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***У представленій роботі виконано аналіз даних по застосуванню інноваційного підходу для оптимізації процесу функціоналізації поверхні кремнезему в мікрореакторі. На основі квантово-хімічного моделювання молекулярних кластерів було встановлено особливості будови та адсорбційні властивості функціоналізованих матеріалів, що можуть бути використані у водоочистці. Для проведення синтезу таких сполук було підтверджено доцільність застосування проточного мікрореактора***

***Ключові слова: функціоналізовані кремнеземні матеріали, мікрореактор, квантово хімічне моделювання, синтез, стале виробництво, водоочистка***

***В представленной работе выполнен анализ данных по применению инновационного подхода для оптимизации процесса функционализации поверхности кремнезема в микрореакторе. На основе квантово-химического моделирования молекулярных кластеров было установлены особенности строения и адсорбционные свойства функционализированных материалов, которые могут быть использованы при водоочистке. Для проведения синтеза таких соединений была подтверждена целесообразность применения проточного микрореактора***

***Ключевые слова: функционализованные кремнеземные материалы, микрореактор, квантово-химическое моделирование, синтез, устойчивое производство, водоочистка***

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# SIMULATION OF THE PROCESS OF SILICA FUNCTIONALIZATION IN THE MICROREACTOR

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## 1. Introduction

Microreactors as a novel concept in chemical technology enable the introduction of new reaction procedures in chemistry, molecular biology and pharmaceutical chemistry. Microreactors offer several opportunities to optimize the reaction systems due to high specific interfacial area improving heat and mass transfer, the smaller working volumes, continuous mode of operation, efficient operation, low wastage of chemicals and intrinsic safety [1]. Potential advantages of microstructured reactors (MSR) allow successfully use them to complex processes for optimization and scale-up from the laboratory scope to production. These arguments give the background to discuss the realization of the functionalization process using the microreactor.

The process of silica surface functionalization is the effective approach to receive the silica-based adsorbents that are able to extract heavy metals such as mercury from water

and, as a result, have the potential for reducing water pollution and protecting ecosystems [2, 3]. The solution of a wide range of issues related to the real experiment is achieved by modeling the test object with the help of special methods and tools. That is why, it is reasonable to perform computational studies of the microreactor system as well as the structural parameters of functionalized materials. Detailed simulation studies conducted in different operation conditions provide important insights to the reaction behavior in a microsystem environment. Comparison of performances in theoretical and practical experiments has been presented in the literature for different types of reactions, which suggests the adequacy of computing and credibility of the calculated data when integrated process in a laboratory or industrial scale. Thus, modeling of the functionalization process in the microreactor is an actual trend of chemical technology that provides opportunities for the synthesis of innovative materials with prescribed properties.

## 2. Analysis of published data and problem statement

The process of silica surface functionalization opens up the possibility to design the materials for various purposes by varying the nature of the functional group. The laboratory synthesis of such compounds has already been realized in the O. O. Chuiko Institute of Surface Chemistry [2, 3]. But the experiment requires precise control of process conditions and a considerable expenditure of time and reagents that complicates the scaling of the process for production needs. Nowadays, the most promising devices for sustainable chemical synthesis are flow microreactors. Thus, it is reasonable to consider the possibility of carrying out the functionalization process in microdevices. It should also be noted that the literature is not presented studies of this process with the help of microreaction technology. So, at the first stages it is appropriate to conduct a comprehensive modelling of the reaction system.

Several definitions of methods and designing the principles of the theoretical study of microreaction systems can be found in the literature. For example, the evaluation of two different fluids molecular mixing within the micrfluidic channels with grooved surface was carried out in [4] by the solving of incompressible Navier-Stokes and convection-diffusion equations at the steady state using a CFD (computational fluid dynamics) functions of the COMSOL Multiphysics (version 3.1).

In order to analyze the complex phenomena in reactive multiphase systems, in the work [5] was proposed a film-near model as well as a micromixing model in the bulk phase. Here was used the Euler-Lagrange approach implemented in the open-source CFD-package "OpenFOAM".

Vaccaro S. and Ciabelli P. [6] presented the comparison between countercurrent and concurrent flow patterns of endothermic and exothermic reactant streams in the combustion channel. The model was consisted of the material, energy and momentum balances equations for the system under examination and contained the constitutive equations for physical-chemistry properties of the reactants species and kinetic expressions for the reactions. The model solutions were carried out by the FEM software (COMSOL Multiphysics).

