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ORIGINAL PAPER

Removal of yttrium (III) ions from water solutions by alginate compounds

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Abstract The presence of radioactive substances in wastewaters poses a problem for public health due to the lack of the radioisotope-binding materials. In the present study, the yttrium-binding activity of sodium and calcium salts of alginic acid was investigated in a batch sorption system. The results showed that both polymers are able to form complexes with yttrium ions. The effects of contact time, initial concentration of the metal and pH of the media on the yttrium-binding processes were experimentally investigated. The equilibrium time was found to be at least 60 min required for adsorption of yttrium by alginate compounds regardless of the initial metal concentrations. Langmuir and Freundlich sorption models were applied for description of the binding processes. The results showed that the Langmuir model is best fit within the whole range of pH values used in the studies. The maximum adsorption capacity of calcium and sodium alginates was found to be 99.01 and 181.81 mg/g, respectively, at pH 6.0. Kinetic studies showed that reactions between alginate compounds and yttrium are corresponding to the pseudo-second-order model. These results obviously show that alginate salts may be successfully used as materials for elimination of radioisotopes from water disposals.

Keywords Alginate · Yttrium · Biosorption · Adsorption isotherm · Equilibrium · Kinetics

Introduction

Recovery of radioisotopes from nuclear waste is a subject of growing interest in recent years all over the world because of their potential application in various fields of industry. One of the radioisotopes most frequently released from low-level radioactive waste into the environment is strontium-90, which decays with a half-life of 28 years by electron emission (beta minus decay) into yttrium-90 (Lawson 1999). Yttrium is considered as the most dangerous in the working environment because damp and gases containing these ions can be inhaled with air. This can cause lung embolisms especially during long-term exposure. Yttrium can also cause cancer in humans, as it enlarges the chances of lung cancer if inhaled. Finally, it can be a threat to the liver when it accumulates in the human body (Curwin and Bertke 2011).

Also, yttrium is widely used in the fields of medicine, for example, in tumor treatment, in food irradiation procedures, as well as for sewage treatment technologies (Sattlberger and Atcher 1999; Diehl 2002; May et al. 2002). Generally radioisotopes, in particular yttrium ions, are quite dangerous and are not biodegradable; therefore, they must be removed from the polluted streams in order to meet increasingly stringent environmental quality standards. At present, there are no particular materials proposed for effective removal of yttrium ions from water disposals especially when their concentrations are very

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low. Up to date, there are just a few of published studies devoted to investigation of the properties of materials interacting with yttrium ions such as hydroxy-naphthoic acids (Aksoy et al. 2005) and dihydroxybenzoic acids (Aydin and Ozer 2004). Application of these substances for removal of yttrium ions from water disposals is almost impossible due to their low molecular weight and complicated processes of separation from aqueous solutions.

Many methods including chemical precipitation, electrodeposition, ion exchange, membrane separation, and adsorption have been used to treat wastewaters containing heavy metal ions (Kołodyńska 2013; Bora and Dutta 2014). Among these methods, traditional chemical precipitation is the most economic one but it is inefficient for dilute solutions. Ion exchange and reverse osmosis are generally effective, but they have rather high maintenance and operational costs and subjected to fouling. Adsorption is one of the few promising alternatives for this purpose, especially using low-cost natural sorbents such as agricultural wastes, clay materials, zeolites, biomass, and seafood processing wastes (Fu and Wang 2011).

In recent years, the number of studies focusing on biopolymers binding metal ions via chelation mechanism have increased significantly. The chelation ion exchange takes advantage of the three-dimensional structure of the biopolymer molecules holding metal ions (Demirbas 2008). Biopolymers are industrially attractive because they possess a capability of lowering transition metal ion concentration to parts per billion level, they are widely available and environmentally safe (Schmuhl et al. 2001; Khotimchenko et al. 2010).

This study is devoted to investigation of the binding properties of the alginate compounds. The retention of heavy metal ions on calcium alginate gels has become an increasing alternative technique to the treatment of water disposals (Jodra and Mijangos 2001; Khotimchenko et al. 2008). Alginic acid and its salts (alginates) occur mainly in marine brown seaweeds making main part of their polysaccharides and comprising up to 40 % of the dry matter (Brownlee et al. 2005). The structure of alginates is presented with a linear chain of (1–4)-linked residues of D-mannuronic acid and L-guluronic acid in different proportions and sequential arrangements. The most common arrangement is a block of guluronic acid residues (G–G blocks) and similar sequences of mannuronic acid residues (M–M blocks) intercalated between sequences of mixed composition (M–G blocks; Sidsrod and Draget 1996).

