



## Resource recovery of animal bones: Study on sorptive properties and mechanism for Sr<sup>2+</sup> ions

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### ABSTRACT

The interaction between Sr<sup>2+</sup> ions and variously treated animal bones was studied from the aspect of <sup>90</sup>Sr isotope immobilization from the contaminated effluents. As a source of biogenic, poorly-crystalline apatite, bone based materials, in general, were found to exhibit good retention properties towards Sr<sup>2+</sup> cation. Furthermore, sorption capacities of H<sub>2</sub>O<sub>2</sub> treated bone sample and sample annealed at 400 °C were found to be higher in respect to a commercial bone char and synthetic hydroxyapatite. Mentioned treatments induced partial organic phase removal from the pores of the skeletal material that caused the increase of the specific surface area. Higher temperatures provoked an increase of the apatite phase crystallinity, agglomeration of nano-crystals and a decrease of both the specific surface area and Sr<sup>2+</sup> sorption. The immobilization was pH independent in the range 4–10, as a result of sorbents buffering properties. Kinetic data were well represented by the pseudo-second-order reaction model. Sorption isotherms were in better correlation with Freundlich than Langmuir theoretical model, whereas samples heated at 800 °C and 1000 °C showed S-type isotherms which were in a good agreement with sigmoidal Langmuir equation. The ion-exchange with Ca<sup>2+</sup> cations and the specific cation sorption were two recognized mechanisms in the Sr<sup>2+</sup> removal process, with relative contributions strongly dependent on the sorbents physicochemical properties. Sr<sup>2+</sup>-loaded products were the most stable in the neutral and alkaline environments, while Ca<sup>2+</sup> containing and acidic leaching solutions caused increased Sr<sup>2+</sup> desorption.

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### 1. Introduction

Interactions between radioactive strontium (<sup>90</sup>Sr, beta emitter, *t*<sub>1/2</sub> 28 years) and calcium phosphate compounds are of interest not only from the aspect of strontium incorporation in human bones and teeth after nuclear explosions [1], but also due to phosphate applications in the precipitation and sorption technologies of nuclear waste water treatments [2]. Among numerous calcium and phosphorous containing compounds, hydroxyapatite, Ca<sub>10</sub>-(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, (HAP), is the most commonly found in nature as a member of the apatite-group minerals, and with fluoroapatite and their carbonate-substituted varieties represent important mineral component of bones and teeth [3]. While geological hydroxyapatite may occur as large, single crystals, bone and tooth minerals consist of nano-sized particles.

Apatite compounds are generally extremely tolerant to chemical substitutions and structural distortions [4] which, with their low solubility and high geochemical stability, make them promising materials for toxic heavy metals and radionuclide immobilization.

Substitution of Ca<sup>2+</sup> ions with Sr<sup>2+</sup> in the synthetic hydroxyapatite structure is well documented [5,6]. Hydroxyapatite lattice parameters and the unit cell volume increase linearly with Sr<sup>2+</sup> addition, consistent with a larger ion entering the apatite lattice [7]. In nature, strontium is one of the most common substituents in mineral apatite [8]. Sr<sup>2+</sup> can also be incorporated in the apatite phase of animal and human bones [9]. From the biological point of view, stable forms of strontium, at low doses, exhibit beneficial effects on bone formation, trabecular bone density and consequently may be of potential interest in the prevention of osteoporosis [10]. Quite the opposite, radioactive strontium may become a continuing source of ionizing radiation in the human body [1]. The energy of <sup>90</sup>Sr β-decays deposits within a small volume of surrounding tissue, and the damage to the cells may be irreversible, leading to leukemia and bone neoplasm.

The literature has shown that the good retention properties of bones towards <sup>90</sup>Sr ions represent a benefit in respect to <sup>90</sup>Sr removal from aqueous media by bone based sorbents. Apatite II<sup>TM</sup> is a sorbent specially processed from fish bones and residues [11], with general composition Ca<sub>10-x</sub>Na<sub>x</sub>(PO<sub>4</sub>)<sub>6-x</sub>(CO<sub>3</sub>)<sub>x</sub>(OH)<sub>2</sub> where (*x* < 1), along with 30–40% by weight of associated organic materials in the internal porosity of the inorganic structure. Besides excellent sorption properties in respect to heavy metal

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cations such as  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  [12], this sorbent was also found to retain  $\text{Sr}^{2+}$  from solutions containing  $10^{-9}$ – $10^{-8}$  mol  $\text{Sr}^{2+}/\text{dm}^3$  and moderate concentrations of common chelating agents and inorganic salts [13]. Equilibrium [14] and kinetic studies [15] of  $\text{Sr}^{2+}$  removal, conducted using a commercial bone char, also suggested that biogenic materials can be effectively used as a low cost substitute for expensive synthetic hydroxyapatite powders.

The main aim of this study was to investigate  $\text{Sr}^{2+}$  removal efficiency of powdered bovine bones, as well as the possibility of improving their sorption properties by different thermal and chemical treatments. The effectiveness of  $\text{Sr}^{2+}$  removal and the stability of Sr-loaded bone products were tested and compared at various experimental conditions.

## 2. Materials and methods

### 2.1. Bone based materials used as $\text{Sr}^{2+}$ sorbents

The preparation and the characterization of bovine bone sorbents were explained in detail in our previous publication [16]. Briefly, sample B refers to crushed, boiled bones; abbreviations B400–B1000 represent samples prepared by annealing of sample B at different temperatures (400 °C, 600 °C, 800 °C and 1000 °C), whereas  $\text{BH}_2\text{O}_2$  corresponds to chemically treated sample B (oxidation with  $\text{H}_2\text{O}_2$ ). Prior to sorption experiments all samples were milled and sieved to obtain a fraction with particle diameters in the range 45–200  $\mu\text{m}$ .

The morphology of the samples was studied using a JOEL JSM 5800 Scanning Electron Microscope (SEM), at an accelerating voltage of 20 kV.

### 2.2. $\text{Sr}^{2+}$ sorption and desorption experiments

Reactions between aqueous  $\text{Sr}^{2+}$  ions and various bone sorbents were studied in the batch system, by varying initial pH, contact time and initial  $\text{Sr}^{2+}$  concentration. Considering the same chemical reactivity of radioactive and stable  $\text{Sr}^{2+}$  isotopes, in the following experiments bone based materials were exposed to solutions containing non radioactive strontium, for safety reasons. Solutions of different  $\text{Sr}^{2+}$  concentrations were prepared by dissolving calculated quantities of  $\text{SrNO}_3$  (Merck) in distilled water. Desired initial pH values were adjusted adding minimum amounts of differently concentrated KOH or  $\text{HNO}_3$  solutions. All sorption experiments were conducted at room temperature ( $20 \pm 1$  °C) using 0.1 g of sorbent and 20 ml of proper  $\text{Sr}^{2+}$  solution. Suspensions were agitated in 50 ml PVC flasks, for designed periods of time, on a horizontal shaker (120 rpm). Initial  $\text{Sr}^{2+}$  concentration of  $6 \times 10^{-3}$  mol/ $\text{dm}^3$ , initial pH 5 and 24 h of equilibration were applied, unless otherwise stated. For these experimental conditions, structures of  $\text{Sr}^{2+}$ -loaded sorbents were analyzed by X-ray diffraction (XRD), using Bruker D8 Advance diffraction system, with  $\text{Cu K}\alpha_{1,2}$  radiation in theta/theta reflection geometry. The patterns were registered in the  $2\theta$  range from  $8^\circ < 2\theta < 60^\circ$  with a scanning step size of  $0.05^\circ$  and an acquisition time of 4 s/step.

