Preparation of Porous Calcium Alginate Beads and Their Use for Adsorption of O-Nitrophenol from Aqueous Solutions

Sandu PERETZ¹, Manuela FLOREA-SPIROIU², Dan-Florin ANGHEL¹, Daniela BALA², Cristina STOIAN³ and Gheorghe ZGHEREA³

¹Institute of Physical Chemistry *Ilie Murgulescu*, Romanian Academy, Department of Colloids, 202 Spl. Independentei, 060021 Bucharest, Romania E-mail: sanduperetz@gmail.com

²University of Bucharest, Faculty of Chemistry, Department of Physical Chemistry, 4-12 Regina Elisabeta blvd., 030018, Bucharest, Romania E-mail: manu.spiroiu@gmail.com

³University *Dunarea de Jos* of Galati, Faculty of Sciences and Environment, Department of Chemistry, 111 Domneasca St., 800201, Galati, Romania E-mail: stoianc@yahoo.com

Abstract. To increase their adsorbent surface, calcium alginate (Ca-Alg)/Sodium Lauryl Sulfate (SLS) beads were synthesized from sodium alginate with SLS as foaming agent, NaCl as porogen agent, and CaCl₂ as cross-linker. The properties of dried Ca-Alg/SLS beads were studied by FTIR and their size by SEM. The adsorption of *o-NitroPhenol* (NP) is dependent of pH, and their adsorption on porous Ca-Alg/SLS beads reaches a maximum for pH = 7. The adsorption experiments indicated that the removal efficiency increases with the quantity of Ca-Alg/SLS beads, and decreases with increasing the initial pollutant concentration. Adsorption isotherms showed that NP adsorption on porous Ca-Alg beads occurs in accordance with Freundlich model.

1. Introduction

Adsorption is one of the most effective and simplest methods to remove pollutants from aqueous wastes, which using polymeric adsorbent that effectively trap many organic pollutants such as phenol derivatives [1–6]. Nitrophenols are the most common organic water pollutants and have adverse health effects on humans because they are toxic even at low concentrations [7]. The o-nitrophenol is used in the production of azo- and sulfur-dyes, insecticides, wood preservatives, rubber, explosives, processing of leather being present in the resulted wastewaters. Up to

some threshold concentrations the nitrophenols can cause the irritation of nose, skin, eyes or throat. The phenol is widely used in various industries and exposure to this contaminant can lead human beings to serious health problems, including symptoms such as diarrhea, dark urine and hemolytic anemia [8].

Nowadays, the use of natural polymers like polyglycolide, polylactide, gelatin, collagen, alginate, chitosan or hyaluronate as absorbents or cleaners for wastewater has received in recent year's considerable attention. Due to the low cost of production and excellent selectivity, the biopolymers are a better alternative to conventional materials for removal cationic and anionic pollutants [9, 10]. Previous studies have shown that nitrophenolic pollutants from wastewaters can be successfully retained by alginate gel complex [11, 12]. Alginate is one of the most extensively used biopolymer for removing the anionic and cationic pollutants from aqueous solutions [13–15]. It is a hydrophilic, biocompatible and inexpensive biopolymer that forms an interconnected open pore network by cross-linking with calcium ions [16, 17].



Fig. 1. Calcium alginate-Egg-box structure [22].

Alginate is composed of $(1\rightarrow 4)$ - β -D-mannuronic acid (M) and a-L-guluronic acid (G) units in the form of a homopolymeric (MM- or GG-blocks) and heteropolymeric sequences (MG- or GM-blocks) [18, 19]. The blocks can be homogeneous GGGG or MMMM or alternate MGMG. Studies by partial hydrolysis and investigations by ¹³C-NMR spectroscopy method unveiled that the monomer residues are not randomly distributed, occurring in blocks of about twenty units. The D-mannuronic acid is connected in the β -configuration through the 1- and 4- positions and the L-guluronic acid is α -1, 4- linked in the polymer. Because of the particular shape of the monomers and of their linkage in the polymer, the geometries of the G-block, M-block, and the alternating regions are substantially different. Specifically, the G-blocks are buckled while the M-blocks

have a shape referred to as an extended ribbon. If two G-block regions are aligned side by side, a diamond shaped hole results. This hole has dimensions that are ideal for the cooperative binding of calcium ions [20].

