

# Chitosan Impregnated with Phosphonium Groups Used To Strontium Adsorption

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**Abstract:** In this work it was studied the removal of strontium ions from aqueous solution through adsorption onto a biopolymer, chitosan, impregnated with butyltriphenylphosphonium bromide. The impregnation of the butyltriphenylphosphonium bromide onto the chitosan was realised through ultrasonication. The energy dispersive EDX applied to the obtained adsorbents proved the fact that the biopolymer support was impregnated with the studied butyltriphenylphosphonium bromide. The impregnated chitosan developed a maximum adsorption capacity in the removal process of  $\text{Sr}^{2+}$  ions from aqueous solution of 2.65 mg  $\text{Sr}^{2+}$ /g of adsorbent. The equilibrium between the adsorbent and adsorbate was achieved in 60 minutes.

**Keywords:** chitosan, adsorption, biopolymer

## 1. Introduction

The recovery of metal ions from industrial wastes has received increasing attention in view of resource sustainable development and environmental improvement and it is very important today.

Impregnated macroporous or gel-type styrene-co-divinylbenzene polymers, chitosan and cellulose have been tested for the removal of a number of metal ions from wastewaters [1,2]. The ionic liquids bearing phosphonium groups have paying attention for their capability to extract a variety of organic compounds [3], and metal ions [1,2].

Chitosan was the subject of various researches during last years [4-6]. The chitosan is a copolymer of glucosamine and N acetylglucosamine, see figure 1. It is a natural product being considered a non toxic substance. It has a high molecular weight, a poor solubility at neutral pH and a high viscosity in solution [6].

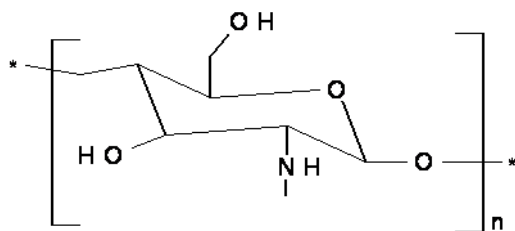


Figure 1. The chitosan structure

In this article, we report the ultrasound-assisted preparation of the chitosan with phosphonium groups and its use as polymer-base sorbent for strontium ions adsorption from aqueous solutions.

## 2. Experimental

### 2.1. Obtaining of biopolymer impregnated with phosphonium salt

In a Erlenmeyer glass (100 mL) were added 5 g of chitosan and 0.5 g butyltriphenylphosphonium bromide dissolved in 25 mL of ethanol. The impregnation was done by ultrasound at 30 °C and at 30 minutes working time. The samples obtained were separated by filtration, washed with ethanol and then dried in an oven at 50 °C for 24 hours. The surface morphology of the impregnated chitosan was studied by scanning electron microscopy (SEM) using a Quanta FEG 250 microscope equipped with a EDAX ZAF detector.

### 2.2. $\text{Sr}^{2+}$ adsorption onto the impregnated biopolymer

The adsorption capacity of the impregnated chitosan with phosphonium groups was studied in the removal process of  $\text{Sr}^{2+}$  ions from aqueous solutions.

The samples with  $\text{Sr}^{2+}$  ions was achieved by shaking and for this was used a MTAKutesz shacker with a

constant speed of stirring and for 240 min contact time. For the studying the adsorption capacities of the chitosan impregnate with phosphonium groups, this was treated with solutions containing different concentrations of  $\text{Sr}^{2+}$  (5, 15, 20, 25 and 30 mg / L) and  $T = 298 \text{ K}$ , agitation speed 200 rpm.

0.1 g of the biopolymer was treated with 25 mL of  $\text{Sr}^{2+}$  solution. The samples were stirred for 1 hour and after stirring were filtered and the concentration of  $\text{Sr}^{2+}$  was determined by atomic emission spectrometry using anatomic absorption spectrometer Varian 280 SpectrAA with air/acetylene flame. The effect of contact time between the adsorbent and adsorbate on the adsorption capacity of the impregnated chitosan was determined.

The adsorption capacity was determined using the following equation:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

where:  $C_0$  - initial concentration of  $\text{Ni(II)}$  ions in solution, mg/L;  $C_t$  - concentration of  $\text{Sr}^{2+}$  ions in solution after time  $t$  (min), mg/L;  $v$  - volume of the solution, L;  $m$  - mass of the adsorbent employed, g.

The experimental data regarding the effect of contact time between the adsorbant and adsorbate were modeled using the pseudo-first-order kinetic model and the pseudo-second-order kinetic model.