The influence of process variables on the amount of  $\text{Sr}^{2+}$  retained and corresponding sorption mechanisms was investigated by varying the contact time in the range 15 min to 48 h, the initial  $\text{Sr}^{2+}$  concentration in the range  $10^{-4}$  to  $6 \times 10^{-3}$  mol/ $\text{dm}^3$  and the initial pH in the range 4–12.

After filtration, the final solution pH values were measured. The exact initial and final concentrations of  $\text{Sr}^{2+}$ , as well as concentrations of  $\text{Ca}^{2+}$  ions discharged into the liquid phase, were determined by Perkin Elmer Analyst 200 Atomic Absorption Spectrometer (AAS). Analyses of blanks containing only  $\text{Sr}^{2+}$  solu-

tion ( $10^{-4}$  mol/ $\text{dm}^3$  or 8.76 ppm) equilibrated 24 h at initial pH values considered in this study, revealed that the retention of metal cations by the system components was in the range of AAS experimental error, therefore sorbed amounts of  $\text{Sr}^{2+}$  were calculated as a difference between initial and final  $\text{Sr}^{2+}$  concentrations. Due to a large number of sorbents and factors which influence was analyzed, a limited number of experiments were performed in duplicate and the differences between duplicate measurements were found to be <3%.

The reversibility of the process was tested using bone particles which were previously loaded with  $\text{Sr}^{2+}$  by equilibrating sorbents with a  $6 \times 10^{-3}$  mol/ $\text{dm}^3$  solution, at solid to liquid ratio 1:200, for 24 h. Solid residues were washed with distilled water, dried at 105 °C, transferred to PVC flasks and shaken with 20 ml of different leaching solutions, for another 24 h. Leaching solutions of pH 2, 5, 7 and 9, prepared using distilled water and appropriate amounts of 0.01 and 0.1 mol/ $\text{dm}^3$   $\text{HNO}_3$  or KOH, were applied, as well as  $10^{-3}$ ,  $10^{-2}$  and  $2.5 \times 10^{-2}$  mol/ $\text{dm}^3$   $\text{Ca}(\text{NO}_3)_2$ . From the quantities of  $\text{Sr}^{2+}$  ions initially sorbed and that released into the leaching solutions, percentages of desorbed metal ions were calculated.

## 3. Results and discussion

### 3.1. Characteristics of bone sorbents

Physicochemical properties of bone sorbents [16] are presented in Table 1. Characterization of obtained products revealed that heating at 400 °C and the chemical oxidation process caused partial removal of bone organic components (mainly collagen) with preservation of the poor apatite phase crystallinity. Heating at higher temperatures, especially  $T > 600$  °C, caused a complete organic phase removal, sintering of HAP nanocrystals and a decrease of the specific surface area. Extremely high  $\text{pH}_{\text{PZC}}$  values of B800 and B1000 powders were related to CaO and MgO traces, observed in the XRD spectra [16].

SEM images (Fig. 1), obtained at lower magnification, revealed the irregular morphology of crushed bone particles. The microstructure of sample B was highly dense, due to the presence of organic components. Quite the opposite, SEM images of processed powders,  $\text{BH}_2\text{O}_2$  and B400 in particular, showed a coarser structure, as a result of organic phase exclusion. Treatments at 800 °C and 1000 °C caused agglomeration of hydroxyapatite nanocrystals. The observed facts are in accordance with other physicochemical characteristics such as HAP phase crystallinity and Sp (Table 1), as well as with data published in the literature [17,18].