Borovinskaya E. S. [7] developed a complex Kinetic program for the kinetic modeling of processes in the microreactor in case the limiting stage is the reaction kinetics. In the thesis [7] was presented the mathematical model of the phenylacetonitrile alkylation process and the modified methods of the kinetic parameters interval estimating.

However, in the recent time, the number of investigations of separation unit operations like absorption, stripping, extraction and distillation in microdevices has been increasing. Such processes can be widely used for environmental concerns in terms of water disinfection, air cleaning, etc. In this sense, the attention of worldwide research has mostly been focused on porous membranes and sieves. Cipes and Engstrom [8], for example, reported the microfluidic device with porous membranes that is able to desorbs traces of toluene from an aqueous phase. It was shown that mass transfer in the micro device was more intensive than in a conventional column. Aota et al. [9, 10] presented a micro extraction device, in which the upper half of the microchannel for the organic-phase flow was supplied with a hydrophobic surface, whereas the lower half for the aqueous-phase flow was supplied with a hydrophilic surface. As the result, it was found that the extraction performance of several theoretical stages could be achieved.

The applicability of microreaction technology was also successfully confirmed for gas-liquid systems. Hibara et al. [16] performed oxygen stripping from water with nitrogen. It was shown that more than 90 % of the dissolved oxygen could be removed within a contact time of 19s. A novel micro device for separation operations, e. g., adsorption, stripping and extraction was presented in [17]. Chasanis et al. exemplified the toluene stripping from water and developed the computational fluid dynamics (CFD) based model. This investigation demonstrated that the overall mass transfer capacity coefficients are one to two orders of magnitude higher than the coefficients for conventional packed towers.

According to the investigations described above, the development of the adequate mathematical model of the process and its implementation in the professional software package allow us to describe the conversion of reactants at a real experiment. Based on modelling data it is possible to formulate clear guidelines for the directed synthesis of functionalized materials. In this work, the structure of materials was studied by quantum-chemical modeling and the synthesis of sorbents is proposed to carry out with the help of micro-reactor in continuous mode.

## 3. Purpose and objectives of the study

The key purpose of this paper is to explore new sorption materials as well as identifying new techniques for their preparation.

In accordance with the set goal the following research objectives are identified:

– to study the adsorptive properties of functionalized silica materials with different groups by means of quantum-chemical calculations. In this paper is presented an example of modeling the silica surface functionalized with thiourea-containing fragments;

– to investigate the approaches to the modeling of different reactions and processes in microreactors with the help of special software tools. The finite purpose of this task is to develop the mathematical model of the microreactor which could be effectively used for the synthesis of functionalized materials.

## 4. A general characteristic of functionalized silica-based materials

Back in the early 90 s of last century, hybrid organic-inorganic materials which include functionalized organosilicon materials have received serious attention from many scientists due to the potential of properties combination for creating the novel structures [2]. In general, the class of hybrid organic-inorganic materials contains compounds that are composed of inorganic (according to our investigation, it is silicon dioxide) and organic (various radicals) components. This result can be achieved by: 1) impregnation of the inorganic part or introduction of the organic part into inorganic one in the absence of covalent bond between them; 2) formation of covalent bond between the components [3]. It should be noted that the latter type of materials is the most progressive in research and in the production scale as well.

## 5. Methods of functionalized silica-based materials synthesis

A sol-gel method and a template method are the most promising approaches for obtaining functionalized silica materials. Materials received by means of the sol-gel technique are usually amorphous or have randomly arranged domains. The template synthesis method permits to obtain an ordered structure, but there are some difficulties regarding the intrinsic properties. Firstly, basic products and by-products of the reaction cannot be divided because of their covalent bonding with the silica surface. Secondly, the number of functional groups reduces significantly when the number of synthesis steps increases [3]. However, these (and other) shortcomings can be avoided by using the "direct" method of functionalization.

The core of the sol-gel method is the alkoxy-(or chlorine) silanes hydrolytic polycondensation reaction. In describing the process of transformation competing ways include: hydrolysis of bonds at the silicon atom with the formation of silanol, and polycondensation with the siloxane formation [2, 3]. But the key feature of the sol-gel synthesis is the ability to introduce different functional groups that are capable to interact selectively with the substances of various nature.