In some previous studies, alginate compounds were proposed for effective removal of radioisotopes of several isotopes such as uranium and cesium from water solutions (Bai et al. 2013; Vipin et al. 2013). Metal-binding activity of alginates is elucidated by the “egg-box” model (Plazinski 2011). This model suggests that covalent and ionic bonds are formed between carboxyl groups of the polysaccharide being in contact with the metal ions. Since alginic acid rarely occurs in natural sources, the great interest is given to its salts. Usually, sodium and calcium salts are used in experiments. As sodium and calcium have quite different properties and presented in water soluble and insoluble forms of alginates, respectively, it is of interest to compare these two types of alginate salts regarding their metal-binding capacity.

In this study, the equilibrium sorption of three-valence yttrium ions by sodium and calcium salts of alginic acid was investigated. The influence of experimental conditions such as pH, initial and equilibrium concentrations was studied. The Langmuir and Freundlich equations were used to fit the equilibrium isotherm. Two simplified kinetic models such as pseudo-first-order and pseudo-second-order equations were selected for investigation. This will be useful for further application of system design in the treatment of the waste effluents. This study was carried out in June–August 2013 in A. V. Zhirmunski Institute of Marine Biology, Far Eastern Branch of Russian Academy of Sciences. Precise determination of the yttrium concentration in supernatant solutions was performed in the School of Biomedicine, Far Eastern Federal University, Vladivostok, Russia.

Materials and methods

Alginate preparation and analysis

Sodium alginate (the viscosity of 2 % solution is 3,200 mPa s at 25 °C) was obtained from Qingdao Haiyang Chemical Co. (China). Sodium alginate was used for the preparation of the calcium alginate sample. For preparation of calcium alginate, 200 g sodium alginate was suspended in 1,000 ml of 70 % ethanol. Eight grams of $CaCl_2 \cdot 6H_2O$ was dissolved in 100 ml of 70 % ethanol and then added into the beaker with alginate ethanol solution and intensively shaken. Calcium alginate beads formed in solution were separated with a porous glass filter with 40-m mesh, rinsed with 500 ml of 70 % ethanol, and then dried at 60 °C.

Uronic acid contents in the alginate samples were determined colorimetrically by the m-hydroxydiphenyl method and expressed in percentage (van den Hoogen et al. 1998). The calcium contents in the calcium alginate samples were estimated using atomic absorption spectrometry and expressed as mg/g of a sample. The ratio of carboxyl groups forming a calcium salt was calculated as a calcium: uronic acid content ratio expressed in mg/g and percentage. Intrinsic viscosity of original sodium alginate was determined in 0.05 mol/l Na–Cl/0.005 mol/l Na-oxalate at 25.0 °C and pH 6.0 using an Ubbelohde viscosimeter. The intrinsic viscosity is empirically related to the molecular weight using Mark–Howink relation (Heinzmann and Tartsch 2009).

Experimental procedures

0.1 M stock solution of yttrium ions was prepared using analytical-reagent grade YCl_3. The stock solution was then diluted to give standard solutions with appropriate yttrium concentrations and controlled pH achieved by addition of either 0.1 M HCl or 0.1 M NaOH. Batch sorption experiments were conducted in 20-ml beakers and equilibrated using a magnetic stirrer. Then, 1.0 ml aliquots of these standard solutions were placed in 20-ml beakers with 10 ml of solution containing 0.05 g of dry sodium alginate sample or 10 ml of suspension with 0.05 g of dry calcium alginate. Then, the total volume of the solution prepared was made up to 20 ml by addition of distilled water. Removal of alginate compounds from yttrium solution was performed with the use of centrifugal force unit 3,000 for 10–20 min following with filtration through a glass filter with a pore size 100–120 μm. Concentration of yttrium ions in the supernatant obtained was analyzed using atomic absorption spectrophotometry method. The effect of yttrium adsorption was studied in a pH range from 2.0 to 6.0. The pH of the initial solution was adjusted to the required pH value using either 0.1 M HCl or 0.1 M NaOH. Alginates were equilibrated at the particular pH for about 120 min at 400 rpm and at initial yttrium concentration varying from 0.1 to 0.7 g/l using a bath controlled at 24 °C. Each experiment was at least triplicated under identical conditions. A negative control experiment with no alginate added was simultaneously carried out to ensure that the yttrium removal was caused by the polysaccharide-binding activity and not by beaker or filter. The experimental findings were subjected to a one-way analysis of variance using a software package SPSS (Statistical Package for Social Sciences) for Windows, version 19.0 with a confidence level of 95 % ($P < 0.05$).