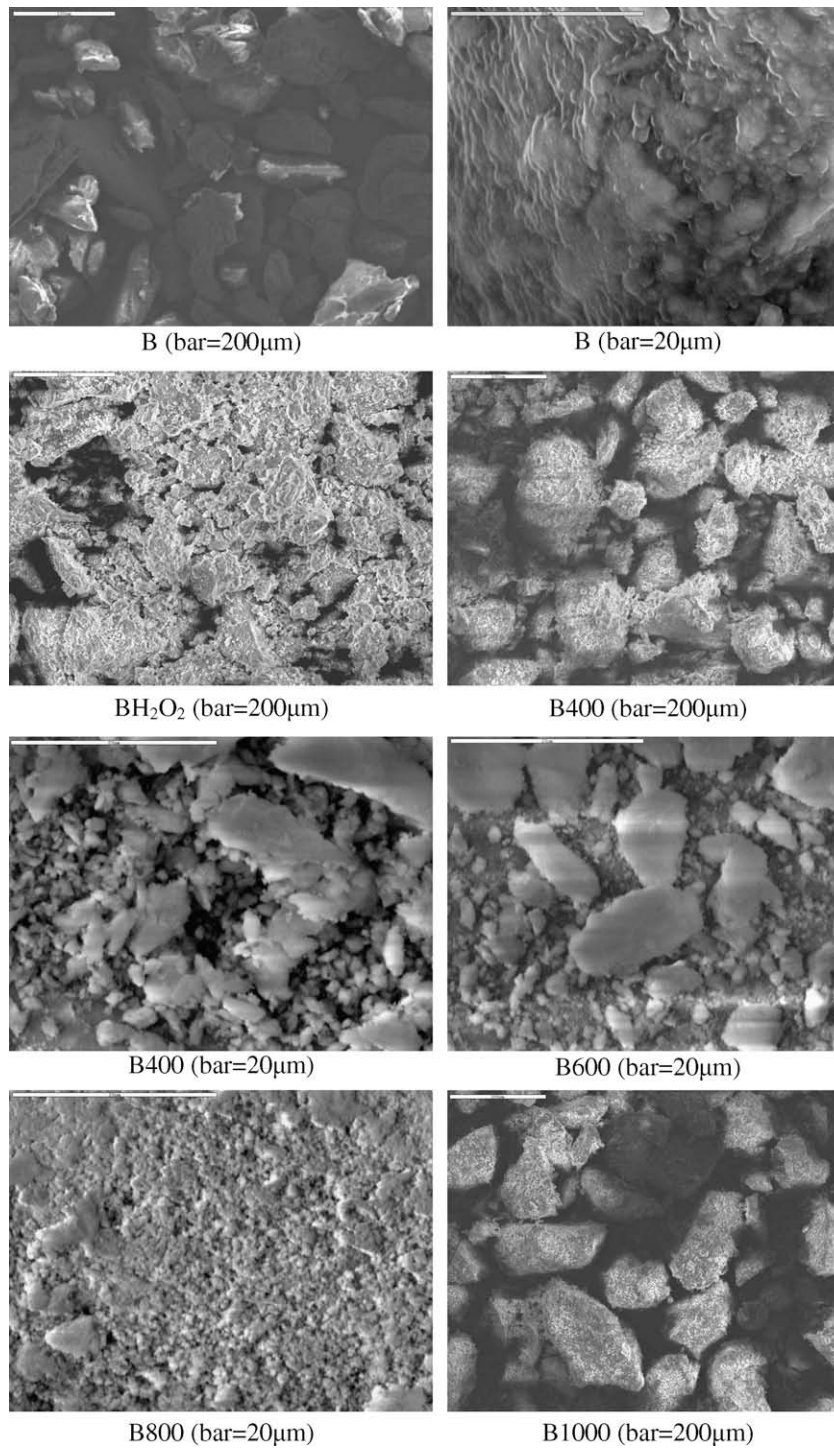
### 3.2. Effect of pH

In order to test the importance of solution pH in the reaction between bone samples and  $\text{Sr}^{2+}$  ions, the initial pH values were adjusted in the range 4–12. Changes of equilibrium (final) pH values, amounts of  $\text{Sr}^{2+}$  sorbed and amounts of  $\text{Ca}^{2+}$  ions released, against initial pH, are presented in Fig. 2. It can be concluded, that both the amphoteric nature of bone samples and the specific sorption of  $\text{Sr}^{2+}$  ions caused pH changes. Equilibrium pH values were relatively constant in the initial pH region  $\sim 4 - \sim 10$ . This buffering range was quite similar for all investigated samples, regardless of their different physicochemical properties. However, differences in the position of the plateaus were observed. In the solution of inert electrolyte ( $\text{KNO}_3$ )  $\text{pH}_{\text{final}}$  values at the plateaus were in the range 6.83–10.15 ( $\text{pH}_{\text{PZC}}$ , Table 1), whereas after  $\text{Sr}^{2+}$  sorption final pH values were in the range 6.1–8.8. In all cases, sorption was accompanied by a certain drop of solution pH in comparison with pH values where no specific cation sorption occurred. The differences between  $\text{pH}_{\text{PZC}}$  and final pH values for various bone sorbents,

**Table 1**

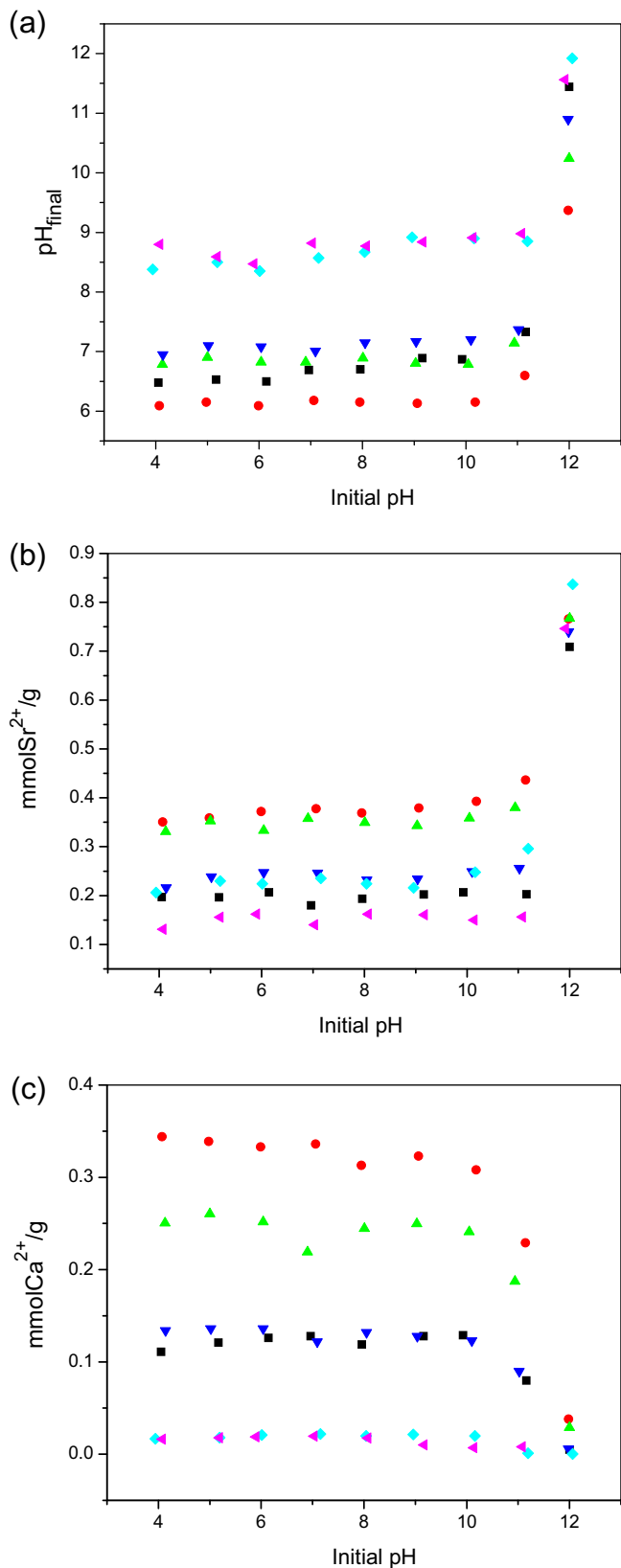
The fraction of crystalline phase, specific surface area and point of zero charge of bone samples (results taken from Ref. [16]).

Sample	B	BH <sub>2</sub> O <sub>2</sub>	B400	B600	B800	B1000
Fraction of crystalline phase (Xc)	0.26	0.27	0.27	0.36	0.93	0.95
Specific surface area (m <sup>2</sup> )	0.1	83.0	85.0	71.7	7.0	2.4
Point of zero charge (pH <sub>PZC</sub> )	7.22	6.83	7.37	7.50	10.15	10.00

**Fig. 1.** SEM micrographs of bone produced sorbents.

decreased in the following way: B800 (1.47) > B1000 (1.20) > BH<sub>2</sub>O<sub>2</sub> (0.71) > B (0.62) > B400 (0.53) > B600 (0.47), sug-

gesting that participation of the specific cation sorption decreased in the same way.



**Fig. 2.** Effect of the initial pH on the: (a) final pH values; (b) amounts of  $\text{Sr}^{2+}$  sorbed; (c) amounts of  $\text{Ca}^{2+}$  released. Sorbents: ■ – B, ● –  $\text{BH}_2\text{O}_2$ , ▲ – B400, ▼ – B600, ◆ – B800, ◀ – B1000.

The rapid final pH increase was observed for initial pH > 10. In these highly alkaline solutions, buffering capacity of bone sorbents

was fully utilized, therefore accumulation of  $\text{OH}^-$  ions and net negative charge occurred at the surface of sorbent materials.

For each sample, sorbed amounts of  $\text{Sr}^{2+}$  (Fig. 2b) were constant in the initial pH range where final pH values were constant as well. On the other hand, for initial pH > 10, along with the rapid increase of final pH, a rapid increase of the amount of  $\text{Sr}^{2+}$  sorbed was detected, due to strong electrostatic attraction forces. A similar pH effect onto  $\text{Sr}^{2+}$  sorption by the synthetic HAP [19] and the commercial bone char [14], was observed.

