthalpy and entropy) of the process. In more chemical elucidation, not kinetics but equilibrium thermodynamics of Ca^{2+} ions replacement for lanthanides ions was investigated [12]. Even if there was a discussion on the mechanism and chemistry of sorption of trivalent ions on hydroxyapatite, there is almost no information on efficiency of these ions (especially lanthanides) sorption, with exception of papers cited above [11, 12] and [13]. Moreover, the investigations described in these papers were carried out with HAP (i.e., $\text{Ca}_5(\text{PO}_4)_3\text{OH}$) that was originally synthesized [11, 13] or purchased as a laboratory reagent [12]. In our investigation, BHAP originally obtained by steam gasification of bones with no additional preparation was used to study the sorption process of La^{3+} and Dy^{3+} (Ln^{3+}) ions from aqueous solutions.

2. EXPERIMENTAL

Preparation of biohydroxyapatite. Raw pork bones from a local slaughterhouse were used for BHAP preparation. In the first step, material was dried for 40 h at 105 °C. The resultant dried substrate was gasified under excess of steam at normal pressure in a quartz tube reactor of a 34 mm inner diameter. The gasification parameters were as follows: heating of the dried bones to 500 °C with a temperature increase of 3 °C/min, heating from 500 °C to 850 °C with the temperature increase of 5 °C/min, heating at 850 °C for additional 2 h, and cooling to ambient temperature with the initial temperature decrease of 20 °C/min. The steam flow was 1.9 g/min when heating to 850 °C and 0.41 g/min during the heating at constant temperature. Pieces of the gasified bones were powdered using an agate mortar and finally sieved. The mass fraction with particle size between 0.071 and 0.16 mm was used in the adsorption experiments.

Methods. X-ray Diffraction (XRD) patterns of BHAP were collected using a Bruker D2 Phaser with a CuK_α radiation source over the 2θ range of 8–90° at the intervals of 0.01° and with a count time of 0.5 s. Sample identification was made by comparing diffraction pattern with this for the HAP standard (JCPDS-09-0432).

Fourier transform middle-infrared (FTIR) spectra of BHAP in KBr pellets were recorded in the range 4000–400 cm^{-1} using a Bruker VERTEX 70V vacuum spectrometer comprising an ATR accessory and an air-cooled DTGS detector. The spectra were recorded at a resolution of 4 cm^{-1} with 128 scans.

The porous texture of the prepared BHAP was determined from nitrogen adsorption isotherms measured at 77 K with a NOVA 2200 (Quantachrome). Moreover, the pore structure of the specimen was determined via mercury intrusion porosimetry. This measurement was performed up to 412 MPa with the Micromeritics AutoPore IV 9500.

Initial and final concentrations of Ln^{3+} ions in solutions before and after the batch treatment with BHAP were determined using an Agilent bench-top inductively coupled plasma optical emission spectrometer (ICPOES), model 720, with an axially viewed Ar-ICP and a conventional pneumatic nebulization sample introduction system. The most prominent analytical lines of La (333.749 and 379.477 nm) and Dy (340.780 nm) were selected for measurements. The operating conditions recommended by the manufacturer of the instrument were applied.

Adsorption experiments. Aqueous solutions of Dy^{3+} ions were prepared by diluting an ICP/DCP stock standard solution ($10150 \mu\text{g}/\text{cm}^3$ in 3% HNO_3 , Aldrich Chemical Company, Inc.). They were neutralized with diluted NaOH (p.a., POCH, Avantor Performance Materials, Poland, S.A.) to the appearance of traces of hydroxide. Final pH was regulated with diluted HNO_3 (p.a., POCH, Avantor Performance Materials, Poland, S.A.). Solutions of La^{3+} were prepared by dissolving crystalline $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (p.a., POCH S.A., Poland) in water; the solutions were clear and there was no need to regulate pH which was 6.01. For adsorption experiments, samples of ca. 0.1 g of BHAP powder were suspended in 10 cm^3 of prepared La^{3+} or Dy^{3+} solutions with varying concentrations of both lanthanides and shaken in vials for 2 h. Particles of BHAP were separated by centrifugation for 25 min at 3500 rpm.

