IRON-CONTAINING POLYMETHYLSILSESQUIOXANE HYDROGELS AS POLYMER BASES FOR SORBENTS OF HYDROGEN SULFIDE FROM ENVIRONMENT

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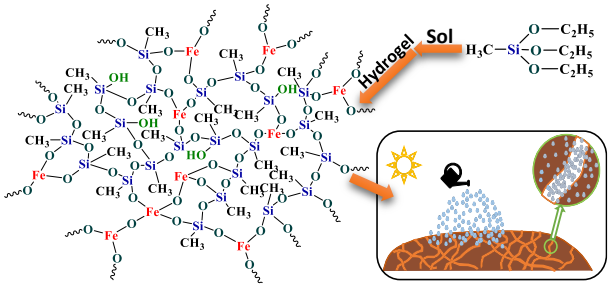
Cite this: *INEOS OPEN*, **2019**, *2 (4)*, 140–144
DOI: 10.32931/io1920a

Received 26 August 2019,
Accepted 1 November 2019

http://ineosopen.org

Abstract

Different methods for production of iron-containing polymethylsilsesquioxane hydrogels are presented. Their sorption properties towards hydrogen sulfide are studied. The structures of the resulting polymethylsilsesquioxane gels are assigned based on the data of high-resolution solid-state NMR spectroscopy.



Key words: polymethylsilsesquioxanes, hydrogels, sorbents.

Introduction

Different issues of environmental protection are actively coming to the forefront of modern life. Nowadays, humanity needs to develop new approaches for cleaning up the environment from technogenic pollution. Among a great variety of sorbents, such as activated carbons [1–4], numerous silicas [5–7], cross-linked polystyrenes [8–11], *etc.*, of particular interest are polymethylsilsesquioxanes (PMSSOs). They are amphiphilic and can be successfully used for the sorption of both organic and inorganic impurities. Furthermore, polymethylsilsesquioxanes are chemically resistant and absolutely safe; the materials on their base find application in medical practice for purification of the gastrointestinal tract from toxins [12, 13].

The technology of production of PMSSOs is based on hydrolytic polycondensation of methyltrichlorosilane and its derivatives. In turn, methyltrichlorosilane results from direct synthesis along with dimethylchlorosilane, which serves as a basic monomer for the production of PDMS. Therefore, methyltrichlorosilane is essentially a waste product of mass production of PDMS.

The application of methyltrichlorosilane in the production of silicone binding agents is generally accompanied by its preliminary partial esterification for the reduction of the probability of gel formation during the synthesis of PMSSO [14]. From the viewpoint of process controllability, the most convenient derivatives of methyltrichlorosilane are methyltriethoxy- and methyltrimethoxysilanes. They were used as bases for the production of PMSSOs featuring strictly defined structures, such as dendrimers [15–17], highly branched polymers [18], and comb-like polymethylsilsesquioxanes with linear PMSSO backbones [19, 20]. Among these materials, of particular interest are PMSSO aerogels, which are close in their properties to classical silica aerogels but differ from them by the elasticity [21–24], and hydrogels, which are the main objects of the present report.

Depending on the conditions of hydrolytic polycondensation and the chemical natures of monomers, PMSSOs can be obtained in various structural forms. Figure 1 depicts different products: from PMSSO macrogels, which represent dry powders used as water repellents, to PMSSO oligomers featuring high contents of hydroxy groups, which are soluble in a water–alcohol medium [25].

Despite the extensive use of PMSSO in medicine, the structures of their hydrogels are not sufficiently studied. It is known that all of them include polycyclic siloxane sequences, in which silicon atoms contain hydroxy groups along with oxygen atoms [13]. The structural formulae mentioned in patents [13, 26] do not withstand criticism since they are not confirmed by the objective data. However, they undoubtedly contain a certain amount of hydroxy groups, which allows for their consideration as hydrogels. Drying of these hydrogels affords hydrophobic PMSSOs, which repeated conversion to the hydrogels is impossible without decomposition of the chemical structures. The ability to retain the residual hydroxy groups, which were formed during hydrolytic polycondensation of monomeric and oligomeric polymethylsilsesquioxanes, explains the paradox of practical application of PMSSOs both as hydrogels and as water-proofing agents, which seemed to defy formal logic. Hence, the presence or absence of hydroxy groups in the PMSSO structures determines their practical application and, to a large extent, their sorption properties. Sorption owing to the formation of hydrogen or chemical bonds in addition to sorption

