

# Calcium alginate and chitosan as potential sorbents for strontium radionuclide

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**Abstract** This work reports the adsorption of strontium(II) from aqueous solutions onto calcium alginate (CA) and chitosan (CH) materials. The adsorption process was studied in batch experiments as a function of the pH of the solution, contact time, and temperature. Freundlich isotherm was found to describe the sorption process comparatively well as the Langmuir model. Laboratory obtained spherical beads of CA seems to be a better sorbent than commercially available materials. A contact time of about 4 h and neutral pH of the initial aqueous solution seem to be optimal conditions for Sr-85 to be removed from contaminated solutions using alginate beads.

**Keywords** Water treatment · Calcium alginate · Chitosan · Strontium-85 · Adsorption · Isotherm

## Introduction

One of the most hazardous radionuclides present in low- and medium-level radioactive wastes (LLW and MLW, respectively) is strontium-90 (Sr-90;  $t_{1/2}$  28.9 years;  $E_{\beta}$  546 keV). Its danger is caused by the long biological half-life of Sr-90 (49.3 years) and the element's chemical similarity to calcium, which implies that it is capable

accumulate in bone tissues. In addition, Sr-89 ( $t_{1/2}$  50.6 days;  $E_{\beta}$  1,495 keV), which in the form of chloride appears to be useful in nuclear medicine for the treatment of bone cancer, and certain compounds of Sr-85 ( $t_{1/2}$  64.8 days;  $E_{\gamma}$  514 keV), used in nuclear medicine as bone imaging agents, may be found in LLW and MLW [1–3].

Different techniques have been used to remove both radionuclides of strontium from aqueous samples and water streams, such as ion-exchange [4, 5], reverse osmosis [6], precipitation [7–9], or electrochemical treatment [10]. However, their routine application is limited both by the high operational cost and production of great amounts of slurries.

Among the main alternative methods, the accumulation of strontium onto inexpensive solid materials of biological origin should be mentioned [11–16]. The carbohydrate polymers: calcium alginate (CA) and chitosan (CH) are two of the most popular biosorbents (Fig. 1).

The aim of the present study was to examine both of the aforementioned biopolymers' usefulness in the removal of strontium radionuclides from aqueous waste solutions. In particular, two types of CA and CH were studied. Sr-85 radionuclide was applied because of the excellent energy of emitted gamma radiation, which implies easy determination of the radionuclide content in the analyzed solutions. This radionuclide is often used to study the condition of bones in the human bodies.

## Experimental

### Chemicals

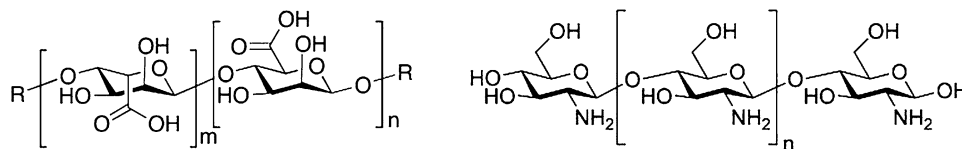
Sodium alginate and alginic acid calcium salt (purum), both powders, came from SIGMA-ALDRICH. Chitosan

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**Fig. 1** Formulas of the polymers of the alginic acid (left) and of chitosan (right)



(molecular weight 100,000; acetylated form) was purchased from ACROS ORGANICS. All inorganic chemicals used in the experiments were purchased from SIGMA-ALDRICH. The solutions were prepared in deionized water with electrical conductivity lower than  $10 \mu\text{S cm}^{-1}$  at  $25^\circ\text{C}$ .

A carrier-free radionuclide of Sr-85 was supplied from Radioisotope Centre POLATOM, National Centre for Nuclear Research (Świerk, Poland).

CA spherical beads were prepared by dropping 0.5 M of  $\text{CaCl}_2$  aqueous solution into a 4 % w/w solution of sodium alginate in water with continuously stirring it at room temperature. The final solution was left to stand for additional 24 h. Grains of the sorbent (ca. 3 mm in the diameter) were stored in a solution containing 0.01 M of KCl and 0.001 M of  $\text{CaCl}_2$ . Before application, CA beads were rinsed carefully with a large amount of the deionized water.