3. RESULTS AND DISCUSSION

3.1. PHYSICOCHEMICAL CHARACTERISTICS OF PREPARED BHAP

The mixture of bones and soft tissue was found to change color during drying at 105°C from original (raw meat) to brown-dark and its weight decreased by 37%. Gasified bones preserved the original form of bone pieces; they were white with a slight brownish tinge on soft parts. The total weight loss of gasified material, including the drying stage, was 62%.

The specific surface area of the powdered bone material S_{BET} was $2 \text{ m}^2/\text{g}$, total pore volume V_t $0.004 \text{ cm}^3/\text{g}$ and micropore volume V_{DR} $0.001 \text{ cm}^3/\text{g}$. The mesopore volume share was 71% and the average pore diameter (L_{AV}) was 3.08 nm. From the intrusion curve, the mercury intrusion porosimetry provided the following information on BHAP sample: the total intrusion volume was $0.6196 \text{ cm}^3/\text{g}$, total pore area $2.063 \text{ m}^2/\text{g}$, median pore diameter (volume) $3.1638 \mu\text{m}$, median pore diameter (area) $0.4025 \mu\text{m}$, average pore diameter ($4 V/A$) $1.2012 \mu\text{m}$, bulk density at 0.0036 MPa $0.9685 \text{ g}/\text{cm}^3$, apparent (skeletal) density $2.4216 \text{ g}/\text{cm}^3$ and porosity 60.0%.

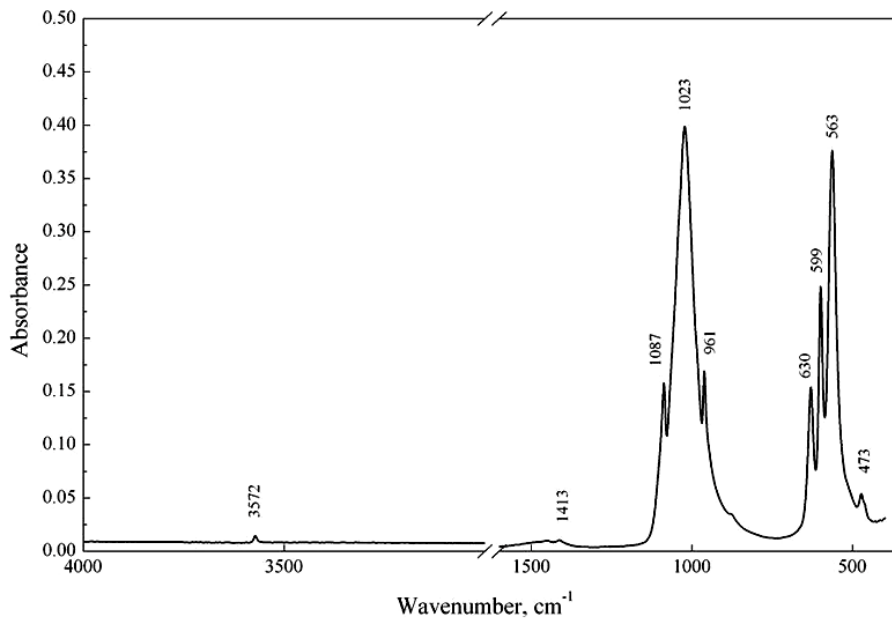


Fig. 1. FTIR spectrum of BHAP prepared by steam gasification (850 °C) of raw pork bones

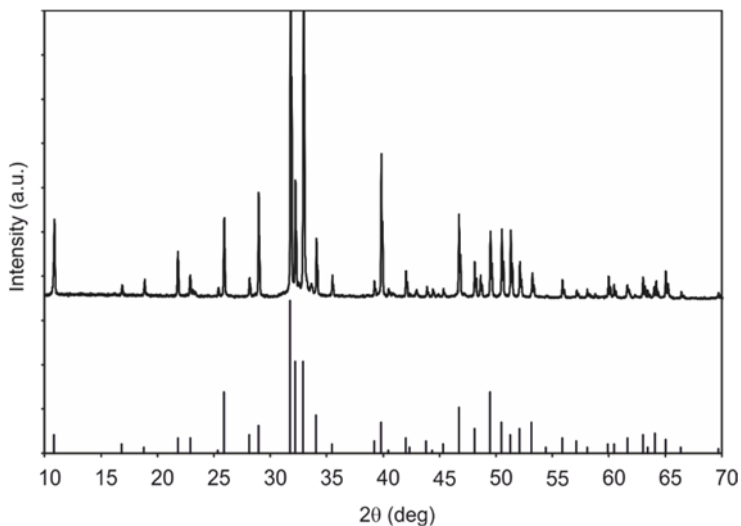


Fig. 2. X-ray diffraction (XRD) pattern of prepared BHAP (upper part) and the HAP standard, JCPDS-09-0432 (lower part)

