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CONTENTS

COMPUTER SCIENCE & ENGINEERING

Porozova S., Volianskyi R. Inplementation of Mackey-Glass chaotic generator with Arduino Mega 2560 demoboard 20
Cherevatenko A. On solutions properties of continuous linear problems of optimal multiplex-partitioning of sets without constraints 22
Safonyk A., Koval S. Computer modeling and automation of process of cleaning liquids from ferromagnetic impurities 26
Shpotyuk M., Kovalenko A., Yakhnevych U., Teslyuk D. Gamma-Induced Changes in Optical Transmission of As-S Semiconductor Glasses 30
Hlukhova A. Modified Multiplying Matrix for Galois field GF(2^m) Multiplier Structural Complexity Evaluation 32
Holub Z. Development of Manipulation Detecting Algorithm as a Constituent of the Internet Community Management System 34
Mykich K., Burov E. Knowledge-based situational awareness systems 38
Krasniuk R. The Optimization of Databases Distribution in a Distributed Computer Networks 42
Fisunenko A. One Approach for Computing Simple Polygons on a Given Point Set in the Plain 44
Melnyk R., Dubytskyi A. Blood Cells classification by Image color and intensity features clustering 46
Artemenko O., Popyk I. Geoinformation technologies for tourist's travel support 50
Lysenko V., Dudnyk A. Intelligent control systems of electrical complexes in biotechnological objects 52
Zavuschak I., Burov E. Automatization design of the user interface based on the knowledge that describes ontology 54
Melnyk R., Boyko I. Image Structure Evaluation by Statistical Intensity Features 56
Zheliznyak I. Valid formation of scientific schools 58
Melnyk V., Kit A. Program Loading and Execution in Self-Configurable Computer Systems using the Conventional Operating System Loader 60
Rybchak Z., Lytvyn V., Kunanets N. The Use of Ant Colony Optimization Algorithms for the Problem of Optimal Route Search 62
Mohammed Kadhim Rahma. Galois Field Operational unit For Elliptic Curve Cryptography Digital Signature 66
Tytyk R., Tkachenko R., Izonin I., Hrytsyk K. Neural Network Technology for Image Downscaling 72
Kryvyy R., Kovaliuk O. Research and development of methods to select the optimal location of vehicles on the parking lot 74
Ihnatovych A. Effectiveness evaluation of modified block ciphers using standardized NIST statistical tests 76
Mandrona M., Maksymovych V., Kostiv Yu., Harasymchuk O. Development of a statistically reliable pseudorandom bit sequence 80
Berezko O. Implementing Social Knowledge Environments for NGOs: Key Research Questions 82
Markelov O., Basalkevych O. Automation of prototyping the pattern tests from an electronic compendium of lectures 84
Kostyk A., Hlukhov V., Zholubak I. Features of multiplication execution of operations in binary and ternary Galois fields 88
Rybchak Z., Basyuk T. Design of an intelligence information system of airport services automation 90