### Sorption experiments

The sorption of Sr(II) was studied as a function of the contact time, initial pH, and temperature in separate experiments. About 0.1 g of each sorbent was added to 2.0 mL of strontium aqueous solution (in polyethylene vials) and shaken in the thermostatic shaker at a temperature of 10, 25, or  $50^\circ\text{C}$  respectively. In all experiments, except those of time dependence, solid sorbents had contact with the liquid phase for 4 h. The initial concentration of Sr(II) radionuclide in the solutions was kept  $\sim 100 \text{ kBq mL}^{-1}$  and has been determined radiometrically, simultaneously with the equilibrium concentrations.

Because of the low Sr(II) initial concentration, it is practical to present the results in terms of the distribution coefficient ( $K_d$ ):

$$K_d = (C_2/C_1) \cdot (V/W) = (C_0 - C_1) \cdot V / C_1 \cdot W \quad (1)$$

where  $C_2$ ,  $C_1$ , and  $C_0$  are the concentrations ( $\text{kBq mL}^{-1}$ ) of Sr(II) on the sorbent, residual Sr(II) concentration in the equilibrium solution, and in the initial bulk solution, respectively. Factor  $V$  is the volume of the aqueous phase (mL) and  $W$  is weight of the sorbent (g).

This term describes the ratio of the total analytical concentration of a substance in the sorbent to its total analytical contents in the aqueous phase in equilibrium [17].

In each experiment, the mean value of  $K_d$  was estimated from triplicate measurements.

### Sorption isotherms

Studies were carried out in the batch mode experiments as described above. A series of experiments was carried out with aqueous phases containing well-defined initial concentrations of the radionuclide in the  $nca$  scale. The range of the concentrations was expressed in  $\text{kBq}$  and raised from  $\sim 53$  up to  $\sim 425 \text{ kBq mL}^{-1}$ . Initial and equilibrium samples of Sr-85 were analyzed in an automatic well-type gamma ray detector ( $E_\gamma = 514 \text{ keV}$ ) after its calibration in a gamma radiation calibrator.

The linearized form of the equations used were:

$$\text{Freundlich equation : } \log(q) = \log(k) + (1/n) \cdot \log(C_e) \quad (2)$$

where  $q$  is the equilibrium metal uptake capacity and  $C_e$  the residual metal concentration at equilibrium. The constant  $k$  is a measure of the adsorption capacity and  $1/n$  is the intensity of adsorption.

$$\begin{aligned} \text{Langmuir equation : } 1/q &= 1/(q_{\max} \cdot b) \cdot (1/c_e) + (1/q_{\max}) \end{aligned} \quad (3)$$

The constant  $q_{\max}$  represents the maximum specific metal uptake and  $b$  is the ratio of the adsorption/desorption rates related the adsorption energy through the Arrhenius equation.

### Chemical equilibrium diagrams

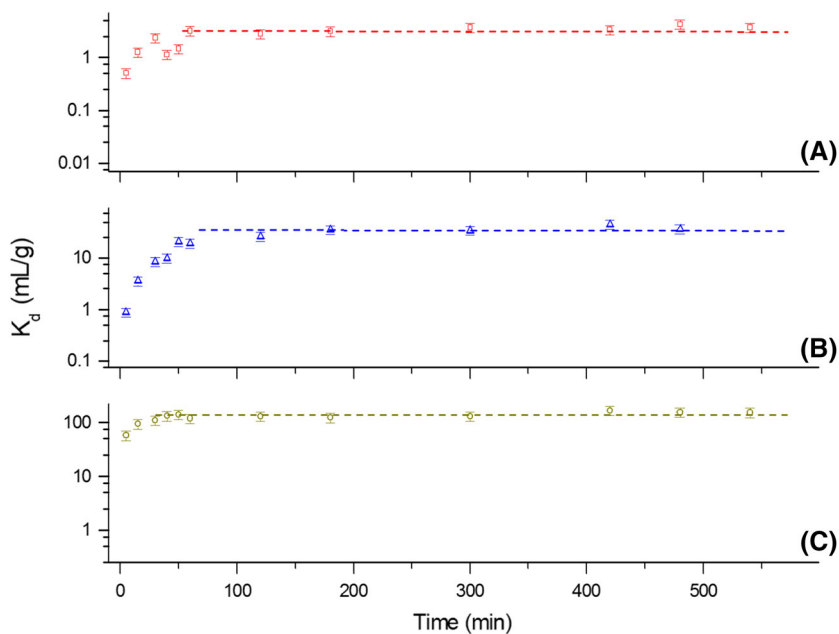
The calculations done by Hydra-Medusa Software (Make Equilibrium Diagrams Using Sophisticated Algorithms [18]) were performed to create chemical equilibrium diagrams.