The FTIR spectrum of BHAP is shown in Fig. 1. Characteristic modes of phosphate groups (PO_4^{3-}) were observed at 473, 563, 599, 961, 1023 and 1087 cm^{-1} . The band at 473 cm^{-1} was attributed to the $\nu_2(\text{PO}_4^{3-})$ bending mode. Two peaks located at 563 and

599 cm^{-1} were due to the $\nu_4(\text{PO}_4^{3-})$ bending mode. The band at 961 cm^{-1} was assigned to $\nu_1(\text{PO}_4^{3-})$ symmetric stretching while the peaks at 1023 and 1087 cm^{-1} were related to the $\nu_3(\text{PO}_4^{3-})$ asymmetric stretching modes. Further, hydroxyl vibration $\nu(\text{OH})$ was observed at 3572 cm^{-1} . The band at 630 cm^{-1} was also attributed to $\delta(\text{OH})$ and a small broad peak at 1413 cm^{-1} corresponded to the stretching vibration of CO_3^{2-} groups. These results are in a good agreement with those reported in literature [14, 15].

The XRD pattern of the prepared BHAP powder is presented in Fig. 2. The d-spacing lines, 2θ angles, and relative intensities observed for BHAP were compared with those for the HAP standard (JCPDS-09-0432). As can be seen, the XRD pattern of prepared BHAP is consistent with that of the HAP standard and the literature data [15]. No additional peaks from other constituents or phases were observed confirming purity of the gasified BHAP product.

3.2. SORPTION EFFICIENCY OF Ln^{3+}

Sorption experiments were performed in a batch mode and using lanthanide solutions with concentrations of La^{3+} and Dy^{3+} varying in the range of 1×10^{-4} – $8 \times 10^{-3}\text{ mol/dm}^3$ and 3×10^{-5} – $6 \times 10^{-3}\text{ mol/dm}^3$, respectively. Parameters of the sorption experiments are given in Table 1 where C^0 and C^e refer to initial and equilibrium concentrations, respectively, and NM is not measured.

Table 1

Parameters of La^{3+} and Dy^{3+} adsorption experiments

$C_{\text{La}^{3+}}^0$ [mol/dm ³]	$n_{\text{La}/\text{NBHAP}}$	$C_{\text{La}^{3+}}^e$ [mol/dm ³]	La^{3+} sorption [%]	La^{3+} uptake [mg La/g BHAP]
8.06×10^{-3}	0.405	6.83×10^{-3}	15.2	17
1.62×10^{-3}	7.68×10^{-2}	7.70×10^{-4}	52.4	11.1
8.64×10^{-4}	4.10×10^{-2}	2.81×10^{-4}	67.5	7.66
4.18×10^{-4}	2.07×10^{-2}	8.32×10^{-6}	98	5.62
1.44×10^{-4}	7.32×10^{-3}	7.41×10^{-8}	100	2.02
$C_{\text{Dy}^{3+}}^0$ [mol/dm ³]	$n_{\text{Dy}/\text{NBHAP}}$	$C_{\text{Dy}^{3+}}^e$ [mol/dm ³]	Dy^{3+} sorption [%]	Dy^{3+} uptake [mg Dy/g BHAP]
5.68×10^{-3}	0.285	4.46×10^{-3}	21.6	19.9
3.39×10^{-3}	0.167	2.36×10^{-3}	30.5	16.5
1.06×10^{-3}	5.35×10^{-2}	3.65×10^{-4}	65.6	11.4
5.51×10^{-4}	2.64×10^{-2}	1.64×10^{-6}	99.7	8.52
2.81×10^{-4}	1.34×10^{-2}	bl	NM	4.34
1.34×10^{-4}	6.72×10^{-3}	9.78×10^{-8}	99.9	2.17
2.71×10^{-5}	1.35×10^{-3}	8.49×10^{-5}	99.7	0.437

bl – below the limit of detection ($2.0 \times 10^{-9}\text{ mol/dm}^3$).