The effect of agitation period was also studied to determine the optimum conditions for sorption of yttrium ions. For batch kinetic studies, 0.05 g of calcium alginate or 10 ml of solution containing the same amount of dry sodium alginate was equilibrated at optimum condition as mentioned earlier. The sorption system was placed in 20-ml beakers and stirred by a magnetic stirrer. Yttrium solution with different metal concentrations was used in these experiments. At preset time intervals, the aqueous samples (5 ml) were taken and the concentration of yttrium ions was assessed.

Sorption equilibrium studies were conducted at optimum conditions using a contact time of 120 min at pH from 2.0 to 6.0. Bath controlled temperature was 24 °C. Isotherm studies were conducted with a constant alginate amount (0.05 g) and varying initial concentration of yttrium in the range of 0.05–0.7 g/l. Each experiment was at least duplicated under identical conditions.

The metal accumulation (q) was determined as follows:

$$q_{\mathrm{e}} = \frac{(C_0 - C_{\mathrm{e}})V}{W}$$

where C_0 is the initial yttrium concentration (mg/l), C_{e} is the final or equilibrium yttrium concentration (mg/l), V is the volume of the yttrium solution (ml), and W is the weight of the dry samples of sodium or calcium alginate (g).

In all experiments, the concentrations of yttrium ions were determined by atomic absorption spectrometry ("Nippon Jarrel Ash," model AA-855) according to the instruction given in the manual guide. The amount of the metal ions bound by the alginic compounds was expressed as mg/g of the dry polysaccharide.

Results and discussion

Alginate substrate

The uronic acid concentration of the sodium and calcium alginate used in experiment was 77.3 %. The intrinsic viscosity of original sodium alginate used for the preparation of calcium alginate was 1,270 ml/g. Calculated molecular weight of the original sodium alginate and prepared calcium alginate used in experiments was 403×10^3 Da. The average calcium content of the calcium alginate sample was 38 mg/g of the polysaccharide or 3.8 % indicating that 82.5 % of carboxyl groups are presented in calcified form. In contrast to the sodium alginate samples, calcium alginate beads were not soluble in water.

Effect of initial metal concentration on yttrium adsorption

The influence of metal concentration on the velocity of interaction between yttrium and alginic polysaccharides was studied at pH 4.0 using stirring speed 200 rpm. The plots reflecting yttrium adsorption by calcium and sodium alginates as a function of time with various initial metal concentrations are given in Fig. 1. It can be seen that adsorption process at different concentrations is quite rapid in the initial stages and then gradually decelerates until the equilibrium is reached. Comparison of the two sets of plots shows that sodium alginate binds larger amount of yttrium ions with faster rate than calcium alginate. The amount of yttrium bound by calcium alginate at equilibrium varied from 24.60 to 97.79 mg/g as the initial concentration

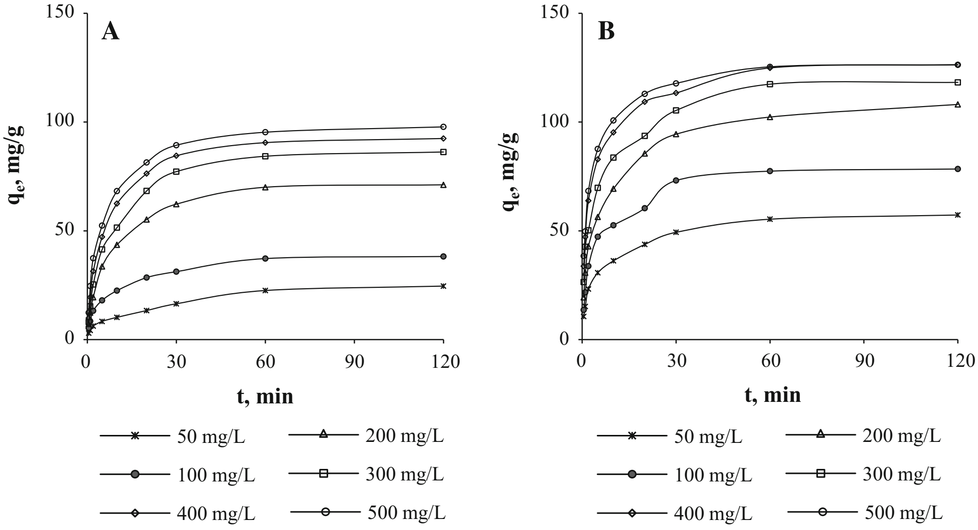

Fig. 1 Effects of agitation period on the yttrium-binding capacity of calcium alginate (**a**) and sodium alginate (**b**)

