CHEMICAL ENGINEERING TRANSACTIONS
VOL. 47, 2016
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Angelo Chianese, Luca Di Palma, Elisabetta Petrucci, Marco Stoller

ISBN978-88-95608-38-9; **ISSN** 2283-9216
DOI: 10.3303/CET1647016

Diffusion of Nano-Particles in Gels

Boris G. Pокusaev, Sergey P. Karlov, Andrey V. Vyazmin*, Dmitry A. Nekrasov

Moscow State University of Mechanical Engineering, ul. Staraya Basmannaya 21/4, Moscow, 105066, Russia
av1958@list.ru

An optical method is used to study the diffusion in the gels. This method allows a real-time visualization of the introduced impurities spreading in gels. The decomposition of the spectrum of the passing radiation in the optical range allows one to get more information not only about the nature of the diffusion distribution of the considered impurities, but also on the state of the gel itself. This paper presents results of temporal dynamics of transparency spectrum evolution during the formation of gel from silicic acid, when there are added nano-particles of silver in the media. The diffusion these nano-particles in the true gel and the diffusion of $KMnO_4$ (given the molecular homogeneous solution with water) in the silica gel containing silver nano-particles are studied. Experimentally it is found that the presence of nano-partiles delays the shift of the wave length of the spectrum maximum of the transparency to the red range compare to true gel of silicic acid. This demonstrates that the velocity of gel formation decreases with the increase of concentration of nano-particles. At the same time the scattering light in green range of spectrum considerably increases, showing the change of the internal structure of the dispersion media. The fundamental differences in the diffusion velocity in gels between true solutions and solutions containing nano-particles are shown. A physical explanation is suggested for this phenomenon. It is observed experimentally that the diffusion of water solution of $KMnO_4$ in the gel of silicic acid containing nano-particles of silver is about the same velocity that in true gel. The obtained results could be applied for the development of a model system, which can be used for verification of the efficiency of the delivery to cells of necessary preparations in order to control their metabolism during the cells growing in bio-reactors formed 3D printing.

1. Introduction

Usually say that the gels are specific disperse systems with liquid dispersing medium, and the dispersion phase makes up a spatial structured mesh due to intermolecular interaction in the contact sites (Tokita and Nishinary, 2009; Scherer, 1999). Gels have such inherent qualities like a tendency to retain its structure, plasticity, resilience, and also thixotropy, i.e., the quality of restoring the gel original structure after mechanical destruction under isothermal conditions. Gels are micro- or nanostructured media whose internal structure depends on the material and on the method of preparation. The characteristics of gel do not remain constant over time, and can change significantly due the internal recondensation and recrystallization processes that lead to the spontaneous compaction of the dispersed phase (Weiss and Terech, 2006; Deshpande, 1992).
The presence of nano- and microchannels makes gels an exceptional tool for their use in the production of catalysts, sorbents, membrane filters, cosmetic and pharmaceutical formulations (Kajiwara and Osada, 2000). The promising application of gels is the use in regenerative medicine for growth of biological issues, including the problem of culturing stem cells in vitro (Westrin and Axelsson, 1991). These cells may serve as a starting material for the regeneration of living tissues. This capillary network is intended for the delivery of nutrients to individual cells, and to remove products from the metabolism. One of the solutions to this problem is to create a synthetic gel matrix with ordered spatial system of nano-channels. It seems promising the idea that gels can used as a carrier during the formation of ordered bio-structured elements (based on the 3D printing) for additive medical technology. This involves the formulation and the solution of fundamental problems of transport phenomena in micro-and nano-porous gels (Amsden, 1998).
The application of gels containing of nano-particles is very broad. For example, using of nano-particles as fillers in the preparation of nano-composite of polymers has drawn much attention, due to the increased demand for new materials with improved thermal, mechanical, physical, and chemical properties. Recent