Therefore, the main goal of the functionalized silica materials synthesis is the combination of organic and inorganic components. For example, the inorganic component can improve mechanical, thermal, structural stability of new compounds, while the organic component provides the specificity of the actions in these substances. In addition, the sol-gel process allows regulating the degree of interpenetration of organic and inorganic fragments at the molecular level to create the organic-inorganic hybrid materials with prescribed properties [3]. Further the influence on structural and adsorptive abilities as well as physical and chemical properties of the product can be carried out at all stages of the synthesis. The progress of the sol-gel synthesis is schematically shown in Fig 1.

To provide the necessary physical, chemical, structural and adsorptive properties of the sample, it is possible to vary the nature and the value of output ingredients, catalyst, solvent, aging conditions and hydrogels washing and drying. A serious task is to regulate the concentration of ligand groups and their distribution on the silica surface. Furthermore, the essential aspect for the majority of applied problems is the opportunity to form both of the monolayer of molecules on the surface and polymolecular coverage. By virtue of requirements described above, it is reasonable to conduct computer calculations of the materials molecular structure by means of the quantum-chemical modeling. On the basis of the theoretical experiment result the process of silica functionalization can be simulated for determining the technological characteristics of the process in terms of sustainable development. The modeling provides clear guidance for sustainable chemical synthesis and production of new materials with useful properties.

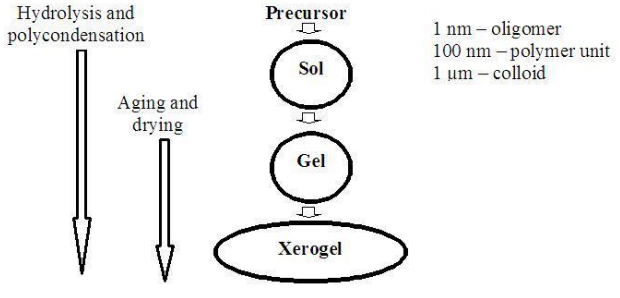



Fig. 1. Scheme of the structure formation at the sol-gel synthesis

## 6. Quantum-chemical modeling of the functionalized silica surface

Construction and previous optimization of structures was performed with a help of the molecular mechanics approximation methods using MM+ force field. The main task of this stage was to find the initial geometrical parameters of the molecules. Theoretical investigations of clusters were carried out by the approach "ab initio" (from first principles). In search of the optimal geometry of clusters there were placed no restrictions on symmetry and the main requirement was to achieve a minimum total energy and a stability of the cluster. For the calculations we used the method of density functional theory (DFT) B3LYP approximation with a local approximation of exchange-correlation potential (basis set 6–31 G(d, p)) [11].

## 7. Implementation of the microreaction systems in chemical production

The next step of the study is to examine the technological characteristics and conditions of the synthesis in order to obtain silica materials functionalized with different groups. The need of the porosity and long reaction times are two among several arguments favoring the use of flow microreactors for the chemical synthesis of such materials. For the previous efficiency estimating of experiment the simulation of chemical process in the microreactor should be performed. As the result, the theoretical calculations provide unprecedented advantages in technological and financial aspects.

In general, microreactors are defined as miniaturized reaction systems fabricated by using, at least partially,

methods of microtechnology and precision engineering [1]. They enable chemical reactions to be conducted in a continuous way instead of the batch processing [12]. The characteristic dimensions of the microreactors internal structures such as fluid channels typically range from the sub-micrometer to the sub-millimeter (Table 1).

Table 1

Size comparison of the macro-, micro- and nanodevices internal channels [13]

| Parameter | Macro | Micro | Nano |
|---|---|---|---|
| Range of sizes | $(1 \div 10^{-3})$ m | $(10^{-3} \div 10^{-6})$ m | $(10^{-6} \div 10^{-9})$ m |
| Measurement unit | 1 mm | 1 μm | 1 nm |
| Surface-to-volume ratio | 100–1000 $m^2/m^3$ | 10000–50000 $m^2/m^3$ | ~100000 $m^2/m^3$ |

A large number of applications within the last decade have clearly demonstrated fundamental advantages for microreactors compared to the lab-scale equipment. Their main feature is to provide the intensification of mass and heat transfer due to the flow regime improvement. Moreover smaller devices require less space, materials, and energy and often have shorter response times.