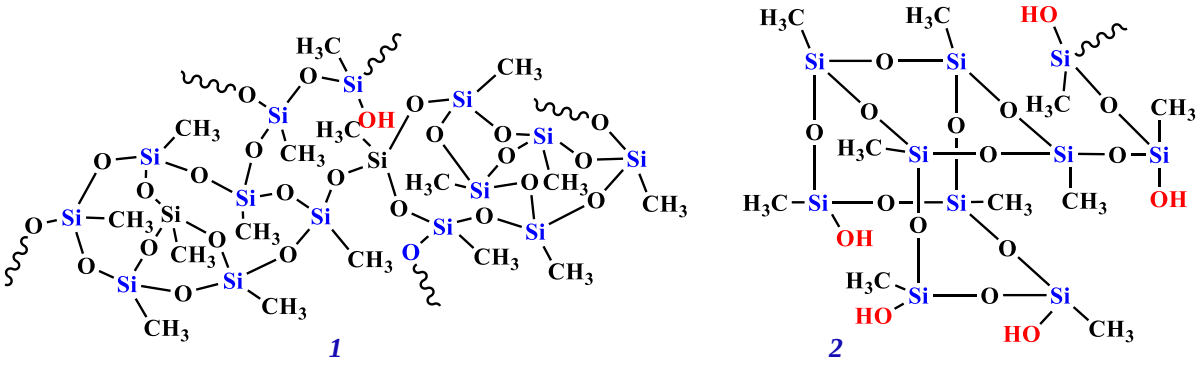


Figure 1. Formulae of PMSSO products: macrogels (***1***), oligomers with the high content of hydroxy groups (***2***).

owing to highly developed surfaces distinguishes PMSSO hydrogels from most of the analogs. At the same time, the presence of active hydroxy groups both in the formed hydrogel and, especially, during the process of its formation allows one to perform the directed modification of a hydrogel to impart some or other specific properties, in particular, selective sorption relative to those or other hazardous impurities.

It is known that the introduction of iron ions into the compositions of sorbents facilitates highly selective sorption of hydrogen sulfide [27–29], which has an irritating effect on the ocular and airway mucous membranes and central nervous system and causes negative impacts (allergic reactions and so on). Therefore, a possibility to modify PMSSO gels is an urgent task.

The goal of this work is to synthesize PMSSO hydrogels modified with iron chloride and to study their structures and sorption properties relative to hydrogen sulfide.

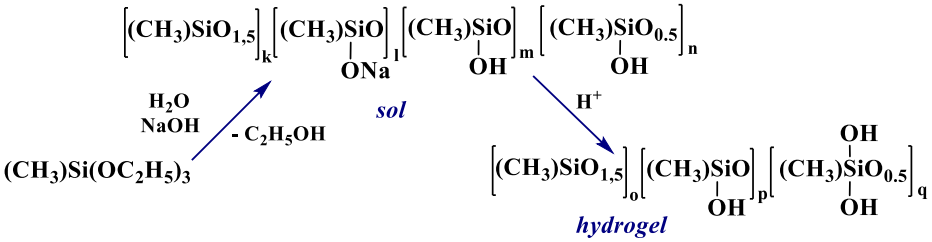
Results and discussion

The synthesis of PMSSO hydrogels from methyltriethoxysilane includes two steps: the hydrolysis and heterofunctional condensation of intermediates resulting in a PMSSO sol followed by the conversion of polyhydroxylated oligomers into a hydrogel *via* homofunctional condensation (Scheme 1).

The first step is carried out using a certain amount of an alkali, which is required to form a soluble sol of sodium methylsiliconate, analogously to the process used in the production of water-repellent compositions [14]. As well as during water proofing, a sol–gel transition occurs in the course of neutralization of the oxygen negative charge in the hydroxy groups, solvated with the aqueous alkali, which hampers the condensation. The second step includes gel aging—the final stabilization of the structure by a system of hydrogen bonds.

Separate process steps can be observed visually. A mixture of methyltriethoxysilane, sodium hydroxide, and water is rapidly homogenized under vigorous stirring. As a rule, this occurs at the moment of almost complete conversion of the ethoxy groups. Then, acetic acid is added to neutralize the charge on the Si–O bond and to initiate gel formation. In several minutes, the blurred solution forms an opalescent gel, which gradually solidifies and converts to a dense semitransparent monolithic gel.