Please cite this article as: Pokusaev B., Karlov S., Vyazmin A., Nekrasov D., 2016, Diffusion of nano-particles in gels, Chemical Engineering Transactions, 47, 91-96 DOI: 10.3303/CET1647016

developments in the synthesis of mono-dispersed, narrow-size distribution of nano-particles by sol-gel method provide significant boost to development of polymer nano-composites (Rahman and Padavettan, 2012). Gels are used in electrophoresis for separation of nano-particles by shapes and size for production of calibrated nano-materials (Hanauer et al., 2007). Recently Rose et al. (2014) show that strong, rapid adhesion between two hydrogels can be achieved at room temperature by spreading a droplet of a nano-particle solution on one gel's surface and then bringing the other gel into contact with it. There is a result (Sorokin et al., 2013) that in the media with silver salts on the surface of life cells there is a generation of silver nano-particles, the number and the size of particles characterize the cells metabolism. These problems emphasize the necessity of the study of interaction of the process of the transfer of nano-particles and liquid phase in gels of different nature.

At present, it seems that the diffusion processes (including diffusion of Brownian particles) in homogeneous liquid media are well studied and understood (Philibert, 2006). However, this is only true in the case of stationary processes and in some simple cases of the unsteady processes. There are a number of different factors that influence diffusion transport in homogeneous media and change classical mass-transfer laws, which follow from Fick's law or from Einstein's formula (Pokusaev et al., 2015a). For example, it has been experimentally established that the unsteady mass-transfer rate in horizontal channels filled with homogeneous liquid depends on the channel width and significantly exceeds the value corresponding to pure diffusion. This movement is caused by the longitudinal pressure gradient that arises when the density of a diffusing substance exceeds the density of the mass-transporting medium. In addition, this is due to the presence of surface forces and is capable of changing the rate of convective flow.

Factors that complicate the diffusion transport can appear also in micro structured media, such as gels. In addition, the transfer processes in gels have such features as nonstationarity, anisotropy and so on; they are determined the nature, structure, and behavior of transfer medium (Muhr and Blanshard, 1982; Amsden, 1998). For example, the selective interaction of the diffusible component with microstructural elements of gel was found (Pokusaev et al., 2015b). The equations of different degree of validity for the calculation of diffusion coefficients in gels are suggested (Lauffer, M., 1961). Nevertheless, it has been increasingly realized that mass-transfer laws in the micro structured media are described by the relationships, which differ from Fick's law, even when it is used with the effective diffusion coefficient (Neuman and Tartakovsky, 2009).

Big difference for diffusion velocity in gels with true solutions and with solutions with nano-particles was found (Pokusaev et al., 2013). For this type of systems the critical aspect is the effect of solute size in comparison with inner scales of microchannels within the transfer medium (Ozturk et al., 2010).

The goal of this paper was experimental study of the formation kinetic and diffusion in gels containing nano-particles by optical methods. The nano-particles change the internal structure of the gel leading to a change in its properties. Gel is micro- and nanoporous medium; therefore, it is natural to expect a difference for diffusion velocity for true solutions and solutions with nano-particles. However, this difference in diffusion velocities of solutes in gels has not been studied yet. Properties containing nano-particles gels as a media for mass transfer of true solutions are particularly interesting.

2. Investigation objects and methods

For experimental study we used gels on the basis of silicates. Such gels are well investigated (Shabanova and Sarkisov, 2012), simply prepared, not toxic, and are stable on times of diffusion. Gels of different density were produced. The stock solution of sodium silicate was diluted with distilled water to the levels of density 1.04, and 1.08 g/cm^3. The gel-generating mixture was prepared by adding the hydrochloric acid to the salt solution, and the mixture pH was adjusted to the range 3.5 – 4.5. The density of silicate solution was controlled by refractometry method through measuring the refractive index with the Abbe refract meter. Since the gel structure might be time-variable, we used only "aged" gels (with lifetime more 24 hours) for study of transfer processes.