Sodium alginate forms gels with interconnected pores by ionotropic gellation in the presence of bi- or trivalent cations [21]. The bivalent calcium cation has the ability to fit into the guluronate structures like eggs in an egg-box [22].

Consequently, this binds the alginate chains together by junction zones, sequentially leading to gelling of the solution.

The purpose of this study is to obtain porous calcium alginate beads, which presents superior performance for adsorption of cationic pollutants, by using sodium lauryl sulfate as foaming agent, sodium chloride as porogen agent, and calcium chloride as cross-linker.

2. Experimental

2.1. Materials

Alginic acid sodium salt and sodium lauryl sulfate (SLS) were purchased from Fluka (Switzerland). Sodium and calcium chlorides (NaCl, CaCl₂), and o*nitrophenol* (NP) were from Merck (Germany). The water used in the experiments was Milli-Q water (MILLIPORE Simplicity UV Lab System–France).

2.2. Synthesis of Alginate/SLS Beads

Aqueous sodium alginate and SLS mixed solution was prepared by dissolving the components in NaCl 1M solution at 60°C under continuous stirring at 2000 rpm for 30 minutes. The aqueous mixture of 2% (wt/v) sodium alginate and SLS 0.2% (wt/v) in form of drops was dried by lyophilization using a ALPHA 1-2 LD plus (Christ) freeze-dryer. Afterwards, the beads were cross-linked by 1,5, and 10 wt % CaCl₂ solutions for 4 hours, and denoted by Alg-1, Alg-2 and Alg-3. They were thoroughly washed with Milli Q water, and after were dried by lyophilization (pressure = 0.021 mbar, temperature = -55° C, for 48 hours).

The calcium alginate/SLS beads (without using NaCl) were obtained by dropping through a needle of a syringe the mixed sodium alginate/SLS solution into a 1 wt % calcium chloride solution; the system was magnetically stirred at 60 rpm. The beads were dried by lyophilization to be analyzed their surface morphology by scanning electron microscopy (SEM).

2.3. Characterization Techniques

The calcium alginate/SLS lyophilized beads were characterized by Fourier Transform Infrared (FTIR-ATR) Spectroscopy using a Nicolet iN10 FTIR spectrometer (Thermo Scientific), in the 550–4000 cm⁻¹ wavenumber range, at a

spectral resolution of 4 cm⁻¹. The pore sizes and the morphology of the dry beads were determined from the SEM images obtained by using a Quanta 3D FEG 200/400 microscope.

The adsorption of o-nitrophenol by the calcium alginate/SLS beads was spectrophotometrically assessed at 282 nm using a Varian Cary 100 Bio UV-Vis spectrophotometer. The concentration of removed NP was calculated at 45 h after reaching the equilibrium, as the difference between the initial concentration and the concentration of non-adsorbed NP remained in the solution. The kinetics regarding the o-nitrophenol uptake by porous calcium alginate (Ca-Alg) beads was obtained by analyzing the samples at determined time intervals. The temperature was maintained at 25° C for all the experiments.

3. Results and discussions

3.1. Beads Morphology

The factors affecting the porosity of the polymeric beads were investigated and corroborated with their mutual effects on the morphology. A porous structure of beads is obtained by using SLS as foaming agent and NaCl as porogen compound.

The SEM image shows that dry alginate beads are relatively spherical, presenting a porous surface, and have micrometrical size (Fig. 2).



Fig. 2. SEM photo of porous calcium alginate/SLS beads.

SEM photos of the surface of alginate beads (see Fig. 3a) does not show an interconnected pore structure because the beads are not prepared in presence of NaCl, and the sodium alginate solution was not frozen. The freezing in presence of NaCl prevents the large ice crystals formation and results in polymeric structures with uniform dimension of the small pores.

The surface of beads is regular showing structures with 3-D interconnected pores. The NaCl porogen, added prior to formation of the three-dimensional

polymer matrices favors pores connection. The presence of anionic surfactant maintains the shape of the pores by repulsion between the micelles and the carboxylate groups of the polymer chain. Addition of $CaCl_2$ cross-linker to the sodium alginate solution entails the alignment of the G-blocks and the calcium ions are bound between the two chains like eggs in an egg box [22]. The reactivity of calcium ions to alginates is the result of calcium-induced dimer association of the G-block regions. The pore size depends on the amount of calcium present in the system. The higher the concentration of $CaCl_2$ leads to more junction zones and increases the number of small pores.