GEODESY, ARCHITECTURE & CONSTRUCTION

Wajs Ja. DTM modelling of open pit mines using unmanned aerial vehicles 96
Petruniak V., Ustenko I. 3D seismic velocity models distribution for complete complex of processing and interpretation of seismic data in Dnieper-Donets Basin 100
Zademlenyuk A., Lysak V. Research of electromagnetic radiation influence of power lines on satellite signals distribution 102
Tretyak K., Dosyn S. Study of Vertical Movements of the European Crust Using Tide Gauge and GNSS Observations 104
Babenko M., Savytskyi M. Development of countryside by the building of agrarian socio-eco-comlexes 106
Verba V., Olovets O. Bearing capacity of steel plate anchor in cellular concrete block masonry. Research aims, programme and methodology 110
Gormakh G. The Potential of Port Buildings and Structures for Further Renovation under Cultural - Community Centers 112
Ozhyshchenko O. Conformity of energy efficiency measures in Ukraine with European requirements 114
Peleshko I., Baluk I., Peleshko S. Efficiency evaluation of stress-strain state calculation method for optimal designing of reconstruction and reinforcement of steel structures 118
Pona O., Gulay B., Shapoval S. Experimental studies of combined heat supply system in the flow mode during the summer period for Lviv 120
Shapoval S. The potential of solar energy in Ukraine 122
Shapoval S., Vengryn I. The efficiency of the combined solar collector in the gravity mode in the southern orientation 124
Onufriv Ya. Research methods of ski resorts' visual perception 126
Pekarchuk O. The formation of a barrier-free environment in the historical apartment buildings in Lviv 128
Chernychuk E., Bazylevych V. Optical illusion: Apogee Development 130
Kyselyova A. A History of Public Art 134
Savchenko-Pichugina N. Methods of formation the experimental spaces. 136
Yuryk Ya. The memory of the city 138
Vegera P., Khmil R., Blikharskiy Z. Shear strength of RC beams strengthened by FRCM system 140
Shekhorkina S. Basic principles of low-rise residential floating buildings design 142

ELECTRIC POWER ENGINEERING AND CONTROL SYSTEMS

Dmytryk B., Ravlyk O. The Detection of Winding Short Circuits in Single-Phase Double-Winding Transformers 148
Chaban B., Lesovoy L. Definition of Equivalent Roughness of Internal Surface of a Measuring Pipeline 152
Yevseienko O., Gapon A., Salnikov D. Searching for Optimal Control Parameters of Thermal Object Using Pulse-Width Modulation (PWM) Control with Predictive Filter 154
Kopchak B. Analysis of Robust Stability of Electromechanical Systems, Described by Fractional Order Transfer Function 156
Muzychak A., Voznyakovska O. The Influence of "Cross-Subvention" on Economic Efficiency of Thermal Insulation of Buildings 158
Muzychak A., Pasternak R. Definition Factors Cubic Approximating Polynomial for Locking Characteristics of Steel Pipelines 160
Kasha L., Bilyakovskyy I. Switched Reluctance Motor for City Electro-Car Drive 162
Yatseyko A., Hyrska K. Ferroresonant Processes in 10 kV Power Grids and There Control 164
Romaniuk O., Kril B. Development of Analyzer for Paper Stock Concentration Measurement 168
Yatseyko A., Andrushko V. Impact of the Operating Mode of Neutral in 35 kV Power Grids on the Arc Overvoltages and Voltage Teasuring Transformers 170
Greh R., Kril O. Development and Research of Bulk Material Moisture Meter 174
Kuznetsova M., Maliovanyy M. Renewable Energy Sources in Hot Water Supply System 176
Fedoryshyn R., Matiko F., Kostyk I., Stefurak K. Mathematical Modeling and Experimental Study of Impulse Lines of Flowmeters 178
Martynyak M. Features of the Boiler (Centralized Heat Supply) During the Heating Season and Hot Water Supply 180
Kurylyshyn O. Mathematical Model for Investigation of Wave Processes in High-Voltage Transformers 182
Semeniuk M., Tutka V. Modeling and Analysis of Processes in Synchronous Generator with PWM Controlled Excitation System 186
Kovalchuk A., Khai V. Determination of Cost of Contra-Rotating Wind Turbine with Transformer with Rotating Half 188
Roman V., Matiko F. Investigation of Ultrasonic Flowmeter Error in Conditions of Distortion of Flow Structure 190
Dzhyhyrei V., Matiko F., Klymkovskyi D. Determining of Volume of Natural Gas Losses Caused by Damages of Distribution Networks 192
Biletskyi Yu. Control Systems of Permanent Magnet Synchronous Machine as Port-Controlled Hamiltonian System 194
Ferensovych R. The Operation of Current Transformer with Open Secondary Circuit 196