A 3 % aqueous solution of potassium permanganate ($KMnO_4$) that forms a true solution, i.e., forms a mixture on the molecular scale with water, was used as a diffusing substance. The color of the specified compound even in low concentrations contrasts well with water and gel that allows one to obtain high-contrast images of the mass-transfer and to observe the displacement of isoconcentration surfaces on them with good accuracy.

Nano-particles of silver are used in the experiments. These particles are stabilized in the form of colloidal solution. The initial solution has mass concentration of nano-particles 4000 ppm. The distribution of nano-particles in sizes is close to the normal distribution. The minimum size is 4 nm, the maximum one is 17 nm. The distribution maximum corresponds to particles with size 9 nm and their mass fraction is 21 %. During the preparation of the gel containing nano-particles, these particles initially added to the liquid sodium silicate. Thereafter hydrochloric acid is added to the mixture for forming of the gel.

To solve the problems that arise during the study of the unsteady mass-transfer processes in macro- and microsystems, the optical methods are widely used. For example, the pattern of hydrodynamic flows during laser heating (Karlov et al., 2013) can be investigated with their use. The optical methods allow one to

visualize the mass transport in the real time conditions, to determine directly the macrokinetic coefficients, and to connect their values with the parameters that characterize the internal structure medium. The optical method was successfully applied for the determination of mass transfer coefficients in gels formed by the dispersion and dispersed phases of different nature (Pokusaev et al., 2013; Helseth, 2011). Bright dyes of various compositions were used in this case to visualize the distribution front of a diffusing substance. Dye visualization is not a unique method for investigating gels; for example, the fluorescent spectroscopy methods as well are widely applied for these purposes (Liu et al., 2004; Michelman-Ribeiro et al., 2007).
For investigation of the kinetics of gel formation with nano-particles and the diffusion transfer the spectroscopic method is used. This method analyses the form of spectrum of transparent, reflected and scattered light of the sample. The experimental setup diagram is shown in Figure 1. The illumination system (1) is made by using of a light source EcoVis (Ocean Optics) with color temperature of 2400 K and emitted light waves in the range of 400 – 2500 nm. For illumination of the sample (2) and receiving of the light signal (5) the optical fiber (Ocean Optics) of 0.1 mm and 0.4 mm diameters are used. These optical fibers work in the range of wavelengths of light from 220 to 1000 nm. Optical system was focused in device for scanning the gel samples (6). The experimental setup has a devise preparation and submission of initial solutions for gel (4) into the measure cuvette. This cuvette (3) is made of quartz glass and it is transparent to full operating range of light. The registration system (8) is able output and analyzes the spectra during the gel formation.
The spectrophotometer (7) USB2000+ (Ocean Optics) including Sony ILX511 2048-element linear silicon CCD array detector is the basis of the experimental setup. These devices provide the instantaneous registration of 2048 channels in spectral range of 200 – 1100 nm. The optical resolution is in average 1.0 nm. The diffused light at 435 nm is less than 0.1 %.

3. Results and discussion

The data obtained from the spectrum of the passing light through the simple are analyzed. The spectrum of the light setup with an empty cuvette is taken as a basis. For the investigation of temporal dynamics of process it is easier to use relative spectra, i.e. related to the basic spectrum.
Characteristic shapes of spectra during the gel formation without nano-particles at different times are shown at Figure 2. The reference time corresponds to the moment of adding in initial mix of the hydrochloric acid. The intensity of the passing light through the sample during the gel formation decreases for all wavelengths, meaning that the optical density of the media increases. This demonstrates the process of the formation of a new dispersed phase. During this formation the absorption and scattering of the green and blue lights (the range of light waves from 480 to 540 nm) considerably increases, the passage of the red light (the range of light waves from 800 to 900 nm) through the sample decreases slightly. The maximum of wavelength of the passing light shifts to infrared range during the gel formation.
For the gel formation of the same density containing silver nano-particles the temporal dynamics of changes in the spectra of the relative intensity of the passing light is similar to that described above. Experimental data on the comparison of rates of formation of different gels are shown in Figure 3. Presented relations are obtained for the light wavelength of 610 nm, corresponding to the maximum of the lighting system spectrum.