The patent literature suggests several formulae of the final product [13, 25], which stem from general concepts in this field. The problem of establishing the real structure of a PMSSO hydrogel consists in the irreversible changes which take place during its drying for analysis. Drying and heating afford a classical PMSSO gel, which is deprived of ethoxy and hydroxy groups and fully conforms to the formula $(MeSiO_{1.5})_x$, where x tends to infinity. However, modern analytical methods enable the determination of the real structures of the sol and hydrogel in its hydrated state. Figure 2 presents the high-resolution ^{29}Si NMR spectrum of the sol in deuterated ethanol. The correlation of chemical shifts of the silicon nucleus signals with the literature data [23] and the values of their integral intensities allows one to establish that the sol represents PMSSO which structure includes a set of the following units $(MeSiO_{1.5})$, $(MeSiO(OH))$, $(MeSiO_{0.5}(OH)_2)$ and $(MeSiO_{0.5}(OEt)_2)$ in 1:2.97:1.18:0.53 ratio, respectively, with an insignificant content (4.5 mol %) of the partially hydrolyzed monomer. The content of the hydroxy groups in the resulting PMSSO gel comprises 73.0 mol % or 19.4 wt %, and that of the residual ethoxy groups—9.3 mol % or 10.2 wt %. The results obtained confirm that PMSSO formed at the sol step features a multifunctional structure with the high content of hydroxy groups, which presence stipulates the solubility of the product of methyltriethoxysilane hydrolytic polycondensation in a water–alcohol medium.



Scheme 1. Synthesis of PMSSO hydrogels.

According to the data of high-resolution solid-state ^{29}Si NMR spectroscopy, the structural composition of a PMSSO component of the hydrogel obtained by the sol neutralization with acetic acid corresponds to the following formula $(MeSiO_{1.5})_a(MeSiO(OH))_b(MeSiO_{0.5}(OH)_2)_c$, where *a:b:c=100:16:0.6*. This allows for the definition of an approximate content of the hydroxy groups in the resulting PMSSO hydrogel: 3.7 wt % or 14.8 mol %.

The modification of a PMSSO gel can be carried by three methods: treatment of the formed hydrogel with iron chloride (Scheme 2, ***Fe hydrogel 1***), introduction of iron chloride instead of the acid for neutralization of the PMSSO sol at the second step (Scheme 2, ***Fe hydrogel 2***), and application of iron chloride as a comonomer in the sol production (Scheme 2, ***Fe hydrogel 3***).

The syntheses of iron-containing PMSSOs were carried out at the Si:Fe ratio equal to 4:1 for all the methods explored. The content of iron in the final product was determined by the elemental analysis after 5–6-fold rinsing of the gel with water followed by its drying. It was found that the content of iron in the resulting sorbents does not depend on the method for hydrogel production and ranges within 11.2–11.8%. The sorption activities of the dried gels were defined by passing hydrogen sulfide, resulting from the interaction of iron sulfide with sulfuric acid. The sulfur content in the samples obtained after sorption studies was controlled by the elemental analysis.

It was established that all the hydrogels obtained can absorb hydrogen sulfide. The Fe:S ratio calculated based on the elemental analysis data for ***Fe hydrogels 1***, ***2*** and ***3*** composed 1:1.37, 1:0.60, and 1:0.46, respectively.