The key advantages of the microreactor are:

Decrease of the linear dimensions

The majority of nowaday's microreaction devices contains microchannels with typical widths from 50 μm to 500 μm; the separating wall material between the reaction and heat transfer channels can be kept down from 20 to 50 μm if it is necessary. As the result, the heat transfer coefficients up to 25.000 $W/(m^2 \cdot K)$ measured in microdevices exceed those of conventional heat exchangers by at least one order of magnitude [1].

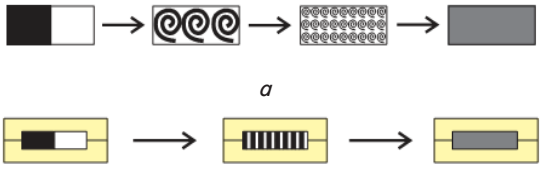
So decreasing the linear dimensions leads to the increasing of driving forces for the heat transfer, mass transport, or diffusional flux per unit volume or unit area.

Increase of the surface-to-volume ratio

As a consequence of the decrease in fluid layer thickness, the corresponding surface-to-volume ratio of the fluid entity is notably increased. Specific surfaces of channels in the microreactor exceed the typical laboratory and production vessels more than 50 times (Table 1) [1]. This increase in the specific vessel surface can be utilized, e. g. in the catalytic gas phase reactors coated with active material on the inner walls.

Improvement of the mass transfer

The main difference between the microstructure and standard volumetric reactor is the laminarity of the traffic flows of liquids and gases that are determined by the Reynolds number [1]. In general, volume division of liquids and gases is possible in two concepts: in the creation of turbulent flow and laminar mixing. In a turbulent regime the fluid entity is constantly subdivided into the thinner and thinner layers by an induced circular motion of fluid compartments, so-called eddies, and the subsequent breaking into fragments. In a laminar regime, a similar breaking of fluid compartments cannot occur due to the high viscous forces. Instead, the fluid entity has to be continuously split and recombined, forming regularly-sized fluid embodiments (Fig. 2, *a, b*).



*a*

*b*

Fig. 2. Schematic picture of stirring: *a* — turbulent mixing; *b* — laminar mixing [1]

Hereby, the application of capillaries in the microreactor allows reaching a good mixing of reagents by means of the repeated mixing of liquid drops because of friction segmented fluids on the microchannels walls.

Increase of the number of units

Unlike the typical industrial installations, enhancement of the microreactor productivity is not achieved by the increase of their size but by the increase of the number of units. The multiple repetitions of basic units is the distinctive feature of microreaction devices. These constituent elements can work both in the cascade style (e. g. devices of pre-selection) or in parallel with the use of a common feed line (production purposes) [1].

Besides the assembling of many units either by parallel or serial means requires fast analysis. A microreactor can be used in combination with analysis systems. This integration serves to speed up analysis times to save the sample material and to eliminate the additional sample transfer.

Production flexibility

It is important to mention that, although microreactors contain microstructures, they are not meant to perform a small-scale chemistry. By using a continuous process instead of the batch processing they can be applied to synthesize a kilogram or even a ton amount particularly in the parallelized arrays [12]. Scaling-up widely guarantees that desired features of a basic unit are kept when increasing the total system size. In addition, a technological project based on the large number of small reaction systems can be changed to perform a variety of reactions by simple modification. In this case, the microdevice may be adapted to the synthesis of various substances using microreactor modules such as "LEGO" system [1].

Safety and sustainability

Structured flow microreactors are called as the global solution of environmental problems for chemical process and technology in terms of sustainable manufacturing [1, 7]. A significant decreasing of the reagents volume reduces the danger of explosion, depressurization and leakage of the reaction mixtures both for the laboratory research and mass production. In addition, small reactor dimensions facilitate the use of distributed production units at the place of consumption. It can help to avoid transport and storage of the dangerous materials.