The amounts of  $\text{Ca}^{2+}$  ions released from the surface of sorbents into the liquid phase (Fig. 2c) followed the general trend: values were relatively constant in the initial pH range 4–10, as a result of stable final pH, whereas decreased at pH > 10. Comparing the amounts of released  $\text{Ca}^{2+}$  ions between different sorbent materials a following trend was observed:  $\text{BH}_2\text{O}_2 > \text{B400} > \text{B600} \geq \text{B} > \text{B800} \geq \text{B1000}$ , indicating that the participation of the ion-exchange mechanism decreased in the same way.

The presented results revealed that changes of pH in the wide range (4–10) caused no significant changes in the  $\text{Sr}^{2+}$  sorption efficiency, due to buffering properties of investigated bone sorbents.

### 3.3. Kinetics of $\text{Sr}^{2+}$ removal

Changes of  $\text{Sr}^{2+}$  sorbed amounts with contact time are presented in Fig. 3a, together with consequent changes of released  $\text{Ca}^{2+}$  amounts (Fig. 3b), and aqueous pH changes (Fig. 3c). It can be observed, that all sorbents under applied experimental conditions, showed a rapid sorption at the beginning of the process, followed by a slower metal uptake and equilibrium at approximately 24 h. However, quantities of metal ion sorbed differed significantly between sorbents (from 0.181 to 0.383 mmol/g, at equilibrium). The affinity of sorbents towards  $\text{Sr}^{2+}$  ion decreased in the order:  $\text{BH}_2\text{O}_2 > \text{B400} > \text{B800} > \text{B} > \text{B1000}$ .

The amounts of  $\text{Ca}^{2+}$ , released per gram of each sorbent, generally increased with time, but these quantities did not fully match the order of samples affinity towards  $\text{Sr}^{2+}$ :  $\text{BH}_2\text{O}_2 > \text{B400} > \text{B600} > \text{B} > \text{B800} \geq \text{B1000}$ . The results suggested different participation of  $\text{Ca}^{2+}/\text{Sr}^{2+}$  ion-exchange process in the overall mechanism of sorption. Solution pH values also increased with time, from initial pH = 5 to equilibrium pH values between 6 and 8. The increase of pH was the most pronounced at the very beginning of the process (first 15 min). On the other hand, all equilibrium pH values were lower than corresponding  $\text{pH}_{\text{PZC}}$  values [16].

The dynamics of the process in terms of the rate constant and the initial sorption rate can be evaluated using sorption kinetic data. The process of  $\text{Sr}^{2+}$  removal from an aqueous phase by different bone sorbents was analyzed using pseudo-second-order mathematical equation [20], which can be expressed in the following linear way:

$$t/q_t = 1/k_2q_e^2 + 1/q_e \cdot t \quad (1)$$

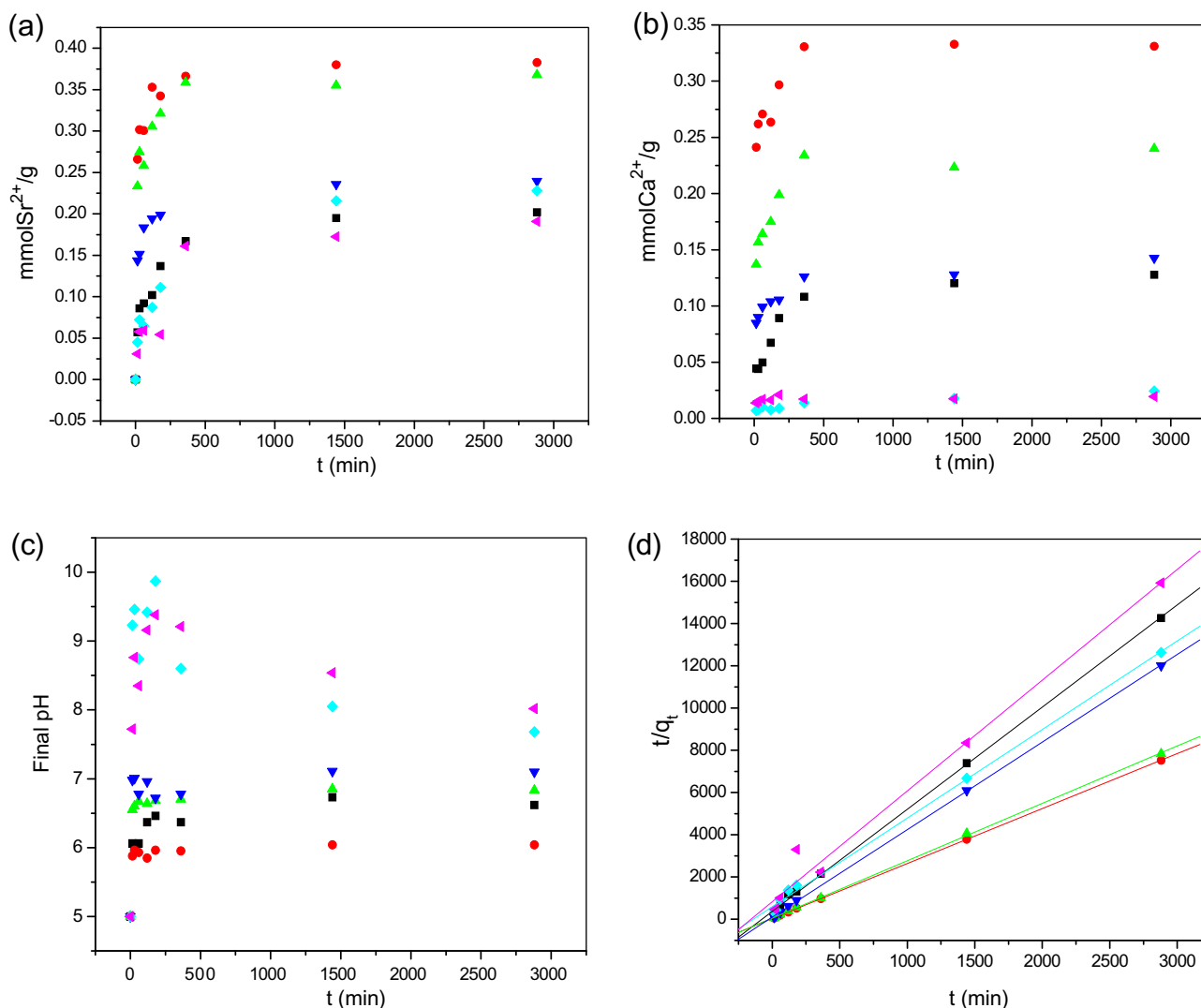
where  $k_2$  (g/mmol min) is the pseudo-second-order rate constant,  $q_e$  (mmol/g) the amount of  $\text{Sr}^{2+}$  sorbed at equilibrium and  $q_t$  (mmol/g) is the amount sorbed at any time  $t$ .