changed from 50 to 500 mg/l. Yttrium uptake of sodium alginate at equilibrium increased from 57.30 to 126.30 mg/g with the initial metal concentration rising from 50 to 500 mg/l as well. The initial concentration provides an important driving force to overcome all mass transfer resistances of the alginates between the aqueous and solid or gel phases. Hence, the higher initial concentration of yttrium contributes the faster process of adsorption. We have registered almost 4-fold increase in the binding capacity at equilibrium for calcium alginate and 2.2-fold for sodium alginate. The equilibrium conditions were reached within 40–60 min for the whole range of concentrations with no dependence on the amount of the metal ions bound.

Effects of pH on yttrium adsorption

Adsorption of Y^{3+} ions by soluble sodium alginate and insoluble calcium alginate beads was studied at pH 2.0, 4.0, and 6.0 with various metal concentrations in standard solutions. In the study with natural polysaccharides, pH of solution should be taken to account. This is an important parameter because the sorption system is strongly pH-dependent due to the properties of both alginate compounds changing their charge and potential at different pH and the solution composition, i.e., metal ion speciation (Lofgren et al. 2002; Schiewer and Patil 2008; Elliott et al. 2013). The number of active binding sites presented with carboxyl group residues of the alginate molecule may also change due to varying pH. Figure 2 shows the sorption curves indicating the amount of metal ions bound by the salts of alginic acid increasing with the rise of the pH values. At pH 2.0, adsorption capacities of both sodium and calcium alginates are significantly lower than that at pH 4.0 and 6.0. The difference between adsorption capacity at pH 4.0 and 6.0 was not significant. Alginate adsorption capacity at acidic pH is lower probably due to the excess of H^+ ions competing with the metal cations for adsorption sites.

In the media with pH values lower than 2.0, all alginic substances are usually precipitated, and this sedimentation also results in dramatic decrease in the binding activity of polysaccharides. Therefore, sodium alginate as well as calcium alginate exerts highest metal-binding activity within the pH range from 4.0 to 6.0.

Adsorption isotherms

Interaction of the polysaccharide samples with ions of yttrium was studied using various concentrations of the metal ions in the batch sorption system. The sorption processes in the batch result in the metal ions being removed from the solution and concentrated on the sorbent sites, until the remaining ions in the solution are in dynamic equilibrium with the ions bound to the active binding sites. Since the data for the curve are obtained at the same temperature, the curve is an isotherm. Therefore, there is a defined distribution of the metal ions in the sorption system, which can be expressed by one or more isotherms (Zhang et al. 2008). Figure 2 shows typical adsorption isotherms obtained in experiments with sodium and calcium alginates interacting with yttrium ions. The isotherms are characterized by the initial region, which is represented as being concave to the concentration axis.

The isotherm reaches a plateau and can typically be described by the Langmuir or Freundlich models, which were used for analysis of the results obtained through this part of experiments. The Langmuir model assumes that the adsorption of metal ions is a process occurring on a homogenous surface with finite number of active binding

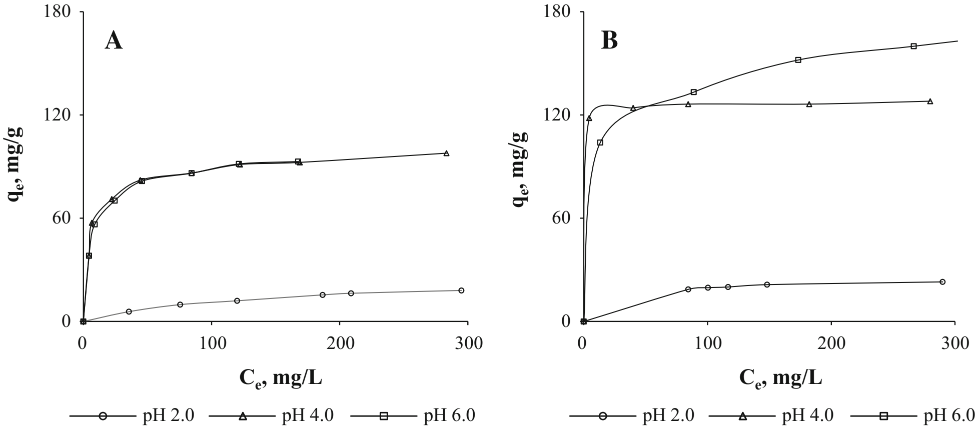

Fig. 2 Isotherm of the yttrium uptake by calcium alginate (**a**) and sodium alginate (**b**) under different pH of the media