Approaches to the modeling processes in the microreactor

To address the problems that occur at designing and optimizing of the microreactor structure, the detailed processes and reactions description is an important aspect. However, measurement inside the small size reactor is a difficult task which can be solved by the help of mathematical modeling of the kinetics of chemical processes. Previous calculations using modern program complexes allow predicting the process conditions, execute the experimental

design and, consequently, significantly reduce the amount of experimental work, consumption of materials and expenditure of the time. Moreover, the macroscopic characteristic of the workspace becomes unbalanced and requires the use of a microscopic approach for describing the interaction on a molecular-kinetic level. Therefore, a complete model should include the equations of material and heat balances of the projected system as well as the basic equations for the physical parameters of the reactants and kinetic equations of reactions transformation occurring in the system. In general, a set of equations has the following form:

$\Sigma G_i=0$ – material balance;
$\Sigma Q_i=0$ – heat balance;
$dX_i/d\tau = kC^m_A C^n_B$ – chemical reaction kinetics;
$dY_i/dZ=f(Re, Pr, Ar)$ – fluid dynamics.

This system includes a set of equations of various types (from the linear to differential equations in partial derivatives) and requires special mathematical methods to solve the specific problems. It should be noted that the determination of boundary conditions and assumptions is the influential stage of modeling [6]. The theoretical calculations aimed at proving of this assumption and, thereby, reliable reproduction of the actual experiment by means of simulation. At present, there are a lot of successful commercial software packages for modeling complex chemical processes. The most popular of them are Aspen HYSYS, Aspen Plus, ANSYS, CHEMCAD, Pro II, Mathcad, COMSOL Multiphysics.

## 8. The possibility of industrial implementation of the investigation

The use of micro- and mini-scale devices offers tremendous prospects for miniaturization of many kinds of chemical plants with the possibility of production sites organization in the desktop scale with the performance of conventional plants. The potential features illustrate that microreactors are promising tools for on-site and on-demand production. Unfortunately, there are no examples of industrial implementation of microdevices in Ukraine. But many well-known chemical and pharmaceutical companies actively implement the new advanced technology for large-scale production, namely [7, 14, 15]:

– Degussa, Germany (propylene oxide, 50 000 t/h);
– Eurodyn G mbH, Germany (nitroglitserin, 16 000 t/h);
– Xi'an Huian Chemical, China (nitroglitserin for medicine, 120 t/h);
– Siemens Axiva, Germany (polyacrylate, 2000 t/h);
– DSM Fine Chemicals, Austria (vitamin D, 100 t/h);
– Synthacon GmbH, Germany (fine chemicals, 200 t/h);
– Sigma Aldrich GmbH, Switzerland (fine chemicals, 20 t/h);
– Clariant, Germany (pigments, 10 t/h);
– Schering, Germany (synthesis of steroids, 15 kg/day).

In turn, the miniaturization of flow reactors is a decisive advantage in the synthesis of nano-sized particles. Due to the efficient heat transfer and optimal mixing, the full control of reaction parameters is affected. Ideal mixing in the microreactor technology determines undeniable benefits of the flow synthesis for carrier surface functionalization with active substances. There are already developed and mastered the receipt and processing of polymer nanoparticles using microreactor units Wingspeed AG (Switzerland) [15]. The main advantage of polymers fabricated in microreactors is the homogeneous particle size distribution. Due to the exact and complete control of parameters of the functionalization reaction in the microreactor (pressure, temperature, stoichiometry, reaction time and flow rate), it is possible to obtain a homogeneous particle size distribution. Thus, new horizons open up both in the basic research of nanomaterials and their mass production.

The data of our calculations may be proposed for such companies as Reachemtrans LLC (Ukraine), Holding Company Menschen Group (Russian), IC "Artalia" (Russia), JSC Sorbent (Russia), United States Environmental Protection Agency EPA (USA), Pall Corporation (USA), AquaNano LLC (USA), Dunwell Group (Chinese National Republic) and others. All of them are engaged in manufacturing of sorbents for water purification. But even a partial implementation of microdevices entails significant financial and technical advantages for these enterprises as well as integrates the technology for producing substances with prescribed properties. Therefore, this study is a complete theoretical experiment that could prove perspectives of practical commissioning of microreaction devices for the synthesis of highly selective sorbents. As a result, innovative sorbents will bring in a serious contribution to the environmental and economic well-being of people generation.

