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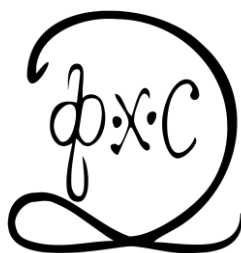
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CONTENT

<i>Volume II</i>	
<i>Organizer</i>	IV
<i>Comittes</i>	V
<i>Sponsors</i>	VI
<i>Material Science</i>	321
<i>Photochemistry, Radiation Chemistry, Photonics</i>	391
<i>Macromolecular Physical Chemistry</i>	395
<i>Environmental Protection, Forensic Sciences, Geophysical Chemistry, Radiochemistry, Nuclear Chemistry</i>	437
<i>Phase Boundaries, Colloids, Liquid Crystals, Surface-Active Substances</i>	513
<i>Complex Compounds</i>	517
<i>Food Physical Chemistry</i>	535
<i>Pharmaceutical Physical Chemistry</i>	565
<i>Index</i>	633



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Fundamental and Applied Aspects of
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and

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MODIFYING MESOPOROUS SBA-15 BY A MICROENCAPSULATION METHOD IN THE MATRIX OF SODIUM ALGINATE

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ABSTRACT

The present work represents hydrogel as a composite based on sodium alginate and mesoporous SBA-15. The hydrogel was obtained by modifying mesoporous SBA-15 by a microencapsulation method of the SBA-15 in the sodium alginate matrix. The solution of CaCl₂ provided a gelation complex of sodium alginate/SBA-15 in a rigid gel-like structure. The sodium alginate/SBA-15 hydrogels beads of about 3 mm diameter were prepared. Composite material was characterized by using powder X-ray diffraction, scanning electron microscopy and energy dispersive X-ray analysis. This composite material may have potential application in removal of metal ions – pollutants from aqueous solutions.

INTRODUCTION

Mesoporous silica materials such as SBA-15 received considerable attention because of their unique large surface area, well-defined pore size and pore shape [1, 2].

Studies have shown that remarkable surface porosity and functionality strongly affect the properties and efficiency of this material and its applications as drug and gene carrier [3, 4-7], material for enzyme loading [8] as well as material for detection and adsorption of metal ions in living systems [3, 9]. Various procedures have been employed on SBA-15 to improve its adsorption capacity [10]. However, the application of SBA-15 has some limitations due to the difficulty of incorporating functional groups on its surface. These limitations can be overcome by encapsulation of mesoporous silica with alginate.

Development of the hydrogel was driven by the idea to modify the mesoporous SBA-15 by a microencapsulation method with alginate used to protect them from degrading by surrounding them with a semi-permeable biopolymeric matrix. Microencapsulation avoids or retarding their contact with, for example, harmful environmental factors.

Alginate is extracted from various species of algae. Alginate is composed of the linear macromolecule in homopolymeric blocks of each monomer. The macromolecules are composed of (1-4)-linked β-D-mannurinate (M) and α-L-guluronate units (G). Properties like low cost, easy use, biodegradability, and biocompatibility make alginate suitable for encapsulation. In the presence of divalent cations, usually, Ca²⁺ alginate is gelling in the form of a rigid gel-like structure, by ion exchange of sodium ions from guluronic acid residues [11-13].

METHODS

Sodium alginate (SA, abcr GmbH), calcium chloride anhydrous powder (CaCl₂, 99.99 %, Sigma Aldrich), Pluronic P₁₂₃ non-ionic triblock copolymer (BASF), tetraethoxysilane (TEOS, 98%, Alfa Aesar) hydrochloric acid and (HCl, 35-38%, MACRON) were used.

The SBA-15 was synthesized according to standard procedures [14] using Pluronic P₁₂₃ as a surfactant and TEOS as a source of silica. A 4.0 g of Pluronic P₁₂₃ dissolved in 30 ml of distilled water and 120 g of 2M HCl and stirred at 35 °C for 1.5 h. The 8.5 g of TEOS was added dropwise

into the solution and vigorously stirred at the same temperature for 1.5 h. This was followed by prolonged stirring and subsequent ageing. According to the method proposed by Zhao et al. [14], the mixture was aged in two steps. Firstly, it has aged at 35 °C for 20 h and then at 80 °C for 48 h. The final product is filtered, washed with distilled water until pH was neutral, and dried at room temperature. Calcination has been carried out in flowing air by slowly increasing the temperature from room temperature to 500 °C for 8 h and holding it at 500 °C for 6 h to decompose the remaining triblock copolymer.