sites without any interactions between adsorbed ions. The adsorption proceeds until a complete monolayer is formed. Langmuir equation is given by:

$$q_{\max} = \frac{q_e \times b \times C_e}{1 + b \times C_e}$$

where $q_{\max}$ is the maximum sorption at monolayer (mg/g), C_e is a final equilibrium concentration of metal ions in solution, q_e is the amount of a metal bound per unit weight of the alginate compound at final equilibrium concentration (mg/g), b is the Langmuir constant related to the affinity of binding sites (ml/mg) and is considered as a measure of the sorption energy.

The following linearized plot of the Langmuir equation giving $q_{\max}$ and b was used in this study:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{q_{\max}} \times b.$$

The widely used empirical Freundlich equation based on the monolayer sorption on a heterogeneous surface with uncertain number of active binding sites is given by:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where K_F (mg/g) and n are Freundlich constants indicating sorption capacity and intensity, respectively. K_F and n can be determined from linear plot of logq_e against logC_e.

The Langmuir and Freundlich equations were used to describe the isotherm data obtained for the adsorption of yttrium ions by each type of alginate over the entire concentration range used in the study. The characteristics of Langmuir and Freundlich equations obtained through the study are shown in Table 1.

These results indicate that the binding processes between yttrium ions and alginate salts are better characterized by Langmuir model according to the values of correlation coefficients. This suggests that alginate molecule contains the finite number of homogenous binding sites and each of them interacts with only one metal ion, which is the basic condition of the Langmuir sorption model. According to the "egg-box" model proposed for description of interaction between non-starch polysaccharides and metal ions (Plazinski 2011), the free carboxyl groups of alginic acid form junction zones consisting of one cation entrapped via covalent and hydrogen bonds. Figure 3 shows the Langmuir plots for the sorption of yttrium ions by calcium and sodium alginates, respectively. Freundlich isotherms of the yttrium ion sorption by alginates are given in Fig. 4. As it was mentioned before at pH 2.0, binding capacity of the polysaccharide is markedly lower than at pH 4.0 and 6.0. Correlation coefficients obtained through mathematical evaluation of the values of yttrium-binding capacity show that at pH 2.0, interactions between alginates and metal ions do not fit neither Langmuir model nor Freundlich model.

Table 1 Langmuir and Freundlich isotherm constants with correlation coefficients characterizing binding of Y^{3+} ions by sodium and calcium alginate

	Langmuir			Freundlich		
	b	$q_{\max}$ (mg/g)	R^2	K_F	n	R^2
Na alginate						
pH 2.0	0.03329	25.4453	0.9997	2.6099	6.035	0.9547
pH 4.0	0.9176	128.205	0.9999	7.8617	53.4759	0.9650
pH 6.0	0.9394	181.818	0.9957	6.3572	6.8399	0.9954
Ca alginate						
pH 2.0	0.0078	25.906	0.9961	0.8730	1.7099	0.9922
pH 4.0	0.1021	99.009	0.9989	4.6927	5.0787	0.8773
pH 6.0	0.1256	97.087	0.9994	4.4602	4.3668	0.9234

Comparison of the metal-binding activity exerted by calcium alginate and sodium alginates on the base of Langmuir coefficients shows that sodium alginate in all experiments is characterized by higher values of $q_{\max}$. This