Fig. 3. SEM photos of Ca-Alg/SLS beads surface: Alg-without NaCl (a), Alg-1 (b), Alg-2 (c) and Alg-3 (d).

The size of pores varies from 5 to 10 μ m in the cross-linked matrices with 1 wt % CaCl₂ (Fig. 3b). However, the pores are smaller ranging from 0.75 to 1.75 μ m when the beads are treated with 5wt % CaCl₂ (Fig. 3c). In presence of high concentration of bivalent cations SLS self-assembles, and forms lamellar micelles. At 10 wt % CaCl₂, the lamellar micelles bind together the alginate chains by electrostatic bonds with calcium ions. This is revealed by the SEM image of

sample Alg-3 (Fig. 3d) and by the FTIR spectrum (Fig. 4d) that indicates a negative effect on the intermolecular hydrogen bonds.

3.2. Evidence of Alginate Cross-Linking - the FTIR Spectrum

The different morphologies of the obtained biopolymeric beads can be explained taking into account the changes in the intermolecular bonds evidenced by FTIR spectrum (Fig. 4).



Fig. 4. FTIR spectrum: Na-Alg (a); Ca-Alg/SLS beads cross-linked with CaCl₂: (b) 1 wt % (Alg-1), (c) 5 wt % (Alg-2), and (d) 10 wt % (Alg-3).

The spectrum of sodium alginate powder shows distinct peaks of hydroxyl (-HO) at 3255 cm⁻¹, carboxyl (-COO) at 1600 cm⁻¹, (-CH) at 1413 cm⁻¹ and (C-O-C) at 1025 cm⁻¹ (Fig. 4a).

Depending on the calcium chloride concentration, the characteristic peaks of alginate are shifted in the cross-linked samples in the presence of anionic surfactant.

Cross-linking decreases the wavenumber of the carboxyl peak from 1600 to 1594 cm⁻¹ for Alg-1, to 1583 cm⁻¹ for Alg-2, and 1597 cm⁻¹ for Alg-3. The highest shift of the carboxyl absorption band (approximate 17 cm⁻¹) corresponds to Alg-2 sample. We can assume that the optimum CaCl₂ concentration for cross-linking of alginate/SLS mixture is an intermediate value between 1 wt % and 10 wt %, more precisely 5 wt%.

The band (-CH) at 1413 cm⁻¹ is also shifted to lower wavenumbers for all the samples.

The characteristic peaks of SLS from 1085 cm⁻¹, 1250 cm⁻¹ and 1220 cm⁻¹ (SO₄) are masked by the absorption bands of alginate [23].

We found also that the peaks of (C-O-C) are shifted from 1025 cm⁻¹ to 1022 cm^{-1} and 1023 cm^{-1} for Alg-2 and respectively Alg-3 samples.

The hydroxyl peak of porous calcium alginate/SLS has a higher wavenumber than that of the sodium alginate. They are shifted from 3255 to 3263 cm⁻¹ for Alg-1, and respectively 3256 cm⁻¹ for Alg-2 sample. In the case of Alg-3 sample (having a lamellar structure) the shifting of hydroxyl peak significantly increase from 3255 to 3319 cm⁻¹, due to a negative effect of intermolecular bond formation involving adjacent hydroxyl groups. It is probably the result of alginate conformational changes by reacting with CaCl₂ in the presence of an anionic surfactant.

3.3. Mechanism of Pollutant Adsorption

In the present study the affinity and the adsorption capacity of calcium porous alginate beads for o-nitrophenol was investigated. The beads used for the organic pollutant sorption had diameters of 700 to 900 μ m.

The ionic exchange takes place in the channels of alginate beads between guluronate blocks charges and the counter ions substrate. Because of this positive charge of the investigated pollutants, we suppose that the sorption process is similar to the metal ion uptake [10].