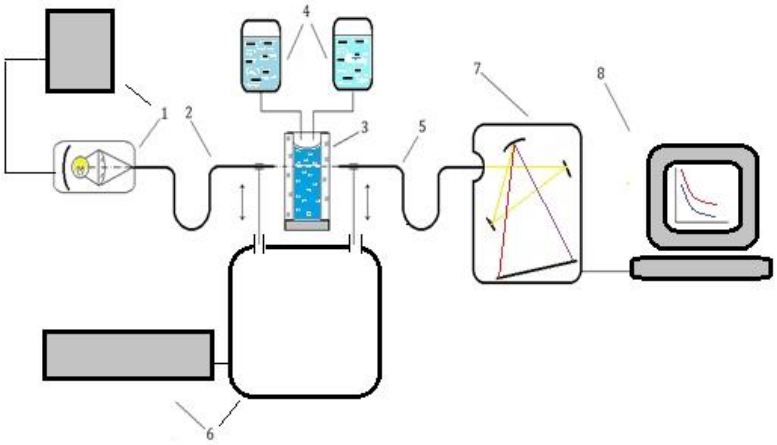

Figure 1: Experimental setup diagram: 1 - illumination system, 2 - supply fiber-optic cable, 3 - sample of the gel,4 - device preparation and submission of initial solutions for gel, 5 - receiving fiber-optic cable, 6 - device for scanning the sample gel, 7 - fiber-optic spectrophotometer USB2000+, 8 - the block of registration and processing of spectra.

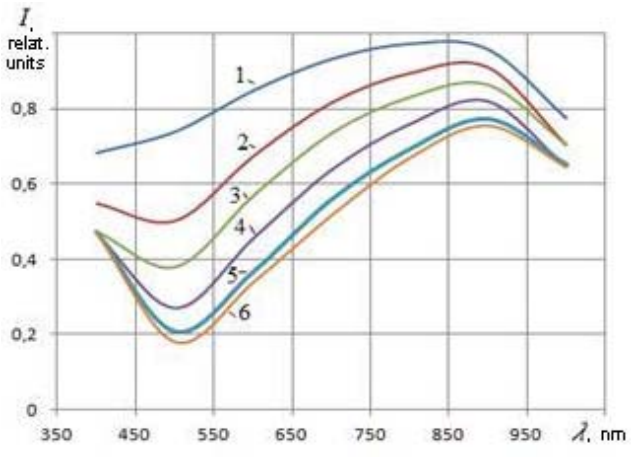

Figure 2: The time evolution of the spectrum of the passing light through the true gel of 1.08 g/cm^3 density: I is the related intensity of the passing light to the light transmittance of the optical system; λ is the wavelength. The curves correspond to spectra at various times: 1 – 20 s; 2 – 40 s; 3 – 60 s; 4 – 120 s; 5 – 300 s; 6 – 600 s.

The graphs show in the presence of nano-particle formation of the gel is almost twice slower. It is seen that the rate of gel formation is dependent on the concentration of nano-particles. It is found that the degree of influence of nano-particle concentration on the rate of gel formation is dependent on the density of the gel. The reason is that at the initial stage of gel formation the silver nano-particles prevent the establishment of normal interatomic relations in the polycondensation of silicic acid, switching them over itself. This slows down the process of formation of the dispersed phase. Large time the process of polycondensation is restored.

At the end of the gel formation the optical density of the gel with nano-particles increases compare to the true gel. The dispersed phase changes its properties due to the fact that a part of the space in the gel pores is occupied by nano-particles. The fractal dimension of the dispersed system increases, which follows from the photos of the scattering of monochromatic light green laser on different samples of the gel shown in Figure 4. In the presence of nano-particles of speckle pattern of the gel under the scattering of light on objects smaller than the wavelength it becomes much denser. This situation corresponds to the complexity the structure of the dispersed phase.