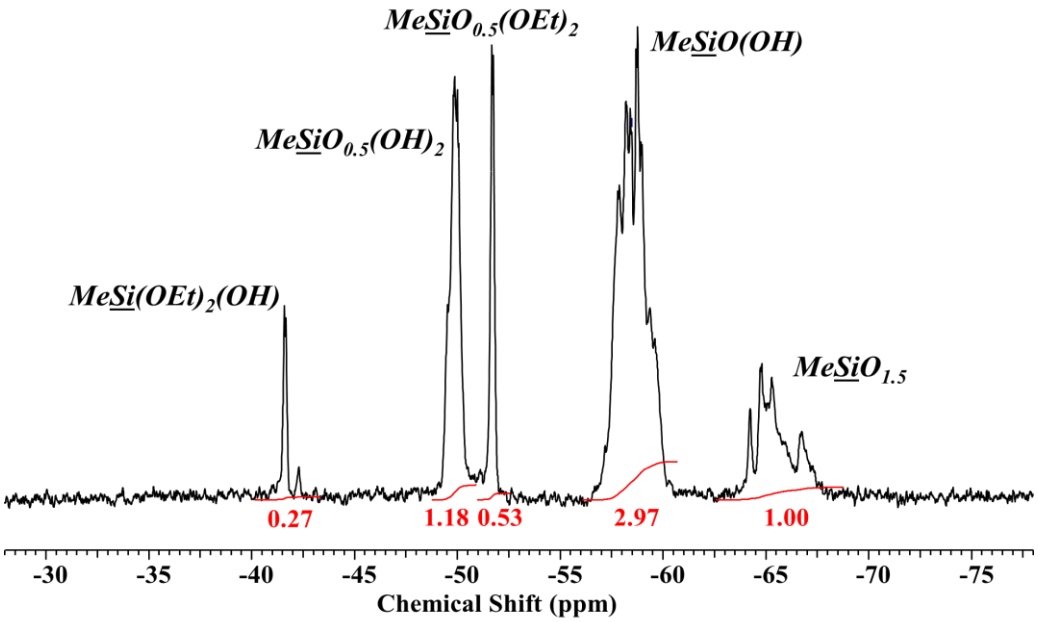
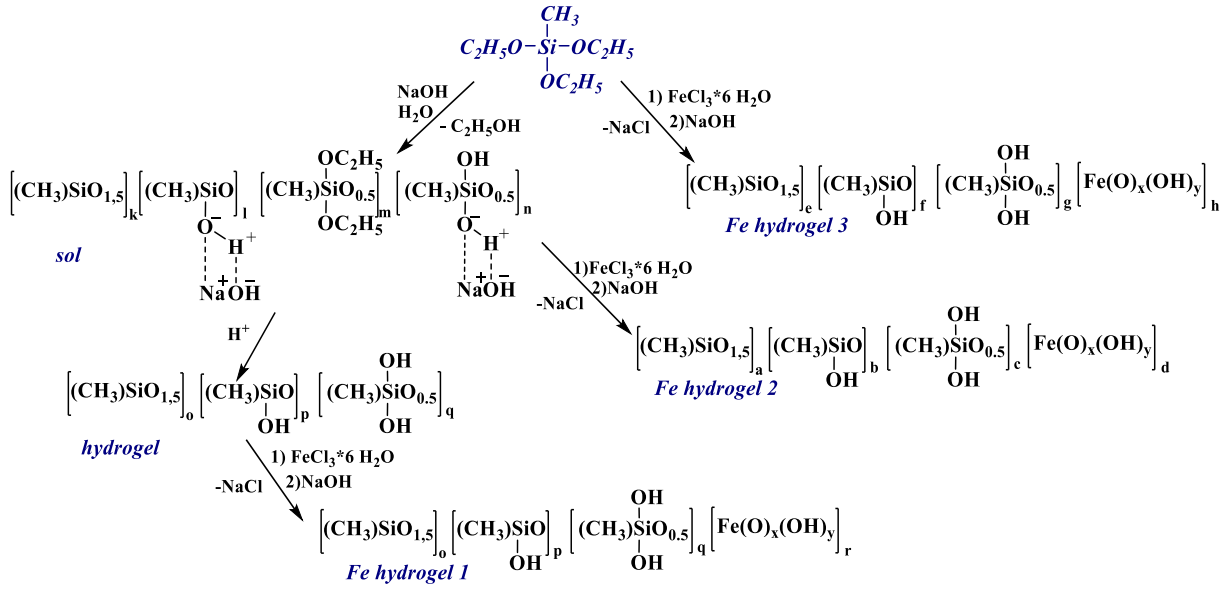


Figure 2. High-resolution ^{29}Si NMR spectrum of the resulting PMSSO sol in *d*-ethanol.



Scheme 2. Syntheses of the PMSSO hydrogels modified with iron chloride.

Such a difference in the sorption activities of the hydrogels is likely to be connected with different locations of iron in the structures of the resulting particles. Thus, in the case of ***Fe hydrogel 1***, the treatment of the preformed PMSSO hydrogel with iron chloride leads to modification of the surface of the sorbent particles, which leads to the higher availability of $Fe(OH)_x$ centers for chemical sorption. During the production of ***Fe hydrogels 2*** and ***3***, iron chloride serves as a structure-forming agent; therefore, a part of the active centers appear to be located inside the sorbent particles and, therefore, are unavailable for hydrogen sulfide. Hence, the most efficient sorbent for hydrogen sulfide is likely to be ***Fe hydrogel 1*** obtained by the modification of the preformed PMSSO hydrogel.