The pseudo-first-order kinetic model:

$$\ln(q_e - q_t) = \ln q_e - k_1 \cdot t \quad (2)$$

where  $q_e$  and  $q_t$  are the amount of the  $\text{Sr}^{2+}$  adsorbed onto the studied adsorbent (mg/g) at equilibrium and after time  $t$ , respectively.  $t$  is the contact time (min),  $k_1$  is the specific sorption rate constant ( $\text{min}^{-1}$ ). The values of the adsorption rate constant ( $k_1$ ) were determined from the  $\ln(q_e - q_t)$  in terms of  $t$  [7-11].

The pseudo-second order kinetic model:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \quad (3)$$

where  $q_e$  and  $q_t$  are the amount of the  $\text{Sr}^{2+}$  adsorbed onto the studied material (mg/g) at equilibrium and at time  $t$ , respectively.  $t$  is the contact time (min),  $k_2$  is the pseudo-second-order adsorption rate constant ( $\text{g}/(\text{mg} \cdot \text{min})$ ). The value  $q_e$  and  $k_2$  are determined from the slope and intercept of  $(t/q_t)$  versus  $t$  [7, 10, 11].

The experimental data regarding the influence of the  $\text{Sr}^{2+}$  initial concentration upon the adsorption capacity were modeled using the linearized isotherm of Langmuir and Freundlich in order to determine the maximum adsorption capacity of the impregnated chitosan in the removal process of  $\text{Sr}^{2+}$  from aqueous solutions.

The linear form of Langmuir isotherm:

$$\frac{C_e}{q_e} = \frac{1}{K_L \cdot q_m} + \frac{C_e}{q_m} \quad (4)$$

where  $q_e$  is the amount of  $\text{Sr}^{2+}$  adsorbed per gram of adsorbent, i.e., metal uptake (mg/g), and  $C_e$  is the equilibrium concentration of adsorbate in the bulk solution after adsorption (mg/L).  $q_m$  is the measure of the monolayer sorption capacity (mg/g) and  $K_L$  denotes the Langmuir isotherm constant related to the affinity between adsorbent and the adsorbate (L/mg) [7-11].

The linear form of Freundlich isotherm:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (5)$$

where:  $K$  and  $1/n$  are characteristic constants that can be related to the relative adsorption capacity of the adsorbent (mg/g) and the intensity of the adsorption, respectively. The logarithmic plot of  $q_e$  against  $C_e$  should result in a straight line that allows computations of  $1/n$  and  $K_f$  from the slope and intercept [7-11].

$$R_L = \frac{1}{1 + K_L C_0} \quad (6)$$

where:  $K_L$  is the Langmuir constant and  $C_0$  is the initial concentration of  $\text{Sr}^{2+}$  ions

### 3. Results and Discussion

#### 3.1. Characterization of the impregnated chitosan

In figure 2 can be seen the SEM image of impregnated chitosan with phosphonium groups.

In figure 3, it is presented the EDX of the phosphonium groups with bromide ions on chitosan. These analyze put in evidence the fact that the chitosan was impregnated with the studied butyltriphenylphosphonium bromide groups.

#### 3.2. Influence of contact time on the adsorption process of $\text{Sr}^{2+}$ from aqueous solutions

The use of impregnated chitosan with phosphonium groups in the removal of  $\text{Sr}^{2+}$  from aqueous solutions presents a link between the benefits of solvent extraction and solid supports. Effect of contact time between the adsorbent and adsorbate of the impregnated chitosan with phosphonium groups, at temperature of 298 K, was determined. The plot of adsorption capacity of the chitosan impregnated with butyltriphenylphosphonium bromide groups versus time is presented in figure 4.