## Results and discussion

### Kinetics of sorption

Figure 2 shows the time profiles of the strontium(II) sorption onto both studied types of CA and (CH). As it can be seen, adsorption of Sr(II) on all examined sorbents was quick and the equilibrium was reached already after 1 h.

**Fig. 2** Influence of contact time on the  $K_d$  of the solutions containing strontium(II); temp. 25 °C: **a** open square box calcium alginate beads, **b** open rectangular box chitosan, pH 5.6, and **c** open circle commercial calcium alginate



After this time sorption is independent from the contact time of equilibrated phases. In detail, the decontamination factors (DF = radiation activity before sorption/radiation level after sorption) at a pH of 5.6 and a temperature of 25 °C are:  $139 \pm 15$  (commercial alginate),  $3.91 \pm 0.77$  (alginate beads), and  $36.6 \pm 4.9$  (chitosan), respectively. Based on these results, in further experiments it was chosen to contact solid sorbents with the liquid phase for 4–6 h.

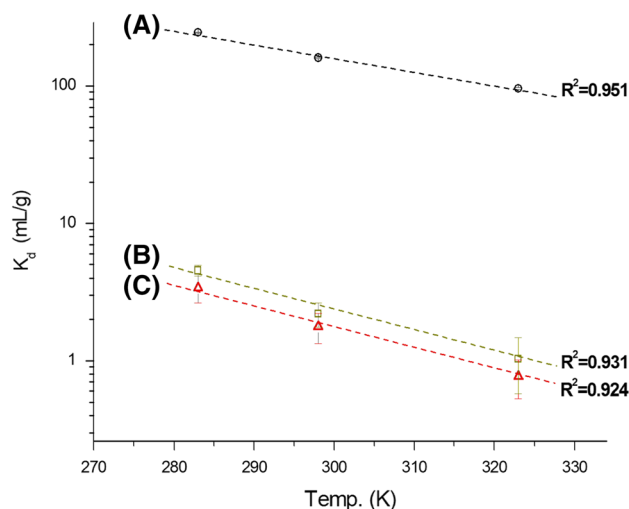
**Effect of temperature**

In order to evaluate the effect of the temperature on strontium removal, thermodynamic parameters such as enthalpy ( $\Delta H^0$ ), entropy ( $\Delta S^0$ ), and Gibbs free energy ( $\Delta G^0$ ) were investigated. Therefore, the sorption of Sr(II) on all sorbents at 10, 25, and 50 °C was studied, and results are shown in Fig. 3.

To estimate the thermodynamic functions, the relationship was used [19].

$$\Delta G^0 = -2.303RT \log K_d = -\Delta H^0 + T\Delta S^0 \quad (4)$$

where terms  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$  have the meaning shown above. T stands for the temperature (°K) and R for the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ). The linear representation of  $\log K_d$  as a function of temperature provides the values of enthalpy and entropy change from the slope and intercept of the plots (see Fig. 3). Their values are tabulated in Table 1 and contain terms due to temperature changes in the activity coefficients of the species involved. Assuming that these changes are similar for the solutions of Sr(II) in



**Fig. 3** Effect of temperature on the sorption equilibrium of carrier-free Sr(II) in the temperature range 283–323 K; (A) open circle commercial calcium alginate, (B) open square box calcium alginate beads, and (C) open rectangular box chitosan

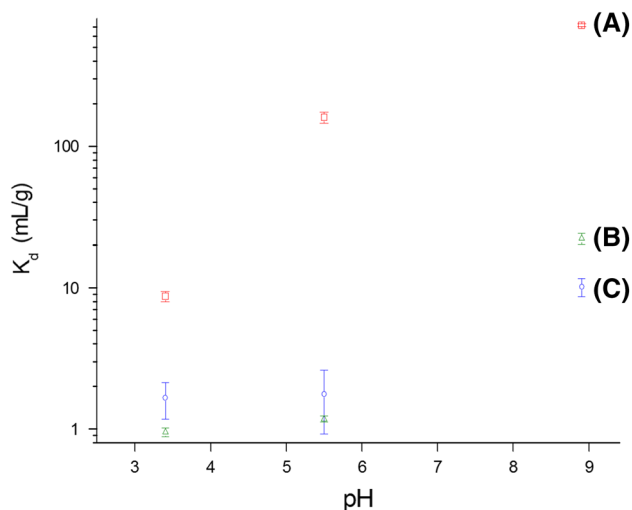
all of the systems studied, the enthalpy and entropy of sorption can be compared.