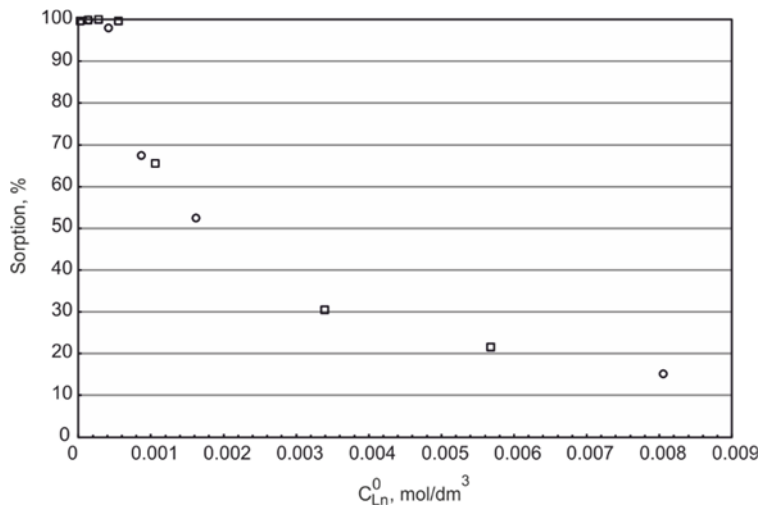


Fig. 3. Sorption efficiency of Ln^{3+} vs. the initial lanthanide concentration (C_{Ln}^0); circles – La^{3+} , cubes – Dy^{3+}

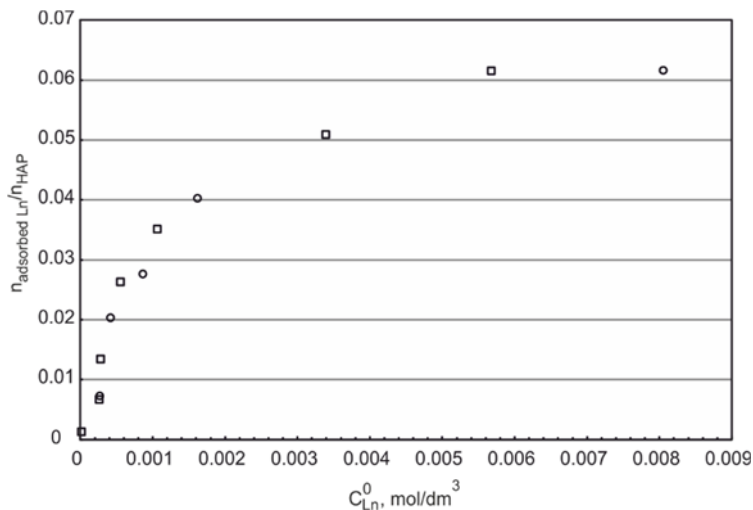


Fig. 4. Sorption efficiency of Ln^{3+} per one mole of BHAP (assuming stoichiometry of $Ca_5(PO_4)_3(OH)$) vs. initial lanthanide concentration (C_{Ln}^0); circles – La^{3+} , cubes – Dy^{3+}

It can be noticed that almost complete sorption of lanthanide ions was achieved only at concentrations lower than $5 \cdot 10^{-4}$ mol/dm³. An increase of the lanthanide ions concentration above this level resulted in a gradual decrease of sorption efficiency (Fig. 3). Taking into account the dependence of number of moles of lanthanide ions adsorbed per mole of BHAP – as shown in Fig. 4, it is clear that the system became saturated.

By fitting this data for both lanthanides with the saturation growth rate equation of the form $n_{\text{adsorbed Ln}}/n_{\text{HAP}} = aC_{\text{Ln}}^0/(b + C_{\text{Ln}}^0)$ where a and b are the parameters of the saturation growth rate equation, it was established that the maximum of the lanthanide uptake is equal to 0.0625 moles of Ln^{3+} per one mole of BHAP.