## 9. Case study of quantum-chemical calculations of the silica surface functionalized with thiourea-containing groups

In order to analyze the process of functionalization in the microreactor firstly we investigated the parameters of structures with different functional groups. Here we presented the molecular structure of silica surface functionalized with thiourea-containing fragment as the case study. This choice is caused by the projected useful properties of such polysiloxane xerogels that are able to sorb ions of noble metals and heavy metals including such dangerous ions for the human as $Hg^{2+}$ (mercury) [2, 3]. In our previous work, we have also described the results of the study on the behavior of nitrogen- and phosphorus-containing groups of functionalized silica surface [18, 19].

Based on the quantum-chemical modeling of silica surface functionalized with thiourea groups [$\equiv(CH_2)_3NHC(S)NHC_2H_5$], it has been shown that hydrogen bonds can be formed between donor and silanol groups both in the presence and absence of the water molecule. Geometry was optimized (Fig. 3) and geometric parameters (Table 2) and spectra frequencies (IR and NMR) were calculated for these fragments.

As a result of the atomic relaxation, it was determined that an adsorption band of the hydrogen bond is slightly shifted to the lower frequencies, but it significantly increases with appearance of the water molecule (Fig. 4).

The theoretical analysis of the NMR spectra of studied fragments permits to identify the causes that determine the behavior of the modified silica surface layer. The values of the chemical shifts of shielding constant at nuclei $^{13}C$ were found when forming the hydrogen bonds between the donor and silane groups. A comparison between the resonance frequencies of the theoretical NMR spectra with the similar experimental values revealed that computer fragments calculations of silica surface functionalized with thiourea groups are in good agreement with the data of synthesized adsorbents (Table 3) [3].

Table 2

Basic geometrical parameters of the optimized fragments [18]

| Bridging | Length (Å) | Valence angle | Value (degree) |
|---|---|---|---|
| $(HO)_2Si(OH)$ $(CH_2)_3NHC(S)NHC_2H_5$ | | | |
| Si1-O3 | 1.666 | O1-Si1-O2 | 111.5 |
| Si1-C1 | 1.865 | N2-C4-S1 | 123.0 |
| S1=C4 | 1.684 | C3-N1-C4 | 124.6 |
| N1-C4 | 1.367 | N1-C4-N2 | 113.5 |
| $(C_2H_5O)_3Si(CH2)_3NHC(S)NHC_2H_5$ | | | |
| Si1-O1 | 1.649 | O1-Si1-C1 | 113.2 |
| Si1-C1 | 1.874 | C3-N1-C4 | 124.4 |
| S1=C4 | 1.686 | C4-N2-C5 | 124.1 |
| N2-C4 | 1.364 | N1-C4-N2 | 113.6 |
| N1-C4 | 1.366 | | |