Fabrication of sodium alginate/SBA-15 hydrogels in the form of beads (SA/SBA-15) was done. The suspension of 1.5 g of SBA-15 powder and 15 ml distilled water was sonicated for 30 min. One and a half grams of alginic acid sodium salt (SA) was added to 110 mL of water at 35 °C while stirring. The suspension of SBA-15 was added into alginate and then homogenized on a magnetic stirrer (600 rpm) for 2 h at 35 °C.

The obtained new suspension was added in drops into CaCl₂ solution through a Pasteur pipette as the next step of synthesizing beads. Gel-type spherical beads were formed during this process. After 3 h of gelation, beads were filtrated and washed with distilled water until pH was neutral. The size of wet beads after filtration was about 3 mm (Figure 1a). After drying at 60 °C, the size of hydrogel beads was about 2 mm. Aqueous CaCl₂ solution was prepared by dissolving 0.623 g of CaCl₂ in 50 ml distilled water under stirring to neutralize the carboxyl-site covalent bond of alginate with the intention to induce inter-molecular ionic bonds between polymeric chains of alginate [11-13].

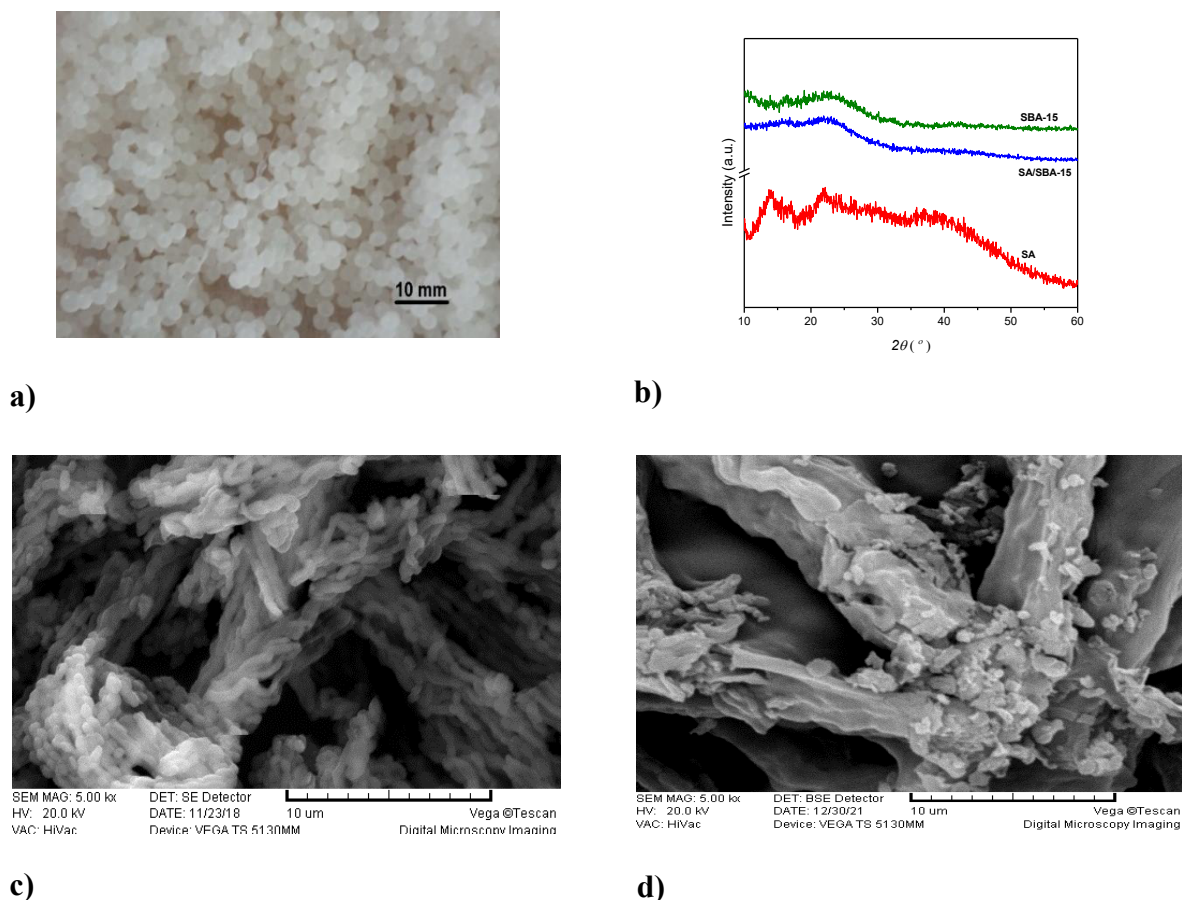


Figure 1. a) Beads of sodium alginate/SBA-15 hydrogel (SA/SBA-15), b) XRD patterns of: SBA-15, SA/SBA-15 and SA and SEM images of c) SBA-15 and d) SA/SBA-15.