3.3. ADSORPTION ISOTHERMS

The Langmuir and Freundlich isotherms were applied to fit the data of adsorption. For the Langmuir model, the saturation growth rate equation $q_e = q_m C^e / ((1/K_L) + C^e)$ was applied for better visualization of the experimental data (it is equivalent to equation $1/q_e = 1/q_m K_L C^e + 1/q_m$ [16, 17]). In this equation, q_e is the number of moles of Ln^{3+} adsorbed in equilibrium on 1 kg of BHAP, q_m – the maximum number of moles of Ln^{3+} adsorbed on 1 kg of BHAP, C^e – the equilibrium concentration of Ln^{3+} in solution (mol/dm^3), K_L – the Langmuir constant (dm^3/mol). Curves fitting the data for La^{3+} and Dy^{3+} are shown in Fig. 5a, b, respectively. For the Freundlich model, the equation $\log q_e = \log K_F + (1/n)\log C$ was applied [16], where K_F is the Freundlich constant, $1/n$ – the parameter of sorption intensity related to heterogeneity of the material. Curves fitting the data for La^{3+} and Dy^{3+} are presented in Fig. 6a, b, respectively. For better fitting of the Dy^{3+} data, one experimental point at the lowest Dy^{3+} concentration was omitted. All the parameters found for both models are given in Table 2.

Table 2

Parameters of the Langmuir and Freundlich model isotherms

Langmuir model, $q_e = q_m C^e / ((1/K_L) + C^e)$			
La^{3+}	q_m	0.1265 mol/kg	SE = 0.0236, r = 0.868
	K_L	2701 dm^3/mol	
Dy^{3+}	q_m	0.1223 mol/kg	SE = 0.0272, r = 0.835
	K_L	3635 dm^3/mol	
Freundlich model, $\log q_e = \log K_F + (1/n)\log C^e$			
La^{3+}	n	5.61	SE = 0.0592, r = 0.989
	K_F	0.283 (mol/kg)·(dm^3/mol) $^{1/n}$	
Dy^{3+}	n	5.82	SE = 0.163, r = 0.929
	K_F	0.306 (mol/kg)·(dm^3/mol) $^{1/n}$	

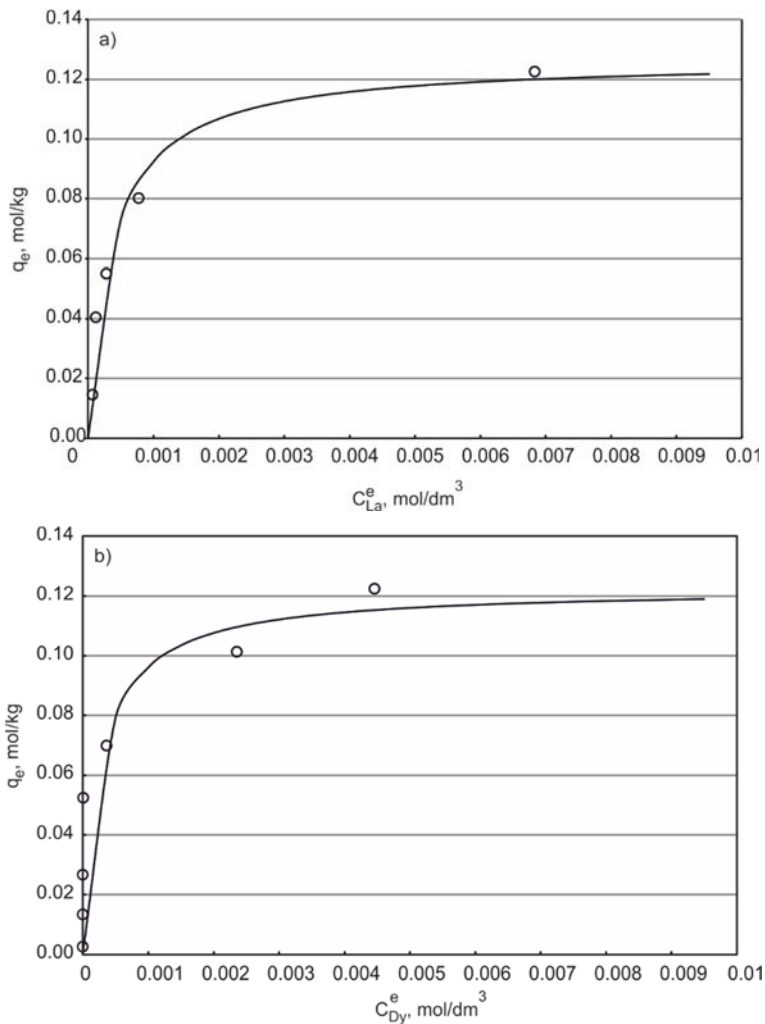


Fig. 5. Langmuir model adsorption isotherm for La³⁺ (a) and Dy³⁺ (b) fitted by the saturation growth rate equation $q_e = q_m C^e / ((1/K_L) + C^e)$; q_e – La³⁺ or Dy³⁺ concentrations on the sorbent (mol/kg), C^e – equilibrium La³⁺ or Dy³⁺ concentration in the solution (mol/dm³)