As seen in Fig. 3, the plots of  $\log K_d$  in the function of temperature are linear. Changes in the standard free energy increase with increasing temperatures regardless of the type of sorbent. This indicates that better adsorption is actually obtained at higher temperatures. The free energy of the process at all temperatures is negative and changes with the rise in temperature. The negative values of  $\Delta G^0$  at all temperatures studied are due to the fact that the adsorption process is spontaneous (does not require the

**Table 1** Thermodynamic data for sorption of Sr(II) by commercial calcium alginate, calcium alginate beads, and chitosan (RT)

Thermodynamic function	Ca-Alg	Chitosan	Alginate beads
$\Delta G_{25} \pm SD_G$ (kJ mol <sup>-1</sup> )	$-12.57 \pm 0.59$	$-1.41 \pm 0.79$	$-1.95 \pm 0.07$
$\Delta H \pm SD_H$ (kJ mol <sup>-1</sup> )	$-17.70 \pm 0.94$	$-27.09 \pm 0.44$	$-27.78 \pm 2.60$
$\Delta S \pm SD_S$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$16.96 \pm 3.13$	$85.99 \pm 1.46$	$85.94 \pm 8.61$

Standard deviation from the mean (the square root of the sum of the squares of the differences between each value and the average, divided by one less than the number of measurements) calculated for the triplicate independent experiments



**Fig. 4** Effect of initial pH on the sorption of carrier-free Sr(II); (A) open square box commercial calcium alginate, (B) open rectangular box calcium alginate beads, and (C) open circle chitosan

delivery of the energy). The positive value of  $\Delta S^0$  suggests increased randomness at the solid and solution interface during the adsorption of metal ions onto adsorbent [20]. The negative values of  $\Delta H^0$  indicate the exothermic nature of the adsorption process.

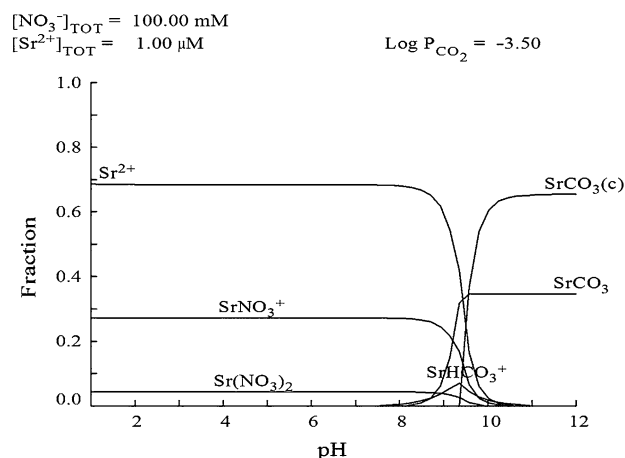
#### Effect of initial pH

The results obtained for strontium(II) sorption for the initial pH ranging from 3 to 9 are illustrated in Fig. 4.

As seen from the Fig. 4, sorption of strontium(II) on all sorbents strongly depends on the initial pH of the solution and raises with an increasing pH as high as 8–9. Furthermore, the distribution coefficients for commercial CA exceed these for CH and CA beads.

The sorption of any metal ion as a function of the initial pH, as a rule, is a complex process. Different forms of metal present in the solution, hydrolyzed and complexed, should also be taken into account. Different forms of the sorbent surface may influence the process as well.

The chemical equilibrium calculation shows that content of the Sr(II) species remains nearly constant in the pH region of 1–9 (Fig. 5).  $\text{SrHCO}_3^+$  and  $\text{SrCO}_3$  (formed with



**Fig. 5** Speciation of strontium in aqueous  $\text{SrCl}_2$  solutions, calculated by means of the Hydra-Medusa software. Total strontium concentration  $10^{-6}$  mol L<sup>-1</sup>, nitrate concentration  $0.1$  mol L<sup>-1</sup>

carbon dioxide present in the air) start to appear at pH of above 8.5. These species are not highly soluble in water (e.g.,  $\text{SrCO}_3$  ca  $4 \times 10^{-5}$  mol L<sup>-1</sup> [21]), so their appearance in solutions of pH higher than 8 containing microamounts of Sr(II) should be taken into account.