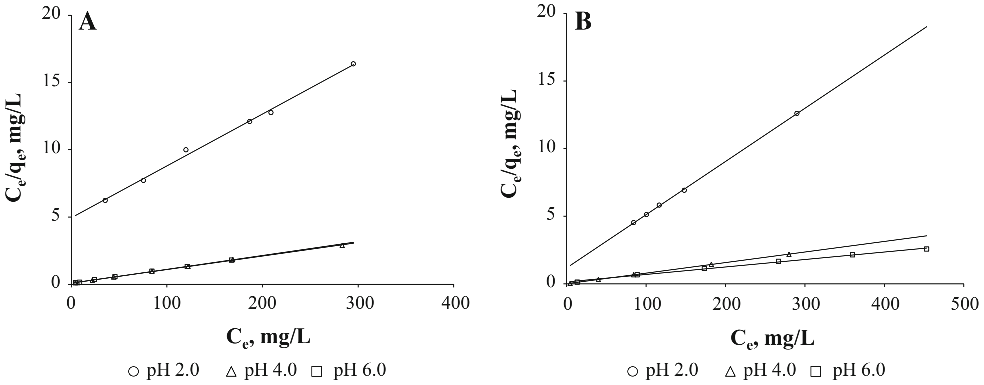

Fig. 3 Langmuir plots reflecting adsorption of yttrium ions by calcium alginate (**a**) and sodium alginate (**b**)

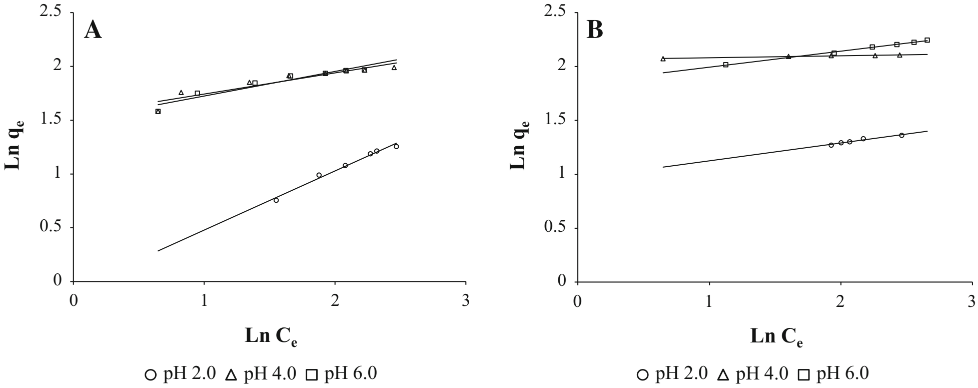

Fig. 4 Freundlich plots reflecting binding processes between yttrium and calcium alginate (**a**) and sodium alginate (**b**)

means that sodium alginate in correspondence with "egg-box" sorption model is capable to form more junction zones entrapping metal ions. Such conclusion is confirmed by the form of isotherms showed in Fig. 2. The monolayer adsorption capacity according to this model for sodium alginate reached 181.81 mg/g at pH 6.0, whereas this for calcium alginates was only 99.009 mg/g. The more important parameter of the Langmuir model is *b* reflecting affinity of the adsorbent to the metal ions. Evaluation of this parameter showed that affinity increases with alkali shift of pH, and affinity of calcium alginate to yttrium ions is a bit higher than that of sodium alginate.

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, R_L that is used to predict whether a binding system is "favorable" or "unfavorable" (Malik 2004). The separation factor, R_L is defined by:

$$R_L = \frac{1}{1 + bC_0}$$

where C_0 is the initial metal concentration (mg/ml), and *b* is the Langmuir adsorption equilibrium constant (ml/mg).

It is supposed that if results are in the range between 0 and 1, the sorption can be considered as favorable. The R_L values of both alginate compounds studied were within the range of $0 < R_L < 1$ (Table 2), which indicates that the sorption of yttrium by calcium and sodium alginates is favorable.

Thus, the results showed that sodium alginate was more effective than calcium alginate interacting with ions of yttrium. The metal ions contacting with the polysaccharide chains were trapped in a junction zone composed of the carboxyl groups located in the alginate molecules through formation of covalent and hydrogen bonds and acting as the binding site. Therefore, the mechanism of these reactions is chemisorption.

The main difference between the samples of the alginate compounds is the metal ion bound to the initial sample of polysaccharide. Sodium is a one-valence metal and its bonds with polysaccharides are easily broken.

Table 2 R_L values based on the Langmuir equation

Metal initial concentration (mg/ml)	R_L value	
	Ca alginate	Na alginate
pH 2.0		
0.2	0.996701	0.978358
0.4	0.993423	0.957633
0.6	0.990167	0.937768
0.8	0.986932	0.918710
1.0	0.983718	0.900411
pH 4.0		
0.2	0.971074	0.738255
0.4	0.943775	0.585106
0.6	0.917969	0.484581
0.8	0.893536	0.413534
1.0	0.870370	0.360656
pH 6.0		
0.2	0.975494	0.987601
0.4	0.952160	0.975505
0.6	0.929916	0.963702
0.8	0.908688	0.952181
1.0	0.888407	0.940933

Chemical bonds between alginate and calcium are much stronger, and calcium ions are competing with yttrium ions. Therefore, comparison of the yttrium-binding activity of these two salts of alginate is interesting. It was found earlier that activity of alginate to majority of the bivalent and trivalent ions is much higher than to calcium (Hartmeier et al. 1992; Jodra and Mijangos 2001). Therefore, the ion-exchange process occurs due to the release of calcium ions from alginate molecule with the simultaneous sorption of the yttrium ions. Results of the measurement of the yttrium sorption capacity showed that both polysaccharides bind similar amount of yttrium ions under given conditions.