A schematic diagram of the o-nitrophenol adsorption is shown in the Fig. 5. According to the "egg-box" model of gelation mechanism [18] each "cavity" formed in the alginate gel can trap the cationic contaminant (NP) by involving the carboxyl groups from participating uronate residues. The hydroxyl groups, not shown in the figure, serve to stabilize the formed contaminant-alginate complex.



Fig. 5. Schematic diagram of the contaminant adsorption by calcium alginate beads. (1) calcium bound; (2) Na^+ ions that remains in the gel to balance the unoccupied carboxyl groups; (3) free, unbound Ca⁺² ions in the gel phase; (4) free, unbound cationic contaminants in the gel phase; dashed lines electrostatic represent interaction between NP and unoccupied carboxyl groups.

3.4. Effect of pH on Pollutant Adsorption

The experimental data obtained at various pH values of the medium, at 45 hours after the reaching the equilibrium, are shown in the Fig. 6. The effect of the pH on the removal efficiency was studied in the pH range of 1.5 to 7.5. The uptake of contaminants shows reduced values at low pH, and increases with increasing pH in the range of 4 to 7. The data show that the efficiency for all the removal process of the cationic contaminants is strongly dependent of the pH value. The sorption of o-nitrophenol is low (between 5–15%) in the range of pH = 1.5–3, for all the samples. A significant increase of the contaminant adsorption (about 40–45%) appears at pH above 4, and the maximum value is reached at pH = 7. For further increase of pH value the curve show a slight decrease. The results are consistent with the explanation that increasing of pH, the charged sites of the Ca-Alg porous beads becomes more negative.



Fig. 6. Influence of pH on NP adsorption for different types of porous Ca-Alg beads, at two contaminant initial concentrations: 2×10^{-5} M (empty symbols) and 10×10^{-5} M (black symbols).

3.5. Influence of Adsorbent Dosage on the Efficiency of NP Removal

The adsorption experiments were conducted to obtain information of NP adsorption efficiency by dry porous calcium alginate beads varying the pollutant initial concentration from 2×10^{-5} to 10×10^{-5} M, and the amount of the Ca-Alg beads (samples Alg-1, Alg-2 and Alg-3). The obtained results are presented in the Figs. 7a, b and c.

We observe that the NP retention increases with the quantity of beads, and it is dependent of the initial pollutant concentration. By using a quantity of 0.22 g of Alg-2 and Alg-3 porous calcium alginate beads, the pollutant removal is significant, reaching 94–95%. These results are good enough compared to previous adsorption experiments performed on non-porous Ca-Alg gel beads, when maximum removal reached was only 55–59% [12].



Fig. 7. Effect of Alg-1(a) Alg-2 (b) Alg-3 (c) quantity on the efficiency of NP adsorption, for different initial contaminant concentrations, at pH = 7.

3.6. Kinetics Experiments

The kinetics of adsorption is important in order to evaluate the qualities of the adsorbent and its efficiency of pollutant removal. The NP adsorption versus time was determined for various amounts of dried porous alginate beads (Fig. 8).

The biggest amounts of adsorbed pollutant were obtained for quantities of 0.22 g porous calcium alginate beads, and for the Alg-2 samples.



Fig. 8. Adsorption of NP versus time, for different quantities of porous Ca-Alg beads. Samples: (a) Alg-1, (b) Alg-2, (c) Alg-3.

The Fig. 8 depicts the kinetics of the NP adsorption, which has three different stages. In the initial stage, occurring in the first 15 hours, a sharp increase of the adsorption is observed. It indicates that the pollutant is adsorbed at the exterior of the beads. In the second stage, from 15 to 45 hours, a slow adsorption process is noticed, and is probably due to the diffusion of the pollutant into the beads pores, when reaching the equilibrium. In the last stage, beyond 70 hours, the uptake of the NP is very small or remains constant. It is the result of solid biopolymer sorbent saturation by the solute.

3.7. Adsorption Isotherms

The adsorption at equilibrium is usually described by an isotherm equation characterized by specific parameters, which express their surface property and the affinity of the sorbent. In the case of o-nitrophenol adsorption onto porous calcium alginate beads, we have investigated which of the two classical models, Langmuir or Freundlich can be applied to our system.