HUMANITIES & SOCIAL SCIENCES

Peleschyshyn A., Bilushchak T. Analysis and classification of historical-oriented Internet sources 200
Kaspryshyn A. Gender Metaphors in Modern American Prose 202
Blagosmislov O. Training the future teachers of technologies to work with students in extracurricular scientific and technical institutions 204
Firsov O. Boris Loutzky – the founder of Ukrainian aircraft engine-building 208
Pochapska O. Manifestation of Stylistic Devices in German Media Texts on Ukraine Crisis 210
Shramko O. Forming intending primary school teachers' social and cultural competence as a means of integrating into European educational space 212
Shurdenko M. The prospect of distance education in Ukraine 214
Nikitin N., Pelmenev V., Nikitina A., Avakyan M. Physical education for people living with HIV: the concept and legal basis 216
Keklyak N. Complex Metaphor in the Novel of Cecelia Ahern "Thanks for the Memories" 220

ECONOMICS & MANAGEMENT

Janiszewski A. Determinants of knowledge transfer as a context for models of knowledge brokers 224
Melnyk O., Adamiv M. Problems and development ways of regulatory-methodological support of socio-economic diagnostics in conditions of European integration 228
Holovko L. Structural Changes and Patterns of Development Economics 230
Ivanytska N., Serhiychuk V. Social and economic efficiency of the decentralization of power in Ukraine (on the example of the Odessa region) 232
Kondrat I., Malets O. IPO of Ukrainian companies on the Warsaw Stock Exchange (WSE) 234
Kosovska V. The development of transfer system as one of the areas of management improvement by industrial enterprises 238
Lynnyk O. "Win-win deal": prospects and risks for Ukraine 240
Romanenko O., Baranyuk Yu. Psychology of relations "teacher-student": expectations and challenges 242
Buriak A. Behavior of Systemically Important Banks on the financial market 244
Dziubińska A. Organizational learning in complex world 246
Petryshyn N., Dziubina K. The Role of Strategic Planning Technologies in Terms of European Cooperation Development 250
Fedorchak O. Three-dimensional model representation of investment attraction for company 252
Khymych O., Shkilna V. Income tax on individuals as a tool impact population welfare 254
Kulyniak I., Koshyk O. The Role of Educational Projects in Ensuring Youth Competitiveness in the Labor Market 256
Muzhelyak M. Problems in the CSR Program Formation and Ways of Their Solution 258
Pelekhatyy A. Ways of Improvement of Tax Administration on Real Estate Distinct from Plot of Land 260

Podolchak N., Kovalchuk G. Evaluation conflicts in the enterprises activities 262
Prokopyshyn-Rashkevych L., Karkovska V. Efficiency of management capacity 264
Anhelko I. Domestic labor market's modern development trends in terms of European integration 266
Kulinich T., Zhayvoronok I. The risk of appearance corrupt practices in the management of assets of private pension funds 268
Joachimiak I. Application of Basic Tools of Experimental Economy in Management Science 270
Kruglov V., Kozyakova D. Tangible and intangible methods of motivation 272
Novikova A., Bilyk O. The peculiarity of thin border between people's chronotypes and the level of labour productivity 274
Olkhova M. The scopes of rational using of road and rail transport while delivering lime bricks in Ukraine 276
Perkhach O. Problems and Prospects for Strengthening Technical and Economic Security of Agricultural Enterprises 278
Zhebchuk R. Estimation of the tax potential as a part of budgetary potential 280
Roman'ko A., Ivanyuk A., Galushko O. Actual trends of projects financing at early stages 282
Tkachenko O. The Impact of Capital Base on the Financial Stability of the Banking System of Ukraine 284
Tosko R., Blynda Yu. Financial Market Stabilization as a Component of Economic Security of Ukraine 286
Zielińska A. Ecologistics Activities in Terms of Communal Waste in Poland 288
Duma O. EU Microintegration: Challenges, Opportunities, Milestones 290