The diffusion process of $KMnO_4$ solution and silver nano-particles for the case of vertical diffusive motion of solutes through a sodium silicate gel with a concentration 1.08 g/cm^3 was studied. The diffusion of $KMnO_4$ solution in the gel matrix takes place with a high velocity; the diffusive smearing of interface is visible, and the visual pattern of diffusion fits the classic idea of diffusion dynamics. As for diffusion of nano-particles in gel, their diffusion velocities are close; the smearing of interface for nano-particles is visible. The difference in diffusion coefficients of true solution ($KMnO_4$) and nano-particle suspension is determined by a difference in sizes of transported particles, which are critical for particle-matrix interaction.

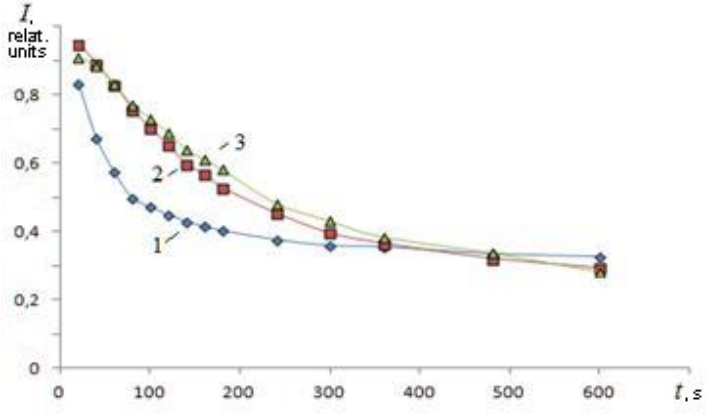

Figure 3: The dependence of relative intensity of passing light I thought different gels on time t at the wavelength 610 nm, 1 - true gel with density 1.08 g/cm^3 , 2 - the same gel containing nano-particles with concentration of 55 ppm; 3 - the gel containing nano-particles with concentration of 110 ppm.

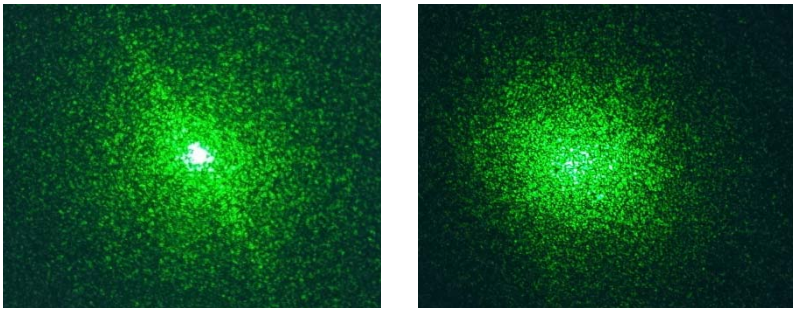

Figure 4: The scattering of light of green laser with wavelength of 532 nm on the gel with the density of 1.08 g/cm^3 (on the left) and on the same gel containing nano-particles with concentration of 110 ppm (on the right).

The Einstein formula for the diffusion of a Brownian particle (and nano-particles suspended in liquid belong to this class) tells that the diffusion coefficient is inversely proportional to the hydrodynamic drag of a particle in viscous fluid. We know that the nano-particle size is about the size of structural mesh of the gel (or possibly bigger), this drag force may be rather high and it prevents spreading of nano-particles in gel (on the molecular level for $KMnO_4$ diffusion, this makes impact on the value of transfer coefficient due to reduction of molecular mobility).