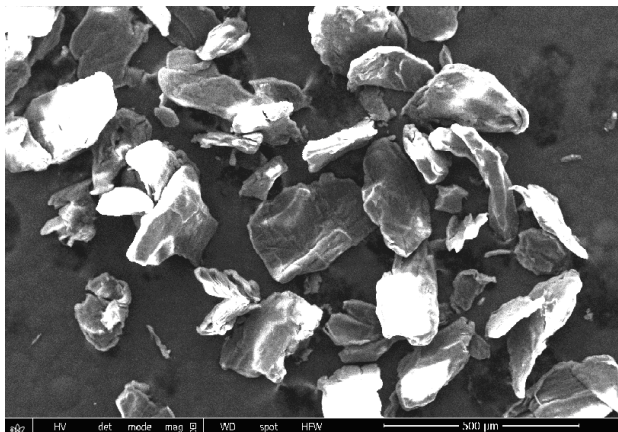


Figure 2. SEM image of impregnated chitosan with phosphonium groups

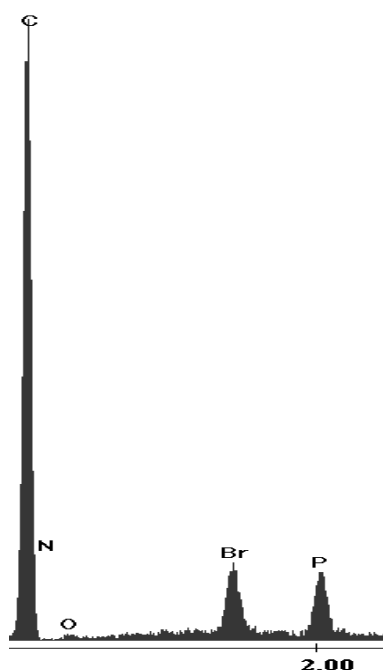


Figure 3. EDX of the impregnated phosphonium groups on chitosan.

In figure 4, it can be notice that the adsorption capacity increase with the contact time increasing until it reaches a constant value. The equilibrium between the adsorbent and adsorbate is reached in 60 minute.

In order to determine the contact time between the adsorbent and adsorbate, kinetic studies were used. Adsorption kinetics was evaluated at temperature of 298 K.

Figure 5 presented the plots of  $\ln(q_e - q_t)$  versus  $t$  for  $\text{Sr}^{2+}$  ions adsorption, onto impregnated chitosan with phosphonium groups. The plots are used to estimate the pseudo-first-order rate constant ( $k_1$ ) and the equilibrium adsorption capacity ( $q_e$ ), respectively. The pseudo second-order rate constant ( $k_2$ ) and the equilibrium adsorption capacity ( $q_e$ ) were obtained from the intercept and slope of  $t/q_t$  versus  $t$  (Figure 6).

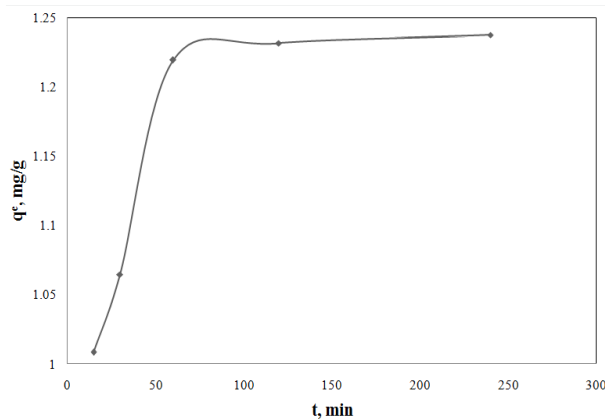


Figure 4. Effect of contact time on the adsorption capacity of the impregnated chitosan with phosphonium groups

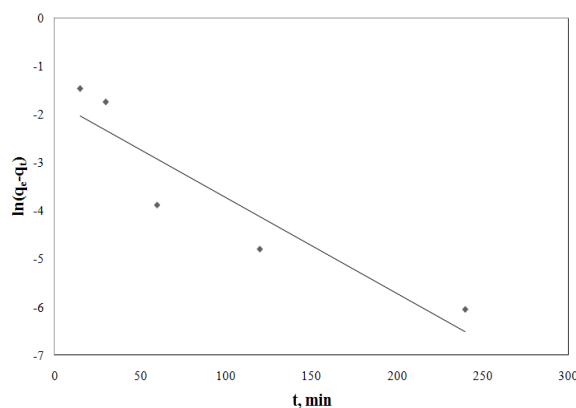


Figure 5. Pseudo-first order kinetic model for  $\text{Sr}^{2+}$  adsorption onto the studied material

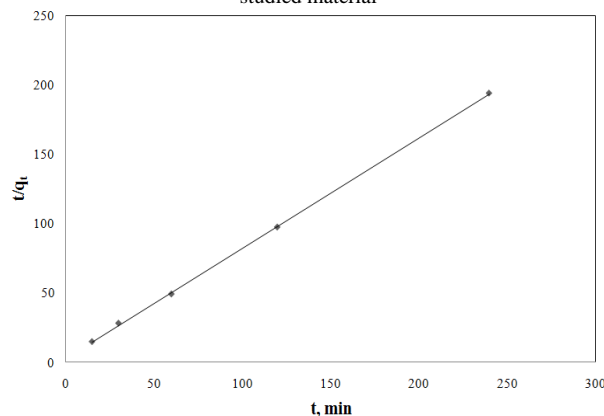


Figure 6. Pseudo-second order kinetic model for  $\text{Sr}^{2+}$  adsorption onto the studied material