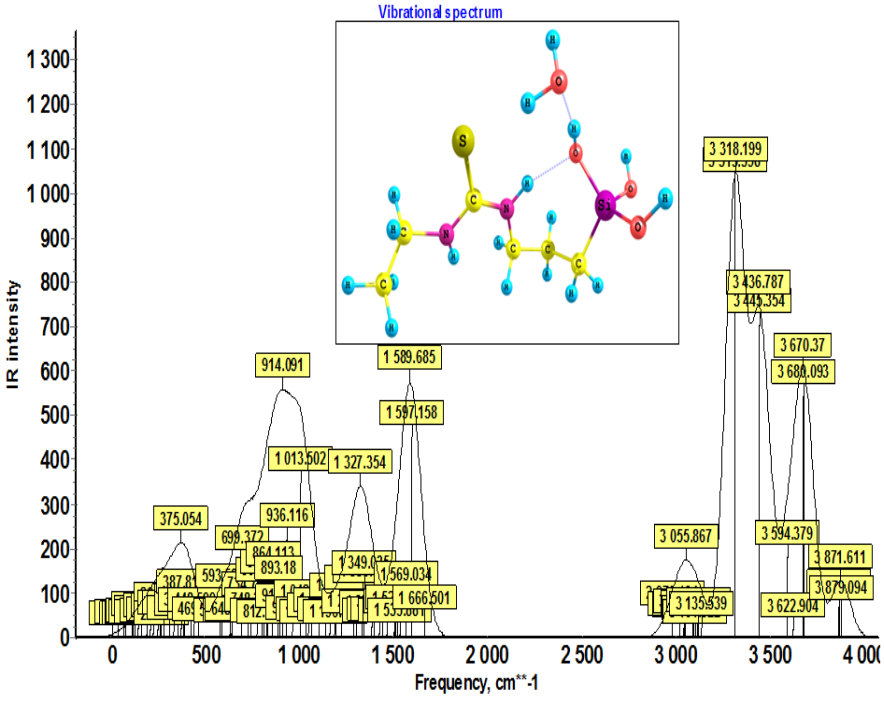
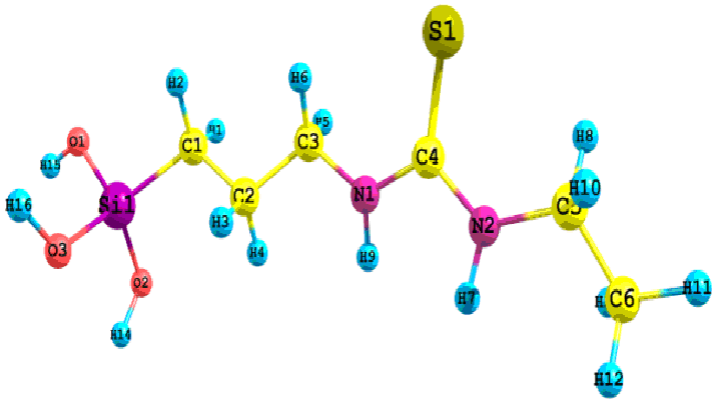
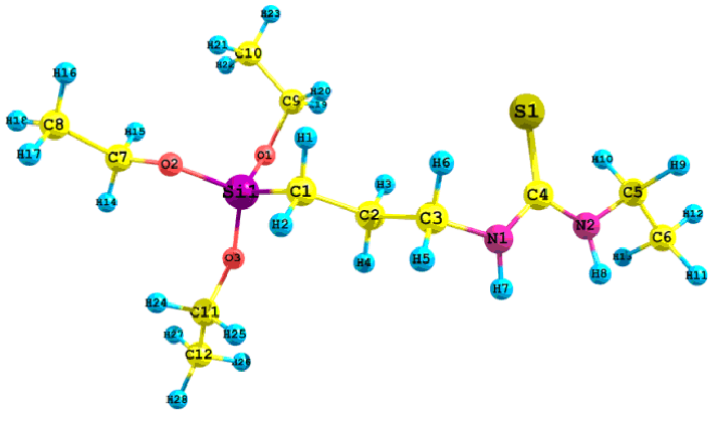



Fig. 4. IR vibration spectrum of the fragment functionalized with thiourea group in the presence of the water molecule




E=−1261.3247 a.u.




E=−1497.1932 a.u.

Fig. 3. Optimized geometry of fragments of silica surface functionalized with thiourea group: *a* – $(HO)_2Si(OH)(CH_2)_3NHC(S)NHC_2H_5$; *b* – $(C_2H_5O)_3Si(CH_2)_3NHC(S)NHC_2H_5$ (where E is the total energy of the fragment) [18]

It should be noted that the lab synthesis of silica compounds with sulfur-containing functional groups has been carried out in the O. O. Chuiko Institute of Surface Chemistry. Yu. Zub reported the experimental results of the adsorption capacity of such materials in his doctoral thesis [3].

He examined the sorptive properties of mesoporous silica surface functionalized with thiourea ligand group regarding mercury ion (II). By virtue of the analysis of adsorption isotherms, it has been shown that the growth in the density of functional groups results in the increase of their inaccessibility when sorbing the metal ions. Consequently, the adsorption properties of mesoporous silica materials containing thiourea group on the surface layer depend on the content of the functional groups and the nature of the porous structure. The low density of ligand groups improves the extraction of mercury while the increase in density of functional groups leads to the impediment of the complexing process. These arguments confirm the necessity of the accurate process control to obtain materials with prescribed properties. Microreaction technology can help to carry out the synthesis under optimal conditions for producing

highly selective sorbents that have the potential for water disinfection and purification.

In the following, we are going to simulate the process of silica surface functionalization in the flow microreactor which could be effectively used for the synthesis of hybrid organic-inorganic materials. It will do so by the solving of the mathematical model process with the help of suitable computer programs and methods of microfabrication technology. Ultimately, functionalized adsorbents could be produced and put into practice for water treatment.