Numerous literature studies reported so far were concentrated rather on biological aspects of the lanthanide uptake by bones and tissues, not the determination of the adsorption parameters. However, some papers are worth considering. Granados-Correa et al. [11] investigated adsorption in aqueous solutions containing La³⁺ and Eu³⁺ ions at very low concentrations between 10⁻⁵–10⁻⁴ mol/dm³ and with a significant molar excess of HAP, i.e. n_{Ln}/n_{HAP} ranging from 0.020 to 0.003, was presented.

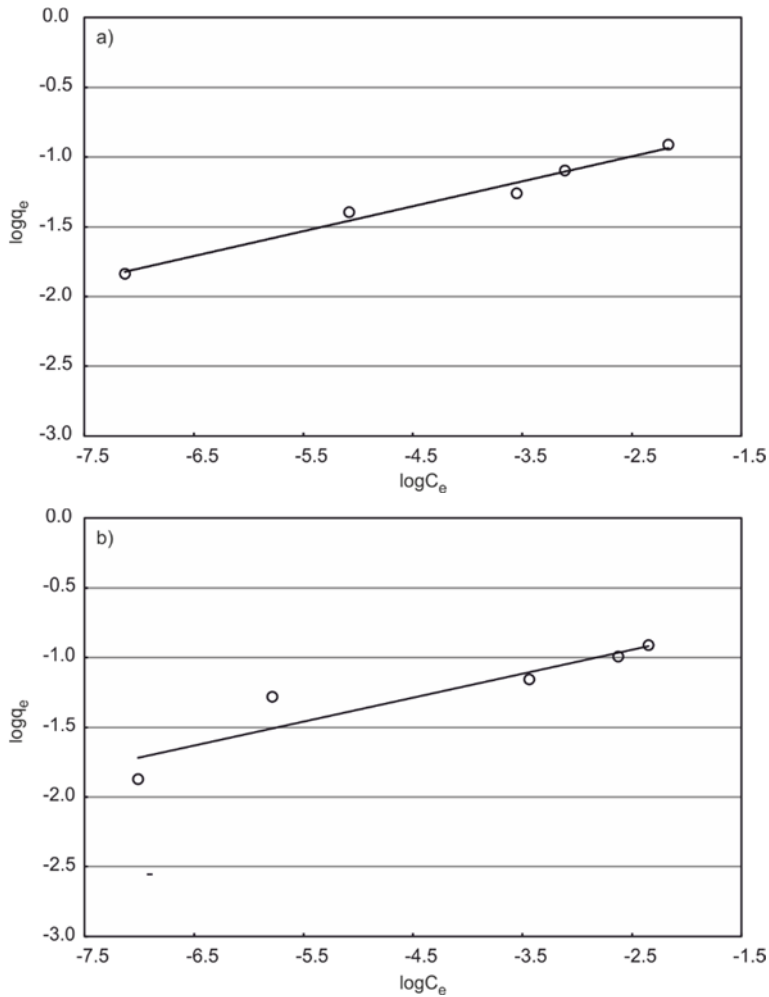


Fig. 6. Freundlich model adsorption isotherm for La^{3+} (a) and Dy^{3+} (b) fitted by the equation $\log q_e = \log K_F + (1/n)\log C_e$; q_e – La^{3+} or Dy^{3+} concentration on the sorbent (mol/kg), C_e – equilibrium La^{3+} or Dy^{3+} concentration in the solution (mol/dm³).

The results of their work [11] appeared rather astonishing; adsorption efficiency was established to increase upon the increasing lanthanide concentration (for La^{3+} it was from 60 to 99%) and hence the Langmuir model was inadequate to describe this phenomenon. However, the use of the Freundlich model gave a good fitting. The authors [11] conducted two sets of experiments with slightly different initial lanthanum concentrations. The following parameters of the Freundlich equation were calculated: $n = 0.21$ or 0.43 and $K_F = 6.3$ or 5.3 (after recalculation to units consistent with those given in

Table 2). The discrepancies between these data and those presented in Table 2 are significant, but it should be kept in mind that the concentration range of the La^{3+} ions applied in [11] was lower by at least one order of magnitude from those applied in the present work, and HAP used was of different origin. Taking into account the slope of the Freundlich isotherm, $1/n$, it may be supposed that cooperative adsorption was observed in [11] (for cooperative adsorption adsorbate has an effect on adsorption of “new” adsorbate molecules [18]). For BHAP used in the present investigation it was rather heterogeneous chemisorption [16]. Moreover, the comparison of the Freundlich constants K_F indicates a higher adsorption capacity of the laboratory prepared HAP used in [11] than that of BHAP used in the present study.