However, the methods for production of ***Fe hydrogel 2*** and ***Fe hydrogel 3*** seem to be more promising from the viewpoint of practical application as sorbents for landfill gases, since they can be formed *in situ* in the landfill body *via* application of their liquid precursors. In this case, the gel formation will occur in the landfill body voids, resulting in a simulacrum of sorption columns (Fig. 3).

Experimental

Materials

The work was concerned with methyltriethoxysilane (Reakhim, Russia), anhydrous sodium hydroxide (Komponent Reaktiv, Russia), hydrochloric acid of reagent grade (Khimmed, Russia), and iron(III) chloride hexahydrate (Reakhim, Russia). All the reagents were used without preliminary processing.

Methods

The compositions and structures of the PMSSO sol and hydrogel were analyzed using solid-state NMR spectroscopy. The ^{29}Si NMR spectra were registered on a Bruker Avance III 400 spectrometer. The analysis of the PMSSO sol was carried out in *d*-ethanol upon addition of $Cr(acac)_3$. The values of the chemical shifts for particular units were as follows: $MeSiOH(OEt)_2$ –41.6 ppm, $(MeSiO_{0.5}(OH)_2)$ –49.9 ppm, $(MeSiO_{0.5}(OEt)_2)$ –51.7 ppm, (MeSiO(OH)) ranging from –57.8 to –58.9 ppm, $(MeSiO_{1.5})$ ranging from –64.0 to –67.5 ppm.

The analysis of the PMSSO gel was carried out using a solid-state sensor under magic-angle spinning with the frequency of 8 kHz with cross-polarization and 1 H decoupling. The value of a chemical shift for $MeSiO_{0.5}(OH)_2$ unit composed –66.3 ppm, that for MeSiO(OH) –55.2 ppm, and that for $MeSiO_{1.5}$ –46.0 ppm.

The sorption of hydrogen sulfide by the hydrogel samples was conducted by the following method: hydrogen sulfide resulting from the interaction of iron sulfide with sulfuric acid was continuously passed through a sample of the dried gel till the constant mass. The amount of absorbed hydrogen sulfide was determined from the data of elemental analysis of the gel sample after hydrogen sulfide passing.

Syntheses

Synthesis of *Fe hydrogel 1*. A solution of sodium hydroxide (6.6 g, 0.167 mol) in water (50 mL) was added to a stirred mixture of methyltriethoxysilane (39.4 g, 0.221 mol) and 96% ethanol (25 mL). The reaction mixture was stirred for 30 min to give 112.7 g of a colorless solution of sodium polymethylsiliconate (a sol). A solution of acetic acid (6.7 g, 0.110 mol) in water (60 mL) was added rapidly under stirring. The gel obtained was left for 12 h for aging and then was rinsed on a filter to a neutral reaction (pH = 7) to yield 185.0 g of the hydrogel with 5.8% of the dry residue. Yield: 68%. Then, this hydrogel (100 g) was treated with a solution of iron chloride hexahydrate (5.84 g, 0.022 mol) in water (50 mL). The resulting solution was stirred and neutralized with sodium hydroxide (2.6 g, 0.065 mol) in water (15 mL). The resulting dark-brown gel (157.8 g) was rinsed with water (5 times; the washing waters were colorless) to give 85.8 g of the gel with 8.5% of the dry residue. Yield: 95%.

The iron content in the dried gel according to the elemental analysis data was 11.2%; the calculated value was 15.0%.

The contents of iron and sulfur after sorption of hydrogen sulfide according to the elemental analysis data were 9.0% and 13.52%, respectively.

Synthesis of *Fe hydrogel 2*. A solution of sodium hydroxide (6.6 g, 0.167 mol) in water (50 mL) was added to a stirred mixture of methyltriethoxysilane (39.4 g, 0.221 mol) and 96% ethanol (25 mL). The resulting mixture was stirred for 30 min to give 112.7 g of a colorless solution of sodium polymethylsiliconate (a sol). Then, a solution of iron chloride hexahydrate (15.0 g, 0.055 mol) in water (25 mL) was added rapidly under stirring. The resulting gel was rinsed with water (5 times) to give 93.5 g of the drained light-brown mass (the washing waters were colorless) with 24.0% of the dry residue. Yield: 100%.