In table 1 are presented the adsorption rate constant, degree of fit  $R^2$  and theoretical adsorption capacity for  $\text{Sr}^{2+}$  sorption onto the impregnated chitosan with phosphonium groups. Such, it can be observed that the degree of fit  $R^2$  for the pseudo-second-order ( $R^2 > 0.99$ ) is higher than those of the pseudo-first-order model ( $R^2 < 0.85$ ). The correlation coefficients found for the pseudo-first-order kinetic model were much lower than those obtained for the pseudo-second-order model.

This shows that the kinetics of  $\text{Sr}^{2+}$  ions adsorption on the studied material is well described by a pseudo-second-order model.

TABLE 1. Kinetic parameters for  $\text{Sr}^{2+}$  sorption onto the studied material

$q_{e, \text{exp}}$	Pseudo-first-order model			Pseudo-second-order model		
	$q_{e, \text{calc}}$ mg/g	$k_1$ , $\text{min}^{-1}$	$R^2$	$q_{e, \text{calc}}$ mg/g	$k_2$ , $\text{min}/(\text{mg/g})$	$R^2$
1.24	0.18	0.019	0.855	1.26	0.225	0.999

### 3.3. Influence of the $\text{Sr}^{2+}$ initial concentration on the adsorption process of $\text{Sr}^{2+}$ from aqueous solutions

The adsorption isotherm of  $\text{Sr}^{2+}$  ions is presented in Figure 7.

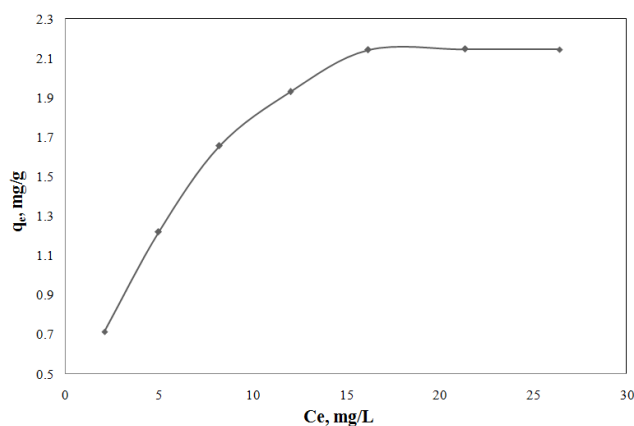


Figure 7. Equilibrium isotherm of  $\text{Sr}^{2+}$  adsorption onto the studied material

In figure 7, it is observed that the adsorption capacities increased with increasing equilibrium concentration of  $\text{Sr}^{2+}$  ions, for the studied material.

At higher concentration the adsorption capacity become constant obtaining a maximum adsorption capacity for the impregnated chitosan with phosphonium groups of 2.15 mg/g, see figure 7. The obtained experimental data were fitted with the linearized isotherms of Langmuir and Freundlich for the determining the maximum adsorption capacity of chitosan impregnated with butyltriphenylphosphonium bromide groups, (see figure 8, 9). The equilibrium data fitted to Langmuir model better than Freundlich model indicating a monolayer adsorption. The adsorption parameters are presented in table 2.

TABLE 2. Parameters of Langmuir and Freundlich isotherms for  $\text{Sr}^{2+}$  adsorption onto the chitosan impregnated with butyltriphenylphosphonium bromide groups

$q_{m, \text{exp}}$ $\text{mg Sr}^{2+}/\text{g}$	Langmuir isotherm			Freundlich isotherm		
	$K_L$ L/mg	$q_{m, \text{calc}}$ mg/g	$R^2$	$K_F$ mg/g	$1/n$	$R^2$
2.15	0.193	2.65	0.991	0.574	0.448	0.934

The value of parameter  $R_L$  provides significant information about the nature of adsorption. The value of  $R_L$  indicated the type of Langmuir isotherm to be irreversible ( $R_L=0$ ), favourable ( $0 < R_L < 1$ ), linear ( $R_L=1$ ), or unfavourable ( $R_L > 1$ ). [7, 10, 11] The  $R_L$  was found to be between 0 and 1 for the entire concentration range, which indicates the favourable adsorption of  $\text{Sr}^{2+}$  onto the chitosan impregnated with butyltriphenylphosphonium bromide groups.