Cawthray et al. [12] do not introduce the concept of adsorption (despite the fact that some experiments were performed in a similar way as those described here) and discuss the ion exchange involving Ca^{2+} and La^{3+} ions. They found that a replacement of Ca^{2+} ions in HAP by La^{3+} ions increased upon increasing La^{3+} concentration in solution up to two moles of La^{3+} per one mole of HAP (what is the equivalent to the replacement of 3 moles of Ca^{2+} out of 5 in the HAP unit). Therefore, a simple recalculation gives the La^{3+} uptake of 553 g La^{3+} /kg or 3.98 mol of La^{3+} /kg of HAP. This is thirty times more than q_m of the Langmuir model (Table 2). However, also in this case, HAP used in [12] was a commercial reagent. On the other hand, according to the opinion presented in [10], hydroxyapatites synthesized by the chemical or biochemical way, do not retain metal cations uniformly and trivalent actinides and lanthanides are incorporated *into the amorphous grain boundaries of the polycrystalline apatite* and there is *no incorporation onto a calcium site within the crystal structure as previously proposed*.

Gok [13] presented results of the Sm^{3+} and Nd^{3+} adsorption by laboratory prepared HAP, that was modified with magnetic Fe_3O_4 nanoparticles. The adsorption data for both lanthanides was very well fitted by the Langmuir model, with correlation coefficients higher than 0.99. However, the parameter q_m of the model, which was equal to (after recalculation) 2.24 and 2.46 mol/kg for Nd^{3+} and Sm^{3+} , respectively, evidently reflects the expected properties of the sorbent. However, the Langmuir constants (K_L) which were equal to 6980 and 3040 dm^3/mol for Nd^{3+} and Sm^{3+} , respectively, (also recalculated), are fairly similar to the ones given in Table 2.

Summarizing the discussion above, surprisingly, only few data on lanthanides sorption on hydroxyapatites has been published [11–13]. A different and somewhat contradictory approach was presented in any of these papers to the lanthanide uptake. The experiments were performed with synthetic HAP or bioHAP not processed at high temperatures. Therefore it seems that in-depth discussion of the presented here results is not justified, especially in the form of non-linear regressions and more sophisticated models of sorption. It should be also kept in mind that biohydroxyapatite processed at high temperature exhibits a little different chemical properties in comparison to those obtained by non-thermal methods. Presented above result, even if limited to the Langmuir

and Freundlich models, clearly point to sorption with chemical reactions undoubtedly associated with alkalization due to decomposition of calcium carbonate from bioHAP.

4. CONCLUSIONS

The authors studied isotherms of adsorption of La^{3+} and Dy^{3+} ions from aqueous solutions (at the concentrations of lanthanides up to 8 mmol/dm³) on BHAP obtained by steam gasification of raw pork bones (an original slaughterhouse product) at normal pressure and temperature of 850 °C. It was established that the uptake of La^{3+} and Dy^{3+} ions increased with the increasing concentration of lanthanides and according to the Langmuir model, reached saturation (q_m) at 0.126 and 0.122 mol/kg of hydroxyapatite for La^{3+} and Dy^{3+} , respectively. The correlation coefficients for the Langmuir model for both lanthanides were noticeably below 0.9. Higher coefficients, above 0.9, were found for the Freundlich model. A relatively high value of the n parameter in the Freundlich equation suggests heterogeneous chemisorption of lanthanides ions. Unfortunately, there is no literature reports on the adsorption parameters of lanthanide ions on calcined or gasified BHAP. There are only few investigations that partially enable to quantitatively evaluate the lanthanides uptake by non-BHAP, however they seem incoherent. The present study on the adsorption of the La^{3+} and Dy^{3+} ions on BHAP certainly helps understanding the sorption process and future application of the raw biomaterial in the enrichment of lanthanides from diluted solutions.

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