The iron content in the dried gel according to the elemental analysis data was 11.8%; the calculated value was 15.0%.

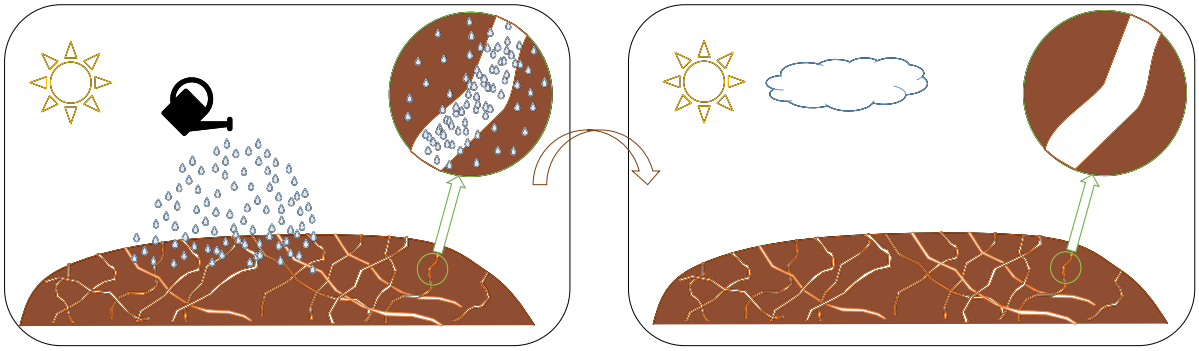


Figure 3. Schematic representation of the formation of absorbing channels based on the hydrogels obtained.

The contents of iron and sulfur after sorption of hydrogen sulfide according to the elemental analysis data were 12.4% and 7.4%, respectively.

Synthesis of *Fe hydrogel 3.* Iron chloride hexahydrate (15.0 g, 0.055 mol) was dissolved in water (6 mL). Then, methyltriethoxysilane (39.4 g, 0.221 mol) was added at room temperature. The resulting mixture was stirred without gel formation for 1 h, and then it was neutralized with a solution of sodium hydroxide (6.6 g, 0.165 mol) in water (100 mL). The resulting brown gel (157.0 g) was rinsed with water (6 times) to give 54.3 g of the gel with 33.5% of the dry residue. Yield: 92%.

The iron content in the dried gel according to the elemental analysis data was 11.8%; the calculated value was 15.0%.

The contents of iron and sulfur after sorption of hydrogen sulfide according to the elemental analysis data were 12.8% and 5.9%, respectively.

Conclusions

The performed investigation showed the possibility to use polymethylsilsesquioxanes as polymer bases for the materials assigned for purification of air. Simple chemical transformations afforded iron-containing PMSSO hydrogels which hold great promise as the sorbents for hydrogen sulfide.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research, project no. 18-29-25053, and the Ministry of Science and Higher Education of the Russian Federation.