MECHANICAL ENGINEERING, MATERIALS SCIENCE, TRANSPORT

Rudyk Yu., Rudko M., Turko B., Rudyk V., Panasiuk M., Kapustianyk V., Vaskiv A. The Effect of Vacuumization on the Photoluminescence and Photoresponse Decay of ZnO Nanostructures Grown by Different Methods 294
Kovbasyuk T., Shapran Yu. Thermo-kinetic Properties of the New Materials for Functional Layers of Flat Heating Elements 296
Litvinova Ya. Optimization of logistics management processes in transport nodes 298
Fiyalko N., Galkin A. City's Parameters Influence on Transportation Servicing of Goods 300
Voitovych A., Mykhalskyi R., Vlakh R. Welded Layers Microstructure Modification on the Basis of Powder Wire Cr10B4 with addition of Al, Mg 306
Ziółkowska M., Grzegorz S. Jodłowski. Energy aspects of arene domain presence in the coal structure under the sorption process 308
Gursky V. Numerical solution of parametric optimization of the resonant vibro-impact system with technological limitations 312
Korendiy V., Vergeles V. Combined Mechanical Systems of Anti-Storm Protection of Horizontal-Axis Wind Turbines 316
Korendiy V., Bushko O., Denderys N. Mobile Robotic Systems with Walking Movers and Mechanisms of Orientation 318
Korendiy V., Vergeles V. Substantiation of Usage Expediency and Analysis of Exploitation Problems of Low-Power Wind Turbines 320
Gurey V., Dmyterko P. Simulation model of dynamic processes during friction hardening of the flat surfaces 322
Novitskyi Yu. Features of Using the Structural Damping in Construction of Cutting Tools 326
Chernega S., Poliakov I., Grinenko C., Krasovsky M. Structure and properties of diffusion boride layers on steels obtained at applying external magnetic field 328
Postranskyy T., Sotnikova A. Analysis of the traffic`s flow distribution by the types of drivers' temperament 332
Duriagina Z., Dvorianyn K., Shvachko S., Pleshakov E., Tepla T. Methods of Rolled Copper Wire Properties Improvement 334

CHEMISTRY & CHEMICAL TECHNOLOGY

Afonin G., Beznosyk Yu., Dzyazko Yu. Modeling of Ni^{2+} exchange on the strong acid ion-exchange resin and the organic-inorganic ionite 338
Miroshnychenko Yu., Beznosyk Yu. Modelling of Heterogeneous Systems in Microreactors 340
Kukushkina O., Vasylkevich O., Bondarenko S., Beznosyk Yu. Analysis of the Process of Obtaining Methyl Esters of Fatty Acids from Waste Vegetable Oils 344
Artyukhov A., Vedmedera V., Kremnyev O. Research of the hydrodynamic and thermodynamic modes of vortex granulator's operation for obtaining of porous ammonium nitrate 346
Melnyk R., Serdiuk V., Kovalenko T. Formation of polymer microcapsules with encapsulated Fe_3O_4 magnetic nanoparticles 350
Sozanskyi M., Shapoval P., Yatchyshyn Yo., Stadnik V., Chaykivska R., Guminilovych R. Investigation the structures ZnS/HgS, HgS/ZnS 352
Kostiv I., Marshalok G., Marshalok O. Effect of the Reactants Molar Ratio on the Kinetics of Cycloaddition of 2,3-Dimethylbuta-1,3-diene to allylmethacrylate 354
Benko R., Havryliv R., Maystruk V. CFD-modeling of gas combustion process in the industrial cyclone-calciner furnace 358
Reutskyy V., Hrynchuk Yu. Influence of surface-active additieves on processes of alkylaromatic catalytic oxidation 360
Orobchuk O., Fuch U., Subtelnyy R., Dzinyak B. Dispersion cooligomerisation of mixture of C_9 fraction unsaturated hydrocarbons 362
Nebesna Yu., Nebesnyi R., Ivasiv V., Lapychak N. Simultaneous Methyl Methacrylate and Methacrylic Acid Obtaining over Zirconium-containing Catalysts 364
Jabłczyńska K., Wojnarowicz M., Tomasz R. Sosnowski. Characteristics of spray drying process of nanocolloidal silica as a method of production of nanostructural powders potentially applicable in inhalation therapy 366
Koval I., Shevchuk L. Cultural features of microorganisms 372
Fedotov R., Ayodeji A. Ijagbuji. "Green" Technology for Nitric Acid Production: Is it Real? 374
Borova S.,Chobit M., Tokarev V. Filling of polymer hydrogels by nanoparticles of the hydroxyapatite 378
Khomyn T., Chobit M., Panchenko Yu. Production of plasticizers from waste alcohol production 380