If the functionality  $t/q_t$  vs.  $t$  is linear, the values of rate constant and the amounts sorbed at equilibrium can be calculated from the slope ( $1/q_e$ ) and intercept ( $1/k_2q_e^2$ ) of the line. Furthermore, when  $t \rightarrow 0$ , the initial sorption rate  $h$  (mmol/g min) can be calculated:

$$h = k_2q_e^2 \quad (2)$$

The results of  $\text{Sr}^{2+}$  kinetic data fitting are presented in Fig. 3 d, and Table 2.

The values of  $R^2$  suggested a good correlation between pseudo-second-order equation and obtained experimental data. A good agreement between experimentally determined and calculated  $q_e$



**Fig. 3.** Effect of contact time on the: (a) amounts of Sr<sup>2+</sup> sorbed; (b) amounts of Ca<sup>2+</sup> released; (c) final pH values, and (d) linear data fitting using the pseudo-second-order equation. Sorbents: ■ – B, ● – BH<sub>2</sub>O<sub>2</sub>, ▲ – B400, ▼ – B600, ◆ – B800, ◀ – B1000.

**Table 2**

The parameters of pseudo-second-order kinetic model.

Sorbent	$q_{e,exp}$ (mmol/g)	Pseudo-second-order model			
		$q_e$ (mmol/g)	$k$ (g/mmol min)	$h \times 10^2$ (mmol/g min)	$R^2$
B	0.207	0.207	0.063	0.270	0.999
BH <sub>2</sub> O <sub>2</sub>	0.383	0.384	0.191	2.816	1.000
B400	0.368	0.368	0.132	1.788	0.999
B600	0.240	0.241	0.176	1.022	0.999
B800	0.228	0.238	0.030	0.170	0.972
B1000	0.181	0.191	0.033	0.120	0.985

values was observed as well (Table 2). The highest values of pseudo-second-order rate constant and the initial sorption rate were calculated for sample BH<sub>2</sub>O<sub>2</sub>, signifying its highest efficiency. Powdered bones calcinated at 400 °C exhibited somewhat lower values of kinetic parameters, and comparable Sr<sup>2+</sup> sorption capacity. In the previous study on Co<sup>2+</sup> removal, ion-exchange and specific cation sorption mechanisms were also found to participate in the overall sorption mechanism of investigated bone materials, and the significant correlation of kinetic data with the pseudo-second-order kinetic model was observed [16]. Samples BH<sub>2</sub>O<sub>2</sub> and

B400 were the most efficient sorbents of Co<sup>2+</sup>, as well as of Sr<sup>2+</sup>, however, the absolute values of calculated parameters  $k_2$ ,  $h$  and  $q_e$  were found to be higher for Co<sup>2+</sup>.

### 3.4. Sr<sup>2+</sup> sorption isotherms

Equilibrium isotherms were determined by shaking a fixed mass of powdered bone sorbents with Sr<sup>2+</sup> solutions of increasing concentration at fixed initial pH 5, for 24 h. Differently treated bone samples differ significantly when sorbed amounts of Sr<sup>2+</sup> ions

as a function of equilibrium  $\text{Sr}^{2+}$  concentration are compared (Fig. 4a).

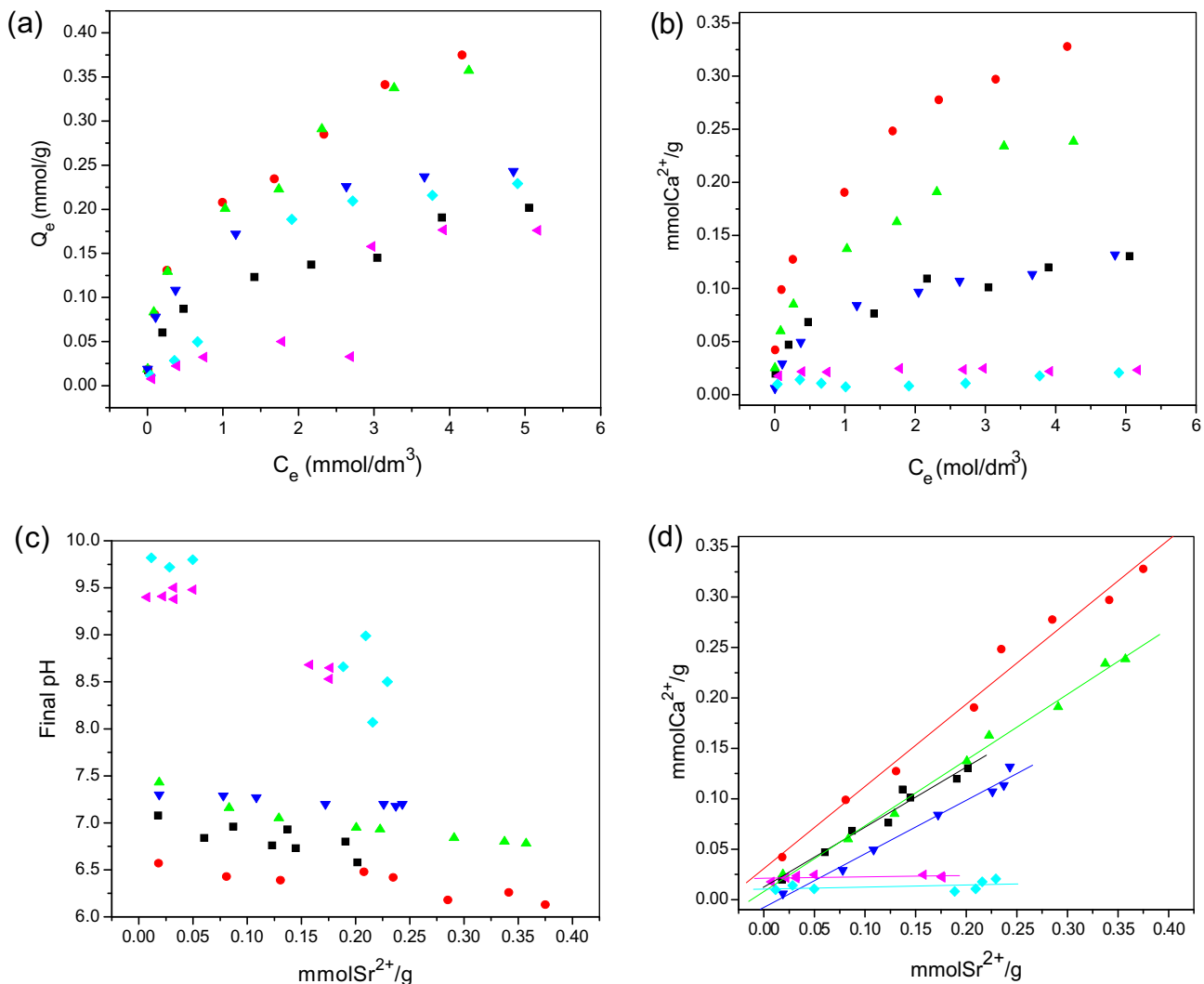
According to Giles et al. [21] the obtained  $\text{Sr}^{2+}$  sorption isotherms can be classified based on their initial slopes and curvatures as Langmuir type (L) for samples B,  $\text{BH}_2\text{O}_2$ , B400 and B600. The ratio between the concentration of the ions remaining in the solution and that sorbed on the solid phases decreased when the sorbate concentration increased, providing a concave curve and suggesting a progressive saturation of the solid. On the other hand, sigmoidal-shape (S) was characteristic for B800 and B1000 isotherms. The S-curve has a point of inflection which can be a result of at least two opposite mechanisms [22].