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References

1. G. Jaria, C. P. Silva, J. A. B. P. Oliveira, S. M. Santos, M. V. Gil, M. Otero, V. Calisto, V. I. Esteves, *J. Hazard. Mater.*, **2019**, *370*, 212–218. DOI: 10.1016/j.jhazmat.2018.02.053
2. J. M. Illingworth, B. Rand, P. T. Williams, *Process Saf. Environ. Prot.*, **2019**, *122*, 209–220. DOI: 10.1016/j.psep.2018.12.010
3. M. Li, R. Xiao, *Fuel Process. Technol.*, **2019**, *186*, 35–39. DOI: 10.1016/j.fuproc.2018.12.015
4. X. Yang, Y. Wan, Y. Zheng, F. He, Z. Yu, J. Huang, H. Wang, Y. S. Ok, Y. Jiang, B. Gao, *Chem. Eng. J.*, **2019**, *366*, 608–621. DOI: 10.1016/j.cej.2019.02.119
5. K. Moeinian, S. M. Mehdinia, *Pol. J. Environ. Stud.*, **2019**, *28*, 2281–2287. DOI: 10.15244/pjoes/91044
6. M. N. Ahmed, R. N. Ram, *Environ. Pollut.*, **1992**, *77*, 79–86. DOI: 10.1016/0269-7491(92)90161-3
7. K. Y. Ho, G. McKay, K. L. Yeung, *Langmuir*, **2003**, *19*, 3019–3024. DOI: 10.1021/la0267084
8. J. Wang, L. Xu, Y. Meng, C. Cheng, A. Li, *Chem. Eng. J.*, **2011**, *178*, 108–114. DOI: 10.1016/j.cej.2011.10.022
9. I. Bekri-Abbes, S. Bayoudh, M. Baklouti, *J. Polym. Environ.*, **2006**, *14*, 249–256. DOI: 10.1007/s10924-006-0018-3.
10. M. P. Tsyurupa, L. A. Maslova, A. I. Andreeva, T. A. Mrachkovskaya, V. A. Davankov, *React. Polym.*, **1995**, *25*, 69–78. DOI: 10.1016/0923-1137(95)00021-A
11. V. A. Davankov, Z. K. Blinnikova, L. A. Pavlova, M. P. Tsyurupa, *INEOS OPEN*, **2019**, *2*, 19–24. DOI: 10.32931/io1903r
12. C. A. Howell, S. V. Mikhalovsky, E. N. Markaryan, A. V. Khovanov, *Sci. Rep.*, **2019**, *9*, 5629. DOI: 10.1038/s41598-019-42176-z
13. RU Patent 2293744, **2005**.
14. L. Khananashvili, K. Andrianov, *Technology of Organoelement Monomers and Polymers*, Khimiya, Moscow **1983** [in Russian].
15. E. Rebrov, A. Muzafarov, V. Papkov, A. Zhdanov, *Dokl. Akad. Nauk SSSR*, **1989**, *309*, 376–380.
16. A. M. Muzafarov, E. A. Rebrov, V. S. Papkov, *Russ. Chem. Rev.*, **1991**, *60*, 807–814. DOI: 10.1070/RC1991v060n07ABEH001112
17. K. Boldyrev, E. Tatarinova, I. Meshkov, N. Vasilenko, M. Buzin, R. Novikov, V. Vasil'ev, E. Shtykova, L. Feigin, A. Bystrova, S. Chvalun, A. Muzafarov, *Polymer*, **2019**, *174*, 159–169. DOI: 10.1016/j.polymer.2019.04.030
18. D. Migulin, E. Tatarinova, I. Meshkov, G. Cherkaev, N. Vasilenko, M. Buzin, A. Muzafarov, *Polym. Int.*, **2016**, *65*, 72–83. DOI: 10.1002/pi.5029
19. M. A. Obrezkova, G. S. Rogul', N. G. Vasilenko, N. V. Demchenko, A. M. Muzafarov, *Dokl. Chem.*, **2008**, *419*, 69–73. DOI: 10.1134/s0012500808030075
20. M. A. Obrezkova, N. G. Vasilenko, V. D. Myakushev, A. M. Muzafarov, *Polym. Sci., Ser. B*, **2009**, *51*, 457–464. DOI: 10.1134/s1560090409110062
21. K. Kanamori, K. Nakanishi, T. Hanada, *J. Ceram. Soc. Jpn*, **2009**, *117*, 1333–1338. DOI: 10.2109/jcersj2.117.1333
22 K. Kanamori, M. Aizawa, K. Nakanishi, T. Hanada, *Adv. Mater.*, **2007**, *19*, 1589–1593. DOI: 10.1002/adma.200602457
23. M. N. Temnikov, Y. N. Kononevich, I. B. Meshkov, M. I. Buzin, V. G. Vasil'ev, G. G. Nikiforova, A. M. Muzafarov, *Polymer*, **2018**, *138*, 255–266. DOI: 10.1016/j.polymer.2018.01.067
24. A. A. Kalinina, D. N. Kholodkov, I. B. Meshkov, M. A. Pigaleva, I. V. Elmanovich, Yu. A. Molodtsova, M. O. Gallyamov, A. M. Muzafarov, *Russ. Chem. Bull.*, **2016**, *65*, 1104–1109. DOI: 10.1007/s11172-016-1419-7
25. UA Patent 27434, **1994**.
26. G. F. Miralamov, *Pet. Chem.*, **2005**, *45*, 368–369.
27. A. Vil'danov, *Doctoral Dissertation (Eng.)*, Kazan, **1998**.
28. V. Ramm, *Absorption of Gases*, Khimiya, Moscow, **1966** [in Russian].
29. R. J. Hook, *J. Non-Cryst. Solids*, **1996**, *195*, 1–15. DOI: 10.1016/0022-3093(95)00508-0