Kot W., Chobit M., Vasilyev V. Modification of the chalk by plant oils 382
Nebesnyi R., Shpyrka I., Shatan A.-B., Lukiyanchuk A., Ivasiv V., Nebesna Yu., Lapychak N. Single Stage Acrylic Acid Obtaining based on Methanol and Acetic Acid 384
Masyuk A., Levytskyi V. Sorption Properties of Metal-containing Polymer-Silicate Fillers 386
Katruk D., Levytskyi V. Influence of poly(vinyl chloride) and polymer-silicate fillers on the properties of polyester resin 388
Ivashchuk O., Suprun O., Reutskyy V. Determination of the catalytic complexes structure in the cyclohexane oxidation 390
Zvir I., Dutka V., Matsyuk N., Matsyuk M., Zastavska G., Kovalskyi Ya. Molecular modeling of the isoquinoline and hinaldyne reaction of oxidation by peroxyacids 392
Stasyshyn H., Zastavska G., Koval M., Dutka V. Peculiarities of the oxidative polycondensation of aniline derivatives in solution of polyvinyl alcohol 394
Rolewicz-Kalińska A. Medical waste management in the pandemic disease conditions 396
Yatsulchak G., Komyshna M., Melnyk Yu. Peculiarities of hydrogel – polyamide composition membranes formation 398
Kharandiuk T., Kosiv R., Palianytsia L., Berezovska N. Effect of heat treatment on brewer's yeast fermentation activity 400

LAW & PSYCHOLOGY

F. W. J. van Geelkerken, Pöhls H. C., Fischer-Hübner S. The legal status of malleable- and functional signatures in light of Regulation (EU) No 910/2014 404
Binas O. The problem of training school psychologists at the University 410
Demnyk V. The problems of gender inequality in the printed media of Ukraine, Poland and Hungary 412
Dorosh I., Malynovych L. Role of the parents in shaping readiness to school education among special needs children 414
Fedan Ya. An inclusive preschool education as the basis of inclusion in the system of education 416
Kitsa M. Unquality advertising in Ukrainian printed media 418
Shyroka A., Kuzo I., Kubay I., Franchuk A. Effects of abuse and neglect on children intelligence 420
Lipiets Z. The importance of applicants' personal qualities in selection and training psychologists 422
Mudra I. Editorial column as self-promotion for publishers 424
Myshchyshyn M., Izotova A. Consideration of the Management Styles for Successful Management of Educational Establishment 426
Myshchyshyn M. The Image of Successful Specialist in Technician and Humanist Students 428
Bulachek K., Semenyuk A. The impact of violence during childhood on personality development 430
Shyroka A., Kobecka D., Danyliv R. Ukrainian students' political decision making after the Revolution of Dignity 432
Tymtsiv I. Psychological aspects of money attitudes 434
Vilchynska Z., Vilchynska V. Lonely life – a new way to happiness of modern human?! 436
Yaroshchuk N. Self-control as pre-condition of success 438
Astakhova O. New social media and intercultural understanding 442
Khomik K., Honcharenko Ye. Towards the abyss: the influence of parents' alcoholism on the development in adolescence 444
Kuta O. Attitude towards psychological knowledge in Ukrainian society 446