On the other hand, the ionization state of functional groups present in the surface region of the sorbents is also highly dependent on pH. It is known from the literature that carboxyl groups in biomass play an important role in metal sequestration, and they are responsible for a major fraction of metal immobilization [11]. The  $pK_a$  value of a carboxylic group existing in biomass varies from about 2 to 4.7 [11]; therefore, at a pH of around 4.5, the extent of its dissociation should roughly approach 50%. Besides, in acidic solutions the majority of amine surface groups in CH may be protonated, inducing less of a negative charge than in the basic conditions<sup>1</sup>; hence, in acidic solutions, their

<sup>1</sup> Appropriate theoretical calculations were carried out by using the SPARTAN 2008 program [22] running on the PC. Geometry optimization and calculation of the atomic charges in the D-glucosamine and N-acetyl-D-glucosamine were performed at the Hartree-Fock level within the model UHF/3-21G(\*). In particular, Natural Atomic Charges of the amine group decrease from  $-0.9246$  and  $-0.7600$  to  $-0.2870$  and  $-0.3280$  in the D-glucosamine and N-acetyl-D-glucosamine, respectively.

interactions with positively charged strontium(II) species are not favored by electrostatic forces.

Sorption isotherms

The adsorption isotherm equation is a description of the processes governing the sorption of a substance from the aqueous environment to a solid phase at well-defined conditions (temperature and pH). The parameters of these equations express the surface properties of the sorbent and its affinity toward the sorbed species. Thus, such a mathematical description is necessary for the design of future sorption systems. Over the years, a wide variety of equilibrium isotherm models have been formulated. All of them are listed and discussed in paper [23], which provides also their linear forms and coordinates used for the diagrams' construction.

Until now, for the two parameter isotherms (e.g. Langmuir or Freundlich), the accuracy of the fit of an isotherm to experimental equilibrium data has been based on the magnitude of the coefficient of determination for the linear regression. This means that the isotherm giving an  $R^2$  value closest to unity was believed to provide the best fit.

The sorption data were analyzed according to the linear forms of the Langmuir and Freundlich models. Illustration of the plots is shown in Fig. 6 and the linear isotherm constants -  $b$ ,  $q_m$ ,  $\log(K_f)$  and  $1/n_f$  - are presented in Table 2. All isotherms were found to be linear over the whole range of studied concentrations. The  $R^2$  values compared for both models applied for description of each system suggest that both isotherms offer equally good modelling. So, it may be justified to conclude that both physical and chemical mechanisms of strontium(II) sorption have their contribution to the overall process in the *nca* scale.

Evaluation of the thermal stability of sorbents

The thermogravimetric (TGA) data (Fig. 7) for all studied sorbents showed a sharp reduction in weight at the temperatures lower than  $\sim 300$  °C. However, thermal decomposition of spherical CA beads occurs at much lower temperatures than of the as-received sorbents. The samples' weight loss to 25 wt% was detected at 156, 545, and 762 °C for the CA beads, commercial chitosan, and commercial CA, respectively. It should be noted that for the sodium alginate (being the substrate), the sample weight to 25 wt% occurs at about 680 °C [24]. The total weight loss curves for both as-received sorbents show three sharply decreasing parts, which may be attributed to the liberation of the adsorbed water and decomposition of the sorbents [25]. It seems that synthesized spherical CA beads at the same time loose water and decompose to the  $\text{CaCO}_3$  in the temperature below 200 °C.