The amounts of  $\text{Ca}^{2+}$  ions released from the surface of sorbents B,  $\text{BH}_2\text{O}_2$ , B400 and B600 increased along with the increase of  $\text{Sr}^{2+}$  sorbed amounts (Fig. 4b). In contrast, samples B800 and B1000 exhibited minor and rather constants values of  $\text{Ca}^{2+}$  released per gram of sorbent. The results also show (Fig. 4d) that, with an exception of sample  $\text{BH}_2\text{O}_2$ , the  $\text{Ca}^{2+}/\text{Sr}^{2+}$  molar ratios were  $<1$ . This trend leads us to a conclusion that the ion-exchange mechanism is less apparent in the bone sorbents removal mechanism than in the mechanism characteristic for synthetic HAP-powders [16], which can be generally explained by: (i)  $\text{Sr}^{2+}$  bonding at the bone organic phase active centers, (ii) high final pH values leading to increased

apatite phase stability and (iii) presence of structural cations other than  $\text{Ca}^{2+}$  that can be substituted by  $\text{Sr}^{2+}$  ions. The final pH values generally decreased with the increase of  $\text{Sr}^{2+}$  sorbed amounts (Fig. 4c), signifying the specific  $\text{Sr}^{2+}$  sorption, in all investigated systems. Furthermore, this mechanism was the most obvious in the case of samples B800 and B1000. XRD analysis of solid residues obtained after  $\text{Sr}^{2+}$  fixation (Fig. 5) provided no evidence of any new solid phase formation. For the purpose of comparison, XRD spectra of pure, synthetic hydroxyapatite [23], is given in the same picture.

Extremely high pH values measured after equilibration of B800 and B1000 samples with  $\text{Sr}^{2+}$  solutions (Fig. 4c) may be a potential reason for sigmoidal-shaped  $\text{Sr}^{2+}$  sorption isotherms.

By definition, S-curve isotherms indicate a change of sorption mechanism in the point of inflection. Although the sorbed amounts of  $\text{Sr}^{2+}$  and final pH values, divided into two separate regions for lower and higher sorbate concentrations, support the concept of sorption mechanism alteration, clear evidence was found only for the specific cation sorption mechanism. The possibility of formation of new solid phases containing  $\text{Sr}^{2+}$  ions, as another sorption mechanism, cannot be excluded, due to the fact that amorphous phases and very low concentrations of crystalline phases cannot be detected by XRD analysis [24].



**Fig. 4.** Effect of equilibrium  $\text{Sr}^{2+}$  concentrations on the (a) amounts of  $\text{Sr}^{2+}$  sorbed and (b) amounts of  $\text{Ca}^{2+}$  released. Relationships between the amounts of  $\text{Sr}^{2+}$  sorbed and (c) final pH values; (d) amounts of  $\text{Ca}^{2+}$  released (solid lines represent linear fitting). Sorbents: ■ – B, ● –  $\text{BH}_2\text{O}_2$ , ▲ – B400, ▼ – B600, ◆ – B800, ◀ – B1000.

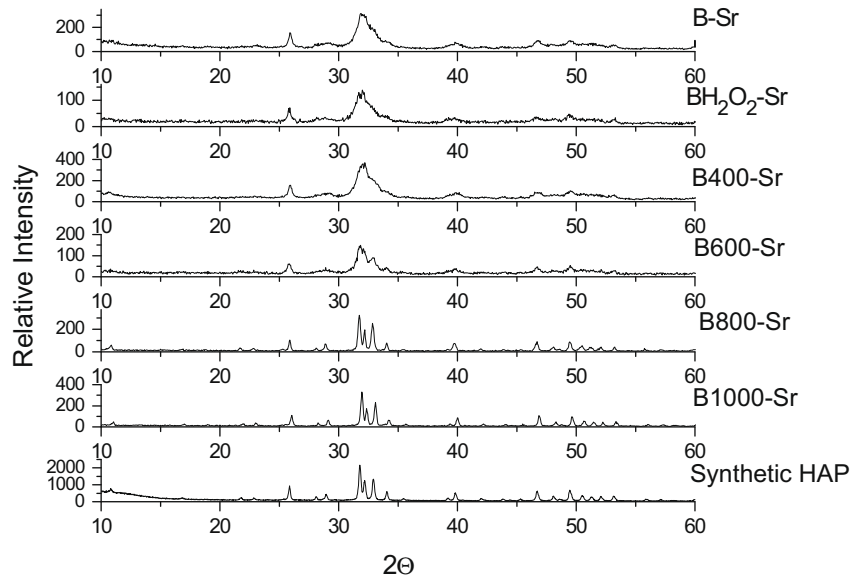


Fig. 5. XRD patterns of  $\text{Sr}^{2+}$ -loaded bone sorbents and synthetic HAP [23].

Obtained experimental data were analyzed in accordance with Freundlich (Eq. (3)) [25] and Langmuir (Eq. (4)) [26] isotherm equations, which are the most commonly used for description of L-type isotherms. In addition, sigmoidal Langmuir equation (Eq. (5)) [22] was applied for S-type isotherms.

$$\log Q_e = \log K + 1/n \cdot \log C_e \quad (3)$$

$$\frac{C_e}{Q_e} = \frac{1}{X_m \cdot K_L} + \frac{1}{X_m} \cdot C_e \quad (4)$$

$$Q_e = \frac{X_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e + \frac{C_e}{S}} \quad (5)$$

In the above presented equations  $Q_e$  (mmol/g) represents the quantity of metal ions sorbed per mass of bone sorbents;  $C_e$  (mmol/dm<sup>3</sup>) is the equilibrium  $\text{Sr}^{2+}$  concentration in solution;  $X_m$  (mmol/g) is the maximum sorption capacity of metal cation;  $K_L$  (dm<sup>3</sup>/mmol) is the Langmuir constant related to affinity;  $S$  (mmol/dm<sup>3</sup>) is the constant related to the limitation of sorption at low concentrations and  $K$  and  $n$  are Freundlich constants related to sorption capacity and intensity, respectively.

The results of equilibrium data fitting are summarized in Table 3, whereas the graphical representation of data fitting is shown in Fig. 6. Generally, Freundlich empirical model provided

better correlation with experimental data in comparison to Langmuir. Both previously described models did not correctly describe the results obtained for B800 and B1000 samples. The values of  $X_m$ , predicted by Langmuir model were 60–70% higher than experimentally derived values. However, reasonably good correlation, with more realistic  $X_m$  values, was obtained when sigmoidal Langmuir model was used (Table 3).