3.7.1. Langmuir adsorption

The Langmuir model is expressed according to the equation [24]:

$$Q_e = \frac{K_L QmC_e}{1 + K_L C_e} \tag{1}$$

where:

Qe (mg/g) - the amount of adsorbed on beads at the equilibrium;

Ce (mg/L) - the concentration of sorbate in solution;

Qm (mg/g) - the maximum sorption capacity corresponding to complete monolayer coverage;

K_L (L/mg) - the Langmuir constant related to energy of adsorption

The above equation can be rearranged to the following linear form:

$$\frac{C_e}{Q_e} = \frac{1}{K_L Qm} + \frac{C_e}{Qm}$$
(2)

A plot of Ce/Qe versus Ce with linear shape, confirm the applicability of the Langmuir adsorption model. The Langmuir constants Qm and K_L can be evaluated from the slope and intercept of linear equation. The Langmuir model assumes monolayer adsorption on a surface with a finite number of identical adsorption sites [25].

The isotherm was found to be linear over concentration range from 2×10^{-5} to 10×10^{-5} M, and the correlation coefficient was $R^2 = 0.948$. Estimated values for the Langmuir constant was $Q_m = 93.45$ mg/g.

The value of the correlation coefficient is satisfactory and shows that the adsorption of NP onto porous alginate beads is not so precisely described by Langmuir equation, probably due to the heterogeneity of the adsorption sites of the calcium alginate.



Fig. 9. Langmuir isotherm for NP adsorbed onto porous Ca-Alg beads.

3.7.2. Freundlich adsorption

The Freundlich model is an empirical equation, based on the sorption onto heterogenous surface [26]:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{3}$$

where:

 $K_F(L/g)$ - the Freundlich constant related to the adsorbent capacity; n - a constant that depends on the adsorption intensity.

If the n value is greater than 1, represent favorable sorption conditions, and it may be attributed to molecular interactions between sorbent and sorbate.

This equation can be represented as:

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

The Freundlich constant (K_F) and the exponent (n) are calculated from the intercept and slope of the plot of log qe versus log Ce.

The experimental data shows that the correlation coefficient is good ($R^2 = 0.998$), indicating that the adsorption isotherm of NP can be described by Freundlich equation.

The sorption isotherms parameters for the two models are presented in the Table 1.

Langmuir model			Freundlich model		
$Q_m (mg/g)$	$K_L(L/mg)$	R^2	$K_F (L/g)$	n	R^2
93.45	0.173	0.948	1.605	1.047	0.998

Table 1. Isotherm constants and correlation coefficients

The isotherms parameters show that there is a better correlation of the adsorption with Freundlich model than Langmuir model.

4. Conclusions

Porous beads with a 3-D interconnected pores and lamellar structures were obtained from sodium alginate in the presence of SLS as foaming agent, NaCl as porogen agent and $CaCl_2$ as cross-linker.

The size of the pores and the structure of alginate beads are influenced by the concentration of calcium ions. By changing the calcium ions concentration, a variation of pore dimension and morphology was evidenced by SEM.

The FTIR and SEM analysis reveal that the optimum concentration of $CaCl_2$ for cross-linking the alginate/SLS mixtures (to obtain the largest adsorption surface) is of 5 wt%. We found that the matrix of calcium alginate/SLS is lamellar for 10 wt% CaCl₂.

The increasing of calcium alginate/SLS porous beads quantity leads to increased adsorption efficiency of the pollutant.

The o-nitrophenol was adsorbed onto calcium alginate beads in three stages. In the first stage reveals a sharp increase in the adsorption process up to 60%. Although in the second and third stage of the process is slow, it is adsorbed 95% of the contaminant.

The kinetic experiments show that NP adsorption onto porous calcium alginate/SLS beads obeys the Freundlich equation.

Acknowledgements. This research was supported by Romanian Academy, *Ilie Murgulescu* Institute of Physical Chemistry. The support of EU (ERDF) and Romanian Government (POS-CCE O2.2.1 project INFRANANOCHEM, No. 19/2009.03.01) and of (UEFISCDI) (Project PN-II-ID-PCE-2011-3-0916, Contract No. 177/2011) is gratefully acknowledged.

References

- [1] B.C. PAN, Y. XIONG, Q. SU, A.M. LI, J.L. CHEN, Q.X. ZHANG, Chemosphere, 51, pp. 953–962, 2003.
- [2] J. HUANG, K. HUANG, C. YAN, J. Hazard Mater. 167, pp. 69–74, 2009.