However, evaluation of the results with use of Langmuir model showed that coefficient of activity of sodium alginate is nine times higher than that of calcium alginate. This may be explained by the presence of intensive ion-exchange process in the case of calcium alginate reducing its activity.

Adsorption kinetics

The study of adsorption dynamics describes the uptake velocity in solution. Evidently, this rate controls the residence time of the metal uptake at the solid–solution interface. The kinetics of yttrium adsorption by calcium and sodium salts of alginic acid were analyzed using pseudo-first-order model described by Lagergren (Plazinski et al. 2009) and pseudo-second-order model proposed by Ho and McKay (1999).

A linear form of the pseudo-first-order equation used in the study is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg/g), k_1 is the rate constant of pseudo-first-order adsorption (mg/g min).

After integration and applying boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of this equation becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t.$$

If pseudo-first-order model is appropriate for description of adsorption of yttrium on alginates, then the values of $\log(q_e - q_t)$ are linearly correlating with t. The plots of $\log(q_e - q_t)$ versus t are shown in Fig. 5. These plots give a linear relationship, from which k_1 can be calculated from the slope. The values of Lagergren's first-order rate constant (k_1) along with the corresponding correlation coefficients are presented in Table 3. It was figured out that the pseudo-first-order model did not fit well. It was also found that the calculated q_e (not given) values do not agree with the experimental q_e values. This suggests that the adsorption of yttrium by both calcium and sodium alginate does not follow first-order kinetics.

The pseudo-second-order kinetics may be expressed as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2,$$

where k_2 is the rate constant of pseudo-second-order adsorption (g/mg min).For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of this equation becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t,$$

which is the integrated rate law for a pseudo-second-order reaction. This equation can be rearranged to obtain the following equation, which has a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e t},$$

where the equilibrium adsorption capacity (q_e), and the second-order constants k_2 (g/mg h) can be determined experimentally from the slope and intercept of plot t/q_t

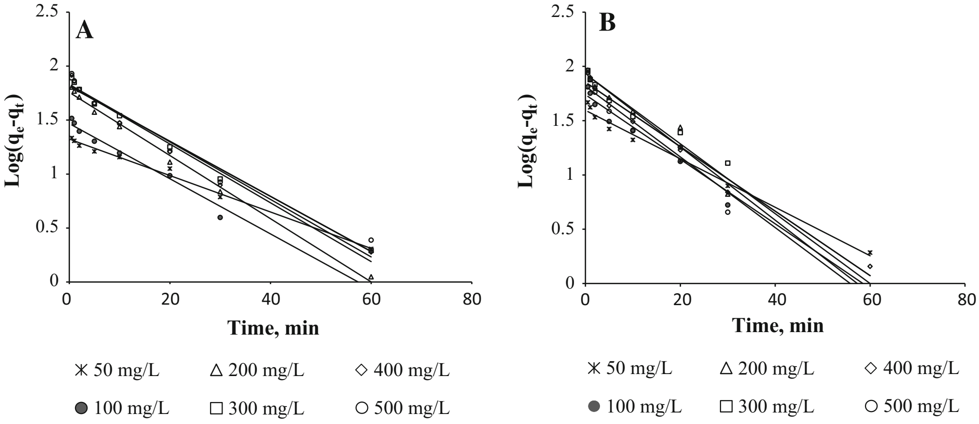

Fig. 5 Pseudo-first-order kinetics of the reactions between yttrium and calcium alginate (**a**) and sodium alginate (**b**)

Table 3 Pseudo-first-order absorption rate constants for calcium and sodium alginate obtained at different initial yttrium concentrations