The visual observation for diffusive front is good for qualitative study only. A more accurate approach is an experiment on measuring the relative transmittance of light through the gel. The data on diffusion of $KMnO_4$ in the gel and same gel with silver nano-particles are plotted in Figure 5, where we have shown the dynamics of light transmittance for a diffusive component at different points of the sample (gel is on the right, and solvent is on the left). Spectral studies demonstrated that measurement of diffusion in microstructure medium with a moving boundary method gave close values for diffusion coefficient for true gel and gel with nano-particles.

A Figure 5 show that gels with a high density (1.08 g/cm^3 unlike 1.04 g/cm^3) has non-uniform longitudinal structure along the length of the cuvette. In experiments, this structure appears in the form of oscillations the intensity of light transmitted through the sample. This can be explained by sedimentation of the gel dispersed phase under the influence of gravity force during the gel formation. The nano-particles makes dispersed phase more dense and homogeneous, but do not alter the characteristic scales of gel pores. This is confirmed by a small change in the diffusion velocity of solution through true gel and gel with nano-particles.

4. Conclusions

Addition into the gel solution of nano-particles leads to the increase of the time of the gel formation. The process rate depends on the concentration of nano-particles and decreases with the increase of the concentration. Effect of nano-particle concentration on the kinetics of gel formation depends on the density of the gel. The gel with nano-particles changes its properties; the structure of the dispersed phase becomes denser and more complex due to the presence of nano-particles.

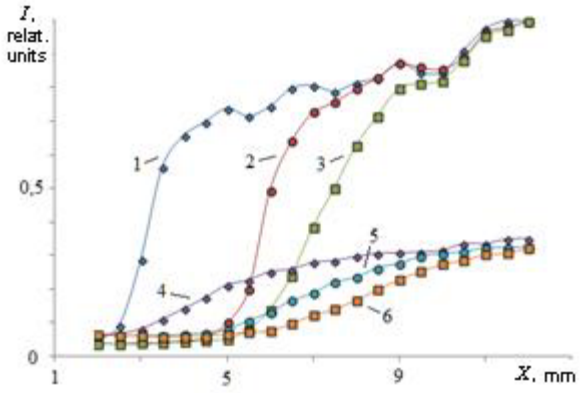

Figure 5: Spectral-revealed curves of $KMnO_4$ solution movement in the true silica gel and gel with nano-particles: X is the distance from the initial solute front while diffusion into the gel; I is the relative transmittance intensity of light with wavelength 610 nm (the transparency in true gel corresponds to 1, the complete absorbance stands for 0). Position of diffusion front: 1, 4 - initial, 2, 5 – 10 min., 3, 6 – 20 min. Dispersed medium: 1, 2, 3 - gel with a density 1.08 g/cm^3, 4, 5, 6 – gel with nano-particles concentration of 15 ppm.

Spectral diffusion studies show that although the gel with silver nano-particles is optically denser, the diffusion velocity of true solutions (for example, $KMnO_4$) is only slightly less than in an ordinary gel of the same density. Though the nano-particles change the structure of the gel, they hardly affect the pore characteristics, providing mass conductivity of the gel by diffusion. Injection of nano-particles in the gel aligns its longitudinal inhomogeneity of density appeared at the moment of the gel formation by sedimentation of dispersed phase during forming time under the action of gravity.

Acknowledgments

This work was supported by the Russian Science Foundation (project no. 15-19-00177).

Reference

Amsden B., 1998, Solute diffusion within hydrogels: mechanisms and models, Macromolecules, 31, 8382-8395.

Deshpande R., 1992, Pore structure evolution of silica gels and microstructural dependence of its properties, PhD dissertation, University of New Mexico, Albuquerque, USA.

Hanauer M., Pierrat S., Zins I., Lotz A., Sönnichsen C., 2007, Separation of nanoparticles by gel electrophoresis according to size and shape, Nano Letters, 7, 2881-2885, DOI: 10.1021/nl071615y.

Helseth L.E., 2011, A simple experiment for visualizing diffusion, Eur. J. Phys., 32, 1193-1197.