- [3] A. LI, Q. ZHANG, G. ZHANG, J. CHEN, Z. FEI, F. LIU, Chemosphere, 47, pp. 981–989, 2002.
- [4] B.C. PAN, X. ZHANG, W.M. ZHANG, J.Z. ZHENG, B.J. PAN, J.L. CHEN, Q.X. ZHANG, J. Hazard Mater., 121, pp.233–41, 2005.
- [5] K. YAMADA, T. TAMURA, Y. AZAKI, A. KASHIWADA, Y. HATA, K. HIGASHIDA, Y. NAKAMURA, J. Polym. Environ., **17**, pp. 95–102, 2009.
- [6] S.H. LIN, R.S. JUANG, J. Environ. Management, 90, pp. 1336–1349, 2009.
- [7] S. PALIWAL, M. WALES, T. GOOD, J. GRIMSLEY, J. WILD, A. SIMONIAN, Anal. Chim. Acta, 596, pp. 9–15, 2007.
- [8] ATSDR, 1998- Toxicological profile for phenol. U.S. Department of Health and Human Services CAS # 108-95-2, Public Health Service, Atlanta, GA.
- [9] J.M. LI, X.G. MENG, C.W. HU, J. DU, Bioresource Technol., 100, pp. 1168–1173, 2009.
- [10] S. BABEL, T.A. KURNIAWAN, J. Hazard. Mater., 97, pp. 219–43, 2003.
- [11] A. ELY, M. BAUDU, J.P. BASLY, M. KANKOU, J. Hazard. Mater., 171, pp. 405–409, 2009.
- [12] S. PERETZ, O. CINTEZA, Rev. Chim., 58, pp. 1129–1133, 2007.
- [13] D. ZENG, D. HU, J. CHENG, J. Environ. Protection, 2, pp. 1370–1374, 2011.
- [14] L.K. JANG, D. NGUYEN, G.G. GEESEY, Water Res., 29, pp. 307–313, 1995.
- [15] M. IORGULESCU, M. FLOREA-SPIROIU, O. CINTEZA, C. PETCU, I. NITA, Annals Univ. Bucharest, XVI, pp. 59–67, 2007.
- [16] G. KLOCK, A. PFEFFRMANN, C. RYSER, P. GROHN, B. KUTTLER, H.J. HAHN, U. ZIMMERMANN, Biomaterials, 18, pp. 707–713, 1997.
- [17] R.J. SCHMIDT, L.Y. CHUNG, A.M. ANDREWS, O. SPYRATOU, T.D. TIRNER, J. Pharm. Pharmacol., 45, pp. 508–513, 1992.
- [18] A. HAUG, B. LARSEN, O. SMIDSROD, Acta Chem. Scand., 20, pp. 183–190, 1966.
- [19] A. HAUG, B. LARSEN, O. SMIDSROD, T. PAINTER, Acta Chem. Scand., 23, pp. 2955– 2962, 1969.
- [20] H. GRASDALEN, B. LARSEN, O. SMIDSROD, Carbohydr. Res., 56, pp. 11–15, 1977.
- [21] Z. WANG, Q. ZHANG, M. KONNO, S. SAITO, Biopolymers, 33, pp. 703–711, 1993.
- [22] E. SCHETTINIA, G. SANTAGATA, M. MALINCONICO, B. IMMIRZI, G.S. MUGNOZZA, G. VOX, Resources, Conservation and Recycling, 70, pp. 9–19, 2013.
- [23] R.B. VIANA, A.B.F. DA SILVA, A.S. PIMENTEL, Adv. Physical Chem., 1, DOI:10.1155/2012/903272, 2012.
- [24] E. TORRES, Y.N. MATA, M.L. BLAZQUEZ, J.A. MUNOZ, F. GONZALEZ, A. BALLESTER, Langmuir, 21, pp. 7951–7958, 2005.
- [25] W. HAN, C. LIU, R.J. BAI Membr. Sci., 302, pp. 150–159, 2007.
- [26] C. MAHAMADI, B. MADOCHA, Am. J. Anal. Chem., 4, pp. 373–378, 2013.