C_{in} (mg/l)	Ca alginate		Na alginate	
	k_1 (1/*h*)	R^2	k_1 (1/*h*)	R^2
50	0.73×10^{-2}	0.9918	0.96×10^{-2}	0.9881
100	1.11×10^{-2}	0.9899	1.29×10^{-2}	0.9814
200	1.27×10^{-2}	0.9939	1.46×10^{-2}	0.9857
300	1.15×10^{-2}	0.9896	1.40×10^{-2}	0.9824
400	1.18×10^{-2}	0.9788	1.29×10^{-2}	0.9800
500	1.11×10^{-2}	0.9669	1.41×10^{-2}	0.9722

versus *t* given in Fig. 6 for both polysaccharides studied. The k_2 and q_e values calculated from this model are presented in Table 4 along with the corresponding correlation coefficients and the initial yttrium adsorption rate values. It can be seen in Table 4 and Fig. 2 that there is a correlation of q_e experimental and q_e calculated values for the pseudo-second-order model. Also, correlation coefficients are always higher than 0.95 indicating that the pseudo-second-order model better represents the adsorption kinetics of the yttrium ions by calcium and sodium alginate.

The initial adsorption rates *h* (mg/g min) can be calculated from the pseudo-second-order model by the following equation:

$$h_{0,2} = k_2 q_e^2.$$

The results are presented in Table 4. It was found that the initial rate of adsorption increases with rising initial yttrium concentration, which would be expected due to the increase in driving force at higher concentration.

Fig. 6 Pseudo-second-order kinetic reactions between yttrium ions and calcium alginate (**a**) and sodium alginate (**b**)

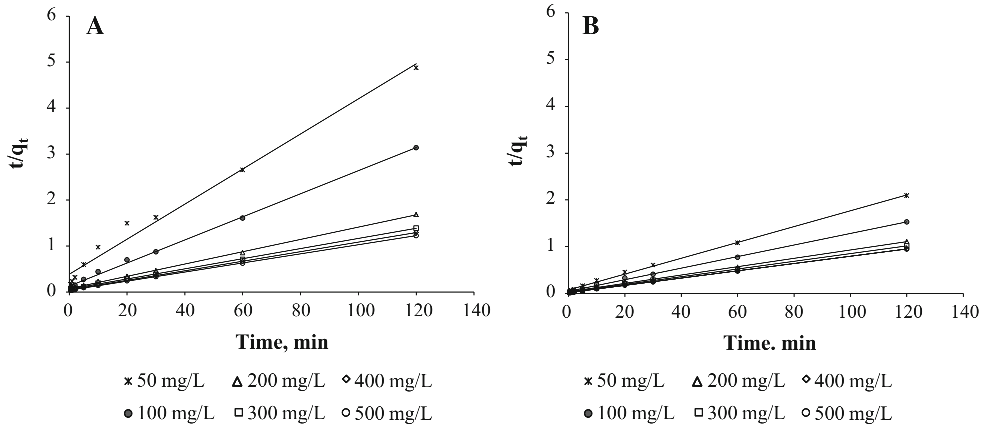

Table 4 Pseudo-second-order absorption rate constants for calcium and sodium alginate obtained at different initial yttrium concentrations

C_{in} (mg/l)	Ca alginate				Na alginate			
	k_2 (g/mg h)	R^2	q_e (mg/g)	h (mg/g min)	k_2 (g/mg h)	R^2	q_e (mg/g)	h (mg/g min)
50	0.39	0.9841	26.25	2.588	0.33	0.9983	59.17	13.387
100	0.68	0.9982	39.84	7.663	0.17	0.9986	80.64	21.930
200	0.40	0.9995	74.63	13.587	0.15	0.9978	112.35	27.027
300	0.35	0.9994	90.91	16.000	0.09	0.9987	121.95	35.842
400	0.21	0.9998	96.15	21.142	0.04	0.9996	114.94	53.476
500	0.16	0.9997	101.01	25.381	0.03	0.9998	128.20	65.789

Conclusion

In this work, the ability of calcium and sodium alginates to remove yttrium ions from aqueous solution was investigated. The results showed that alginate compounds act as effective adsorbents binding yttrium in water solutions. Regardless of the initial metal concentration, the equilibrium time was found to be 60 min for both soluble and insoluble salts of alginate. The results obtained through the experimental studies were evaluated using two equilibrium models: Langmuir and Freundlich. Equilibrium isotherms were best described with the Langmuir equation giving the maximum adsorption capacity at pH 6.0. Kinetics of adsorption interactions are corresponding to the pseudo-second-order equation. Although sodium alginate was found to be more effective than calcium salt of alginic acid, both alginate compounds were figured out to be suitable for removal of yttrium ions from water solutions.

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