Sorption capacities of the investigated samples, decreased in the way:  $\text{BH}_2\text{O}_2 > \text{B400} > \text{BC} > \text{B600} > \text{B800} > \text{B} > \text{B1000}$ , in accordance with the decrease of  $q_e$  values determined from the kinetic data. The amounts of  $\text{Sr}^{2+}$  sorbed at equilibrium increased from 0.176 to 0.357 mmol/g with the increase of the sorbents specific surface area. Sample B was the exception, showing the moderate capacity of 0.202 mmol/g and the lowest Sp. Its organic matter contains polar and negatively charged functional groups [16] that may serve as potential active centers for  $\text{Sr}^{2+}$  ions.

In Fig. 7 the relationships between heating temperature, sorbents Sp values and the experimentally determined  $X_m$  values ( $X_{m,exp}$ ), are illustrated. Heating at 400 °C preserved the low apatite crystallinity, and provoked specific surface area increase due to a partial organic phase removal from the pores of skeletal material [16]. Although organic matter was completely removed at  $T > 600$  °C, these high temperatures also lead to fusion of apatite nanocrystals, and a consequent Sp and sorption capacity drop. The effect of chemical oxidation ( $\text{H}_2\text{O}_2$  treatment) on the bone

Table 3

Equilibrium parameters of  $\text{Sr}^{2+}$  removal by various bone sorbents obtained using Langmuir, sigmoidal Langmuir and Freundlich equation.

Sorbent	$X_{m,exp}$ (mmol/g)	Langmuir model			Freundlich model		
		$X_m$ (mmol/g)	$K_L$ (dm <sup>3</sup> /mmol)	$R^2$	$K$	$N$	$R^2$
B	0.202	0.209	1.509	0.943	0.107	0.383	0.993
$\text{BH}_2\text{O}_2$	0.375	0.393	1.742	0.949	0.204	0.457	0.988
B400	0.357	0.376	1.876	0.947	0.201	0.422	0.989
B600	0.243	0.257	3.012	0.992	0.153	0.369	0.990
B800	0.229	0.398	0.318	0.682	0.086	0.696	0.950
B1000	0.176	0.288	0.130	0.242	0.044	0.692	0.821
<i>Sigmoidal Langmuir model</i>							
Sorbent	$S$ (mmol/dm <sup>3</sup> )	$X_m$ (mmol/g)	$K_L$ (dm <sup>3</sup> /mmol)	$R^2$			
B800	42.86	0.229	42.11	0.981			
B1000	38.10	0.200	9.974	0.918			

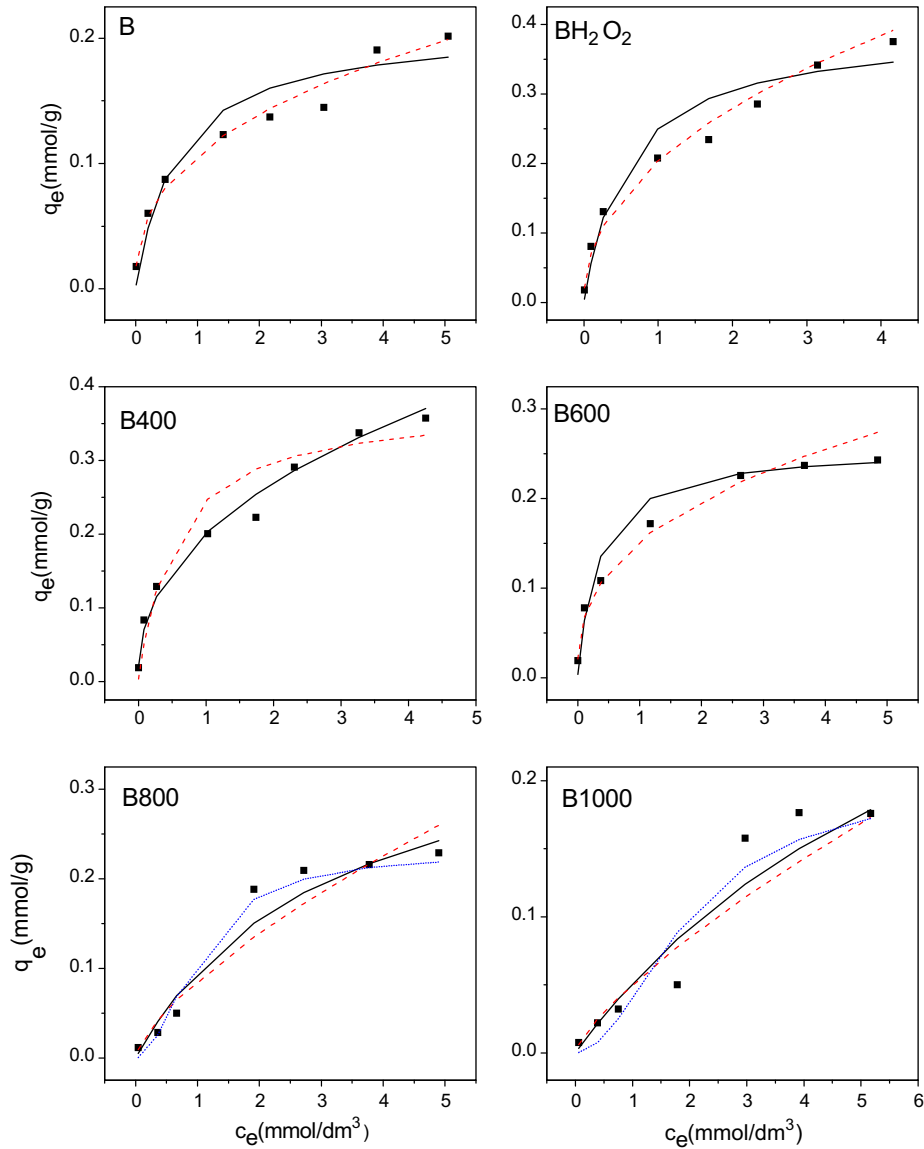


Fig. 6. Equilibrium data fitting. Experimental points (■), Langmuir model (—), Freundlich model (---) and sigmoidal Langmuir model (...).

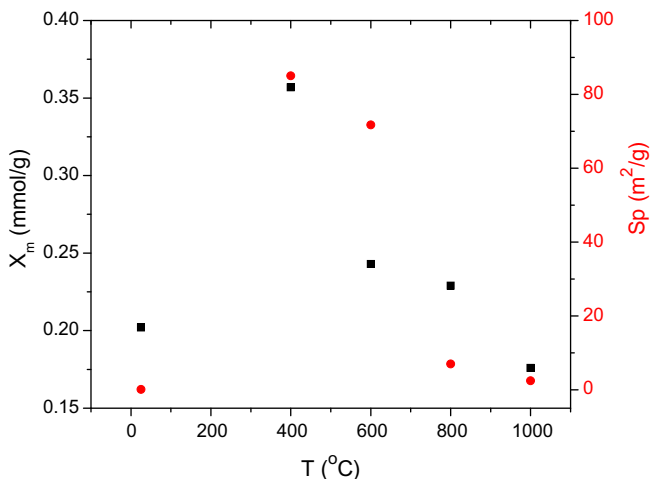


Fig. 7. Correlation between treatment temperature, specific surface area of sorbent materials (●) and  $\text{Sr}^{2+}$  sorption capacities (■).

specific surface area and sorption properties was pretty much the same as heating at 400 °C. These two sorbent materials exhibited sorption capacities higher than those of commercial bone char [14] and of the range of synthetic hydroxyapatite powders [27].