Table 3

Experimental and calculated values of the chemical shifts in the 13C NMR spectra of thiourea-containing fragments

| Type of the nucleus | [≡SiC1H2C2H2 C3H2NHC4(S) NH C5H2C6H3], ppm | [≡SiC1H2C2H2 C3H2NHC4(S)NH C5H2C6H3] (with intramolecular bond), ppm | [≡SiC1H2C2H2 C3H2NHC4(S) NH C5H2C6H3] (experimental values for mesoporous silica), ppm |
|---|---|---|---|
| $^{13}$C1 | 11.9 (7.40)[1] | 12.0 (13.7)[2] | 9.0 |
| $^{13}$C2 | 26.8 (22.36) [1] | 25.0 (24.1) [2] | 23.1 |
| $^{13}$C3 | 51.0 (46.15) [1] | 50.0 (48.1) [2] | 46.8 |
| $^{13}$C4 | 192.5 (181.27) [1] | 194.4 (189.5) [2] | 181.4 |
| $^{13}$C5 | 42.4 (39.20) [1] | 42.5 (42.6) [2] | 39.6 |
| $^{13}$C6 | 14.6 (14.19) [1] | 14.1 (13.7) [2] | 12.8 |

[1] $(C_2H_5O)_3Si(CH_2)_3NHC(S)NHC_2H_5$

[2] $(C_2H_5O)_3Si(CH_2)_3NHC(S)NHC_2H_5+H_2O$

## 10. Conclusions

The adsorption properties of functionalized silica materials were approved in the context of water purification and the implementation of microreactors for the process of silica surface functionalization was discussed.

Quantum-chemical modeling of innovative silica-based materials that can be used for water treatment was performed. Thiourea-containing fragments were considered as the case study for identification of the theoretical experiment technique. The adequacy of the results of quantum-chemical modeling was confirmed by comparing the calculated values of IR and NMR spectra against the similar data of practical experience.

The analysis of approaches to modeling the process of functionalization in the flow microreactor was conducted. The simulation results of various technological operations were studied and the potential benefits of microdevices were confirmed in the context of sustainable manufacturing. The next step of this investigation will be the development of a mathematical model of the functionalized silica materials synthesis in the flow microreactor and its realization in the appropriate software environment. Ultimately, a clear guidance for sustainable chemical synthesis and large-scale production of functionalized sorbents will be provided and used for water treatment.

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***Проведено системний аналіз переваг використання вакуумно-плазмових покриттів для підвищення зностойкості деталей парових турбін. Показані можливості використання структурного підходу до інженерії поверхні для контролю ефективності фізико-технологічних параметрів, які використовували при отриманні покриттів. В якості структурних параметрів експрес контролю функціональних властивостей нітридних покриттів з ГЦК кристалічною решіткою запропоновано використовувати ступінь текстурування і середній розмір кристалітів***

***Ключові слова: лопатка турбіни, вузол тертя-ковзання, покриття, текстура, розмір кристалітів, твердість, зносостійкість***

***Проведен системный анализ преимуществ использования вакуумно-плазменных покрытий для повышения износостойкости деталей паровых турбин. Показаны возможности использования структурного подхода к инженерии поверхности для контроля эффективности, применяемых при получении покрытий, физико-технологических параметров. В качестве структурных параметров экспресс контроля функциональных свойств нитридных покрытий с ГЦК кристаллической решеткой предложено использовать степень текстурированности и средний размер кристаллитов***

***Ключевые слова: лопатка турбины, узел трения-скольжения, покрытие, текстура, размер кристаллитов, твердость, износостойкость***

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# АПРОБАЦИЯ СТРУКТУРНОГО ПОДХОДА ДЛЯ ОПТИМИЗАЦИИ РЕЖИМОВ ПОЛУЧЕНИЯ ПОКРЫТИЙ, ПОВЫШАЮЩИХ ИЗНОСОСТОЙКОСТЬ ЛОПАТОК ТУРБИН

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## 1. Введение

Лопатки роторов паровых турбин являются наиболее сложной и высоконагруженной частью турбины и в значительной мере определяют надежность работы всего агрегата. При этом, лопатки последней ступени цилиндра низкого давления (ЦНД) определяют порог предельной мощности турбины и поэтому надежности их работы уделяется наибольшее внимание [1]. При эксплуатации паровых турбин энергетических станций разрушение лопаток происходит в результате воздействия ряда факторов, в