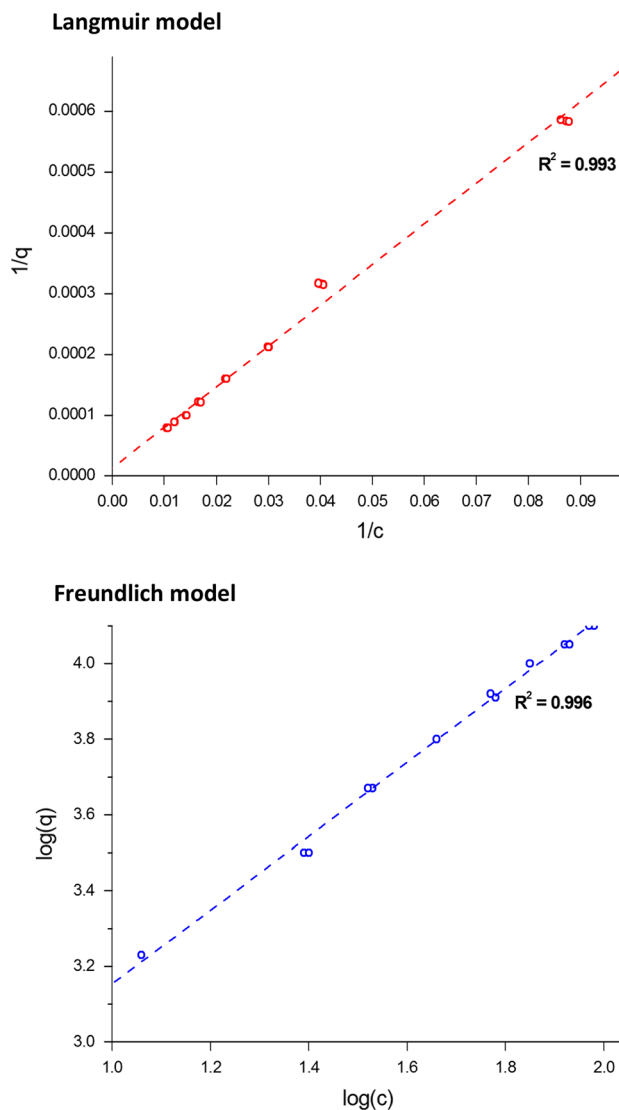
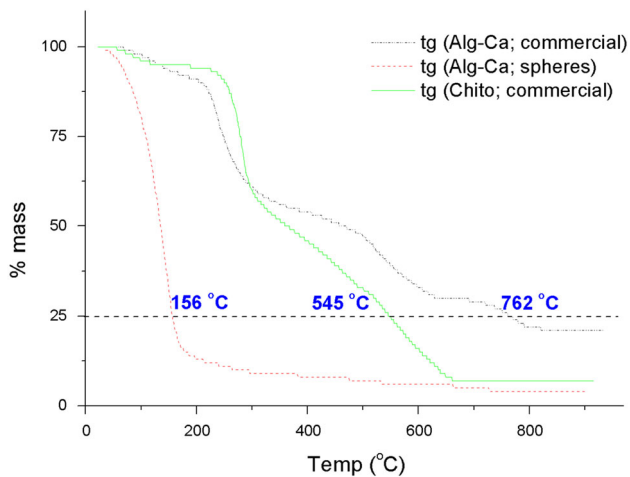


Fig. 6 The Langmuir and Freundlich models presented in their linear forms for Sr(II) sorption on the chitosan

Table 2 Key parameters reflecting the sorption mechanism obtained by using the Langmuir and Freundlich models for the three beads studied; concentration of Sr-85 is given in kBq/g, while the mass of the sorbent and the solution—in grams

	Commercial CA	Commercial CH	CA beads
Langmuir model			
$q_m$ (kBq/g)	$2.50 \times 10^6$	$1.00 \times 10^5$	$3.33 \times 10^4$
$b$ (L/kBq)	$2.32 \times 10^{-9}$	$6.7 \times 10^{-8}$	$4.8 \times 10^{-8}$
$R^2$	0.9991	0.9928	0.9776
Freundlich model			
$\log(K_f)$	2.2398	2.1828	2.7070
$1/n_f$	0.9966	0.9958	1.1603
$R^2$	0.9965	0.9958	0.9641



**Fig. 7** TGA curves of the studied sorbents

## Conclusions

Laboratory obtained beads of CA seem to be a better sorbent than commercially available materials. They are the most effective in strontium(II) adsorption potentially present in aqueous solutions and decompose at lower temperatures giving the opportunity to burn at low temperature of sorbed wastes and by this lower their volume for further long-term disposal. The TGA properties of this material show that pretreatment of the radioactive wastes containing strontium immobilized on the spherical CA beads requires less energy input than on the as-received sorbents.

A contact time of about 4 h and neutral pH of the initial aqueous solution seems to be the optimum conditions for Sr-85 to be removed from contaminated solutions using alginate beads.

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