X-ray diffraction (XRD) analysis of SBA-15, SA/SBA-15 and SA was performed at room temperature using Ultima IV Rigaku diffractometer, equipped with Cu $K_{\alpha 1,2}$ radiations, with generator voltage 40.0 kV and generator current 40.0 mA. The range of 10° - 60° 2θ was used in a continuous scan mode with a scanning step size of 0.02° at a scan rate of 10° /min. Microstructure analysis is performed by scanning electron microscope (SEM, VEGA TS 5130 MM, Tescan). Energy-dispersive X-ray analysis (EDS) was carried out with INCA PentaFET-x3, Oxford Instruments.

RESULTS AND DISCUSSION

The XRD patterns of SBA-15, SA/SBA-15 and SA are shown in Figure 1b. Samples SBA-15 and SA/SBA-15 exhibit a single very broad peak at about $2\theta = 23^{\circ}$, which is the characteristic of amorphous silica. In contrast, XRD of the SA pattern exhibits very broad peaks at about $2\theta = 14^{\circ}$ and 22° .

A glimpse at the SEM micrographs of SBA-15 and SA/SBA-15 and (Figure 1c and Figure 1d) discloses the presence of many rod-like agglomerates were approximately $20\ \mu\text{m}$ in length in all studied samples. As the SEM images showed, the average size of grains in all samples was about $1\ \mu\text{m}$, in which particles have placed themselves along the agglomerated ones like chains. Same chain agglomerate structures (Figure 1c) were reported in an earlier paper [15, 16].

The EDS analysis showed the chemical composition of SBA-15, SA/SBA-15 and SA. The EDS analysis demonstrated that the particles in the SBA-15 sample consist of SiO_2 . High levels of carbon (~ 36 at. %) and oxygen (~ 58 at. %) originate from gases from the air adsorbed by the surface of the SBA-15 [17].

The EDS analysis of SA and SA/SBA-15 showed the presence of C, O, Na, K and Cu in SA (Table 1.) and confirmed the presence of C, O, Si, Cl, and Ca in the sample SA/SBA-15. Elements Ca, and Cl originates from CaCl_2 solution, used as an agent for sphere formation. However, high levels of carbon (~ 22 at. %) and oxygen (~ 59 at. %) originated from SA and air adsorbed by the surface of the samples.

Table 1. Average values of the chemical composition of SA and SA/SBA-15, obtained by EDS analysis (atomic %).

Sample	C	O	Si	Na	Cl	K	Cu	Ca	Ag	Au
SA	56.38	32.56	-	10.21	0.13	0.11	0.11	-	0.08	0.35
SA/SBA-15	21.50	58.71	17.28	-	0.07	-	-	1.65	0.10	0.67

CONCLUSION

Composite hydrogel based on sodium alginate and mesoporous SBA-15 was synthesized by a microencapsulation method of the SBA-15 in the sodium alginate matrix. A gelation complex of sodium alginate/SBA-15 is a form rigid gel-like structure was provided by the solution of CaCl_2 . The sodium alginate/SBA-15 hydrogels were obtained in the form of beads of about 3 mm in diameter. The X-ray diffraction patterns of SBA-15, SA/SBA-15 and SA exhibit a single very broad peak, which is the characteristic of amorphous silica. A scanning electron microscope discloses that many rod-like agglomerates of all investigated samples were approximately $20\ \mu\text{m}$ in length. As the scanning electron microscope images show, the average size of grains of all investigated samples is about $1\ \mu\text{m}$. The Energy-dispersive X-ray analysis of the SBA-15 surface content has demonstrated that the particles in this sample are of SiO_2 . We intend to investigate the possibility of using the obtained hydrogels of sodium alginate/SBA-15 in the form of pearls to remove metal ions from an aqueous solution.

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