### 3.5. Desorption

A strong dependence of the amounts of  $\text{Sr}^{2+}$  released on both the sorbent type and the leaching solution composition was observed (Fig. 8). Generally, investigated materials were more stable in neutral and alkaline solutions than in acidic and  $\text{Ca}^{2+}$  containing environments. This can be attributed to the low apatite stability in acidic pH region, leading to dissolution and release of previously sorbed metal cations, as well as to the ion-exchange of sorbed cations with  $\text{Ca}^{2+}$ . The major difference between desorption of  $\text{Sr}^{2+}$  and other divalent metals (such as  $\text{Co}^{2+}$  [16,28] or  $\text{Cu}^{2+}$  [29]) from apatite based sorbents was that more  $\text{Sr}^{2+}$  was released in  $\text{Ca}^{2+}$  solutions than in acidic media. These data suggested that the competition for active surface sites was more pronounced between



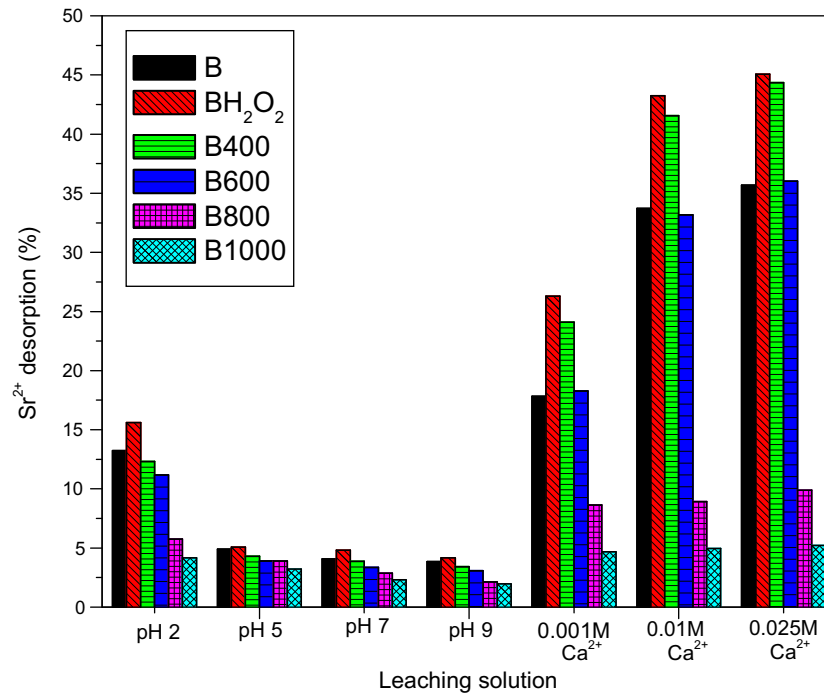


Fig. 8. Relative percentages of Sr<sup>2+</sup> ions desorbed as a function of leaching solutions composition.

**Table 4**  
Solution pH values after Sr<sup>2+</sup> desorption.

No.	Composition	Initial pH	Final pH					
			B	BH <sub>2</sub> O <sub>2</sub>	B400	B600	B800	B1000
1	Distilled water	2.00	4.87	4.70	5.03	5.12	5.12	5.18
2	Distilled water	5.00	7.12	6.83	7.25	7.36	8.09	8.35
3	Distilled water	7.00	7.20	6.92	7.29	7.47	8.27	8.45
4	Distilled water	9.00	7.27	6.90	7.36	7.53	8.33	8.55
5	Ca <sup>2+</sup> 10 <sup>-3</sup> mol/dm <sup>3</sup>	5.55	6.74	6.22	6.84	6.95	7.65	8.08
6	Ca <sup>2+</sup> 10 <sup>-2</sup> mol/dm <sup>3</sup>	5.49	6.58	5.98	6.71	6.86	7.53	7.91
7	Ca <sup>2+</sup> 2.5 × 10 <sup>-2</sup> mol/dm <sup>3</sup>	5.36	6.42	5.75	6.54	6.63	7.13	7.79

chemically similar Ca<sup>2+</sup> and Sr<sup>2+</sup> ions than between Ca<sup>2+</sup> and other investigated divalent metals. Similar conclusions were derived from the fact that Sr<sup>2+</sup> sorption by synthetic hydroxyapatite, in comparison with the sorption of some other divalent metals, was the most affected by the presence of Ca<sup>2+</sup> [19]. In the most acidic solution applied in this study (initial pH 2), sorbents BH<sub>2</sub>O<sub>2</sub> and B released the highest amounts of Sr<sup>2+</sup> ions, in comparison with the previously sorbed amounts, which can be related to the lowest final pH values (Table 4).

When the solutions of initial pH 5, 7 and 9 were compared as leaching media, no significant differences in the amounts of desorbed Sr<sup>2+</sup> were observed for each sorbent, due to buffering properties of investigated materials, and relatively constant final pH values (Table 4).

Furthermore, it can be observed from Fig. 8, that the differences between desorbed amounts of Sr<sup>2+</sup> from various bone sorbents are more obvious in Ca<sup>2+</sup> solutions than in solutions of different initial pH. Sr<sup>2+</sup>-loaded BH<sub>2</sub>O<sub>2</sub> and B400 samples exhibited lowest stability in the presence of competing cation Ca<sup>2+</sup>, which is in accordance with the previously observed highest participation of the ion-exchange mechanism (Fig. 4b and d).

The bonds between high temperature heated powders B800 and B1000 and Sr<sup>2+</sup> ions, have shown the highest stability in all inves-

tigated leaching media, and this was probably the result of the highest final pH values (Table 4) which increased the stability of apatite phase.

#### 4. Conclusion

Animal bones, which represent a rich source of low-crystalline hydroxyapatite, were examined as sorbent material for Sr<sup>2+</sup> ions immobilization. Calcinations at different temperatures, as well as chemical oxidation, were compared as possible treatments for the improvement of their sorption capacity. Removal of organic bone components under conditions that secure low hydroxyapatite crystallinity (heating at 400 °C, and H<sub>2</sub>O<sub>2</sub> oxidation) caused the significant increase of sorbents specific surface area and, consequently, the increase of the overall Sr<sup>2+</sup> sorption capacity. At least ion-exchange and specific cation sorption mechanisms were responsible for Sr<sup>2+</sup> removal by animal bones, with relative contributions dependent on the physicochemical properties of investigated sorbents. Desorption of Sr<sup>2+</sup> ions was generally the most effective in Ca<sup>2+</sup> containing solutions, where 55–95% of previously sorbed Sr<sup>2+</sup> ions remained attached to bone sorbents. These results suggested that further immobilization of spent animal bones is more realistic than their regeneration.

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