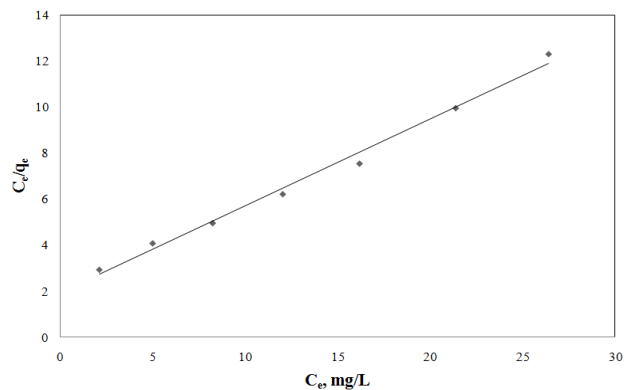


Figure 8. Langmuir isotherm of  $\text{Sr}^{2+}$  adsorption onto the obtained impregnated material

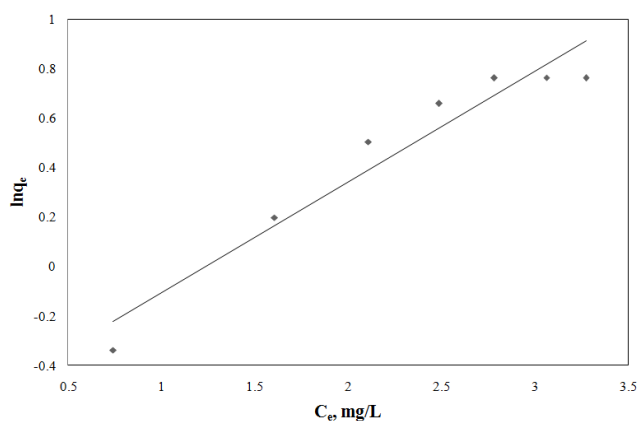


Figure 9. Freundlich isotherm of  $\text{Sr}^{2+}$  adsorption onto the obtained impregnated material

## 4. Conclusions

Chitosan was impregnated with butyltriphenylphosphonium bromide and it presented a maximum adsorption capacity in the removal process of  $\text{Sr}^{2+}$  ions from aqueous solution of 2.65 mg  $\text{Sr}^{2+}/\text{g}$  of adsorbent, obtained from the linearized isotherms of Langmuir. The kinetics of  $\text{Sr}^{2+}$  ions adsorption on the studied material is well described by a pseudo-second-order model.

The use of impregnated chitosan with phosphonium groups in the removal of  $\text{Sr}^{2+}$  from aqueous solutions presents a link between the benefits of solvent extraction and solid supports.

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## REFERENCES

1. Regel-Rosocka M., Cieszynska A. and Wisniewski M., *Przem. Chem.*, 85(8–9), **2006**, 651–654.
2. Camposa K., Domingo R., Vincent T., Ruiz M., Sastre A.M. and Guibal E., *Water Res.*, 42, **2008**, 4019-4031.
3. Martak J. and Schlosser S., *Chem. Pap.*, 60, **2006**, 395–398.
4. Goy R.C., De Britto D. and Assis O.B.G., *Polímeros: Ciência e Tecnologia*, 19(3), **2009**, 241-247.
5. Kong M., Chen X.G., Ke Xing K. and Park H.J., *Int.J. Food Microbiol.*, 144(1), **2010**, 51–63.
6. Li Q., Dunn E.J., Grandmaison E.W. and Goosen M.F.A., *J. Bioact. Compat. Pol.*, 7(4), **1992**, 370-397.
7. Borah D., Satokawa S., Kato S. and Kojima T., *J. Hazard. Mater.*, 16, **2009**, 1269-1277.
8. Kul A.R. and Caliskan N., *Adsorpt. Sci. Technol.*, 27, **2009**, 85-105.
9. Gupta K. and Ghosh U.C., *J. Hazard. Mater.*, 161, **2009**, 884-892.
10. Davidescu C.M., Ciopec M., Negrea A., Popa A., Lupa L., Dragan E.S., Ardelean R., Ilia G. and Iliescu S., *Polym. Bull.*, 70, **2013**, 277–291.
11. Ciopec M., Davidescu C.M., Negrea A., Lupa L., Popa A., Muntean C., Ardelean R. and Ilia G., *Polym. Eng. Sci.*, 53, **2013**, 1117-1124.

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