Kajiwara K., Osada Yo., Eds., 2000, Gels Handbook. Four-Volume Set, Elsevier, Amsterdam, Netherlands.

Karlov S.P., Kazenin D.A., Vyazmin A.V., Pirogova O.V., Okhotnikova K.A., 2013, Convection during the fluid heating by laser emission, Chemical Engineering Transactions, 32, 565-570, DOI: 10.3303/CET1332095.

Lauffer M., 1961, Theory of diffusion in gels, Biophys. J., 1, 205-213.

Liu J., Chen L., Li L., Hu X., Cai Y., 2004, Steady-state fluorescence study on release of camptothecin from agar hydrogel, Int. J. Pharm., 287, 13–19.

Michelman-Ribeiro A., Horkay F., Nossal R., Boukari H., 2007, Probe diffusion in aqueous poly(vinylalcohol) solutions studied by fluorescence correlation spectroscopy, Biomacromolecules, 8, 1595-1600.

Muhr A.H., Blanshard J.M.V., 1982, Diffusion in gels, Polymer, 23, P. 1012-1026.

Neuman S.P., Tartakovsky D.M., 2009, Perspective on theories of non-Fickian transport in heterogeneous media, Adv. Water Resour., 32, 670-680.

Ozturk S., Hassan Ya.A., Ugaz V.M., 2010, Interfacial complexation explains anomalous diffusion in nanofluids, Nano Letters, 10, 665-671.

Philibert J., 2006, One and half century of diffusion: Fick, Einstein, before and beyond, Diffusion Fundamentals, 4, 6.1-6.19.

Pokusaev B.G., Karlov S.P., Vyazmin A.V., Nekrasov D.A., 2013, Peculiarities of diffusion in gels, Thermophysics and Aeromechanics, 20, 749-756.

Pokusaev B.G., Karlov S.P., Vyazmin A.V., Nekrasov D.A., 2015a, Peculiarities of unsteady mass transfer in flat channels with liquid and gel, Theoretical Foundations of Chemical Engineering, 49, 798-807.

Pokusaev B.G., Karlov S.P., Vyazmin A.V., Nekrasov D.A., 2015b, Diffusion phenomena in gels, Chemical Engineering Transactions, 43, 1681-1686, DOI: 10.3303/CET1543281.

Rahman I., Padavettan V., 2012, Synthesis of silica nanoparticles by sol-gel: size-dependent properties, surface modification, and applications in silica-polymer nanocomposites - A review, Journal of Nanomaterials, ID 132424, DOI: 10.1155/2012/132424.

Rose S., Prevoteau A., Elzière P., Hourdet D., Marcellan A., Leibler L., 2014, Nanoparticle solutions as adhesives for gels and biological tissues, Nature, 505, 382-385, DOI: 10.1038/nature12806.

Scherer G.W.,1999, Structure and properties of gels,Cement and Concrete Research, 29, 1149-1157.

Shabanova N.A., Sarkisov P.D., 2012, Sol-gel Technology. Nanodispersed Silica. Binom. Moscow, Russia (in Russian).

Sorokin V.V., Skladnev D.A., Volkov V.V., Tereshchenko E.Yu., Mulukin A.L., Gal'chenko V.F., 2013, The pathways of silver nanoparticles formation by Mycobacterium smegmatis, Doklady Biological Sciences, 452, 325-328.

Tokita M., Nishinary K., Eds., 2009, Gels: structures, properties, and functions. Fundamentals and applications, Progress of Colloid and Polymer Science, 136.

Weiss R.G., Terech P., 2006, Molecular Gels: Materials with Self-Assembled Fibrillar Networks. Springer Science & Business Media, Amsterdam, the Netherlands.

Westrin B.A., Axelsson A., 1991, Diffusion in gels containing immobilized cells: a critical review, Biotechnology and Bioengineering, 38, 439-446.