ENVIRONMENTAL PROTECTION, NATURAL RESOURCE MANAGEMENT AND TOURISM

Gyvljud A., Sabadash V., Gumnitskij Ja. The Kinetics of Oxypropionic Acid on Natural Zeolite 450
Pohrebennyk V., Politylo R., Klochko U. The Influence of Agriculture on Water Quality 452
Malovanyy M., Petrushka K. Determination of Electrical Conductivity of Ion Exchange Resins 454
Shandrovych V., Malovanyy M. Monitoring of Performance of the Municipal Wastewater Treatment Facilities 456
Dzhumelia E., Pohrebennyk V. Environmental Control of Phosphogypsum and Tars of Rozdil State Mining and Chemical Company "Sirka" 458
Politylo R., Borovyk O., Yakovleva V. Radioecological monitoring of water resources in the Chernobyl exclusion zone 460
Nahurskyy O., Tsyhaniuk S. The characteristic's impact on environment of laminated product's plants 462
Ruda M., Pohrebennyk V. Space-functional role of consortiums of ecotones of protective type to ensure the environmental safety on railway lines 464
Iziumova O. Formation of Agrophysical Properties in the Affected Soils of Recultivated Areas 466

Modelling of Heterogeneous Systems in Microreactors

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Abstract* – *In this paper an overview of approaches to the modelling of heterogeneous systems (liquid-liquid) in the microreactor was performed, mathematical models of various chemical reactions in microchannels published in the literature was considered and the comparison of theoretical and practical experiments was executed. Based on the generalized data, it has been proved the feasibility of microstructured reactor application for the process of silica surface functionalization in order to carry out the synthesis of innovative sorption materials. The next stage of this research is to develop a mathematical model of the process and its implementation by means of special software environment.

Key words – microreactor, microchannel, process of functionalization, silica surface, CFD-modelling, heterogeneous system, miniaturization.

I. 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.

II. 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.

III. A general characteristic of functionalized silica-based materials

Back in the early 90s 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.

IV. 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.

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.

V. 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)) [4].

VI. Implementation of the microreaction systems in chemical production

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.

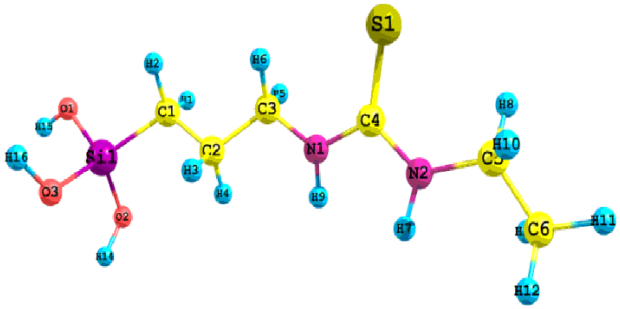
The key advantages of the microreactor are: Decrease of the linear dimensions, Increase of the surface-to-volume ratio, Improvement of the mass transfer, Increase of the number of units, Production flexibility, Safety and sustainability, Approaches to the modeling processes in the microreactor.

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 [5]. 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.

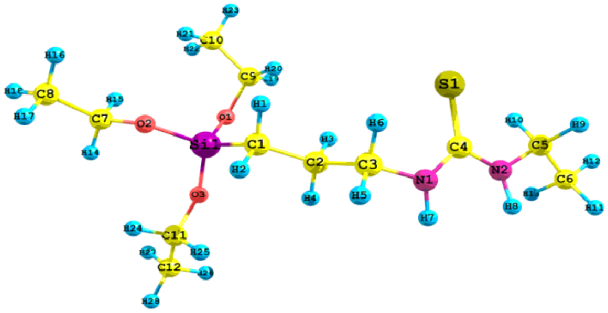
VII. Case study of quantum-chemical calculations of the silica surface functionalized with thiourea-containing groups

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 Hg2+ (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.

Based on the quantum-chemical modeling of silica surface functionalized with thiourea groups [≡(CH2)3NHC(S)NHC2H5], 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. 1) and geometric parameters (Table 1) and spectra frequencies (IR and NMR) were calculated for these fragments.



a) E=-1261.3247 a.u.



b) E=-1497.1932 a.u.

Fig. 1. 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)

TABLE 1

BASIC GEOMETRICAL PARAMETERS OF THE OPTIMIZED FRAGMENTS

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		

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. 2).

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 13C 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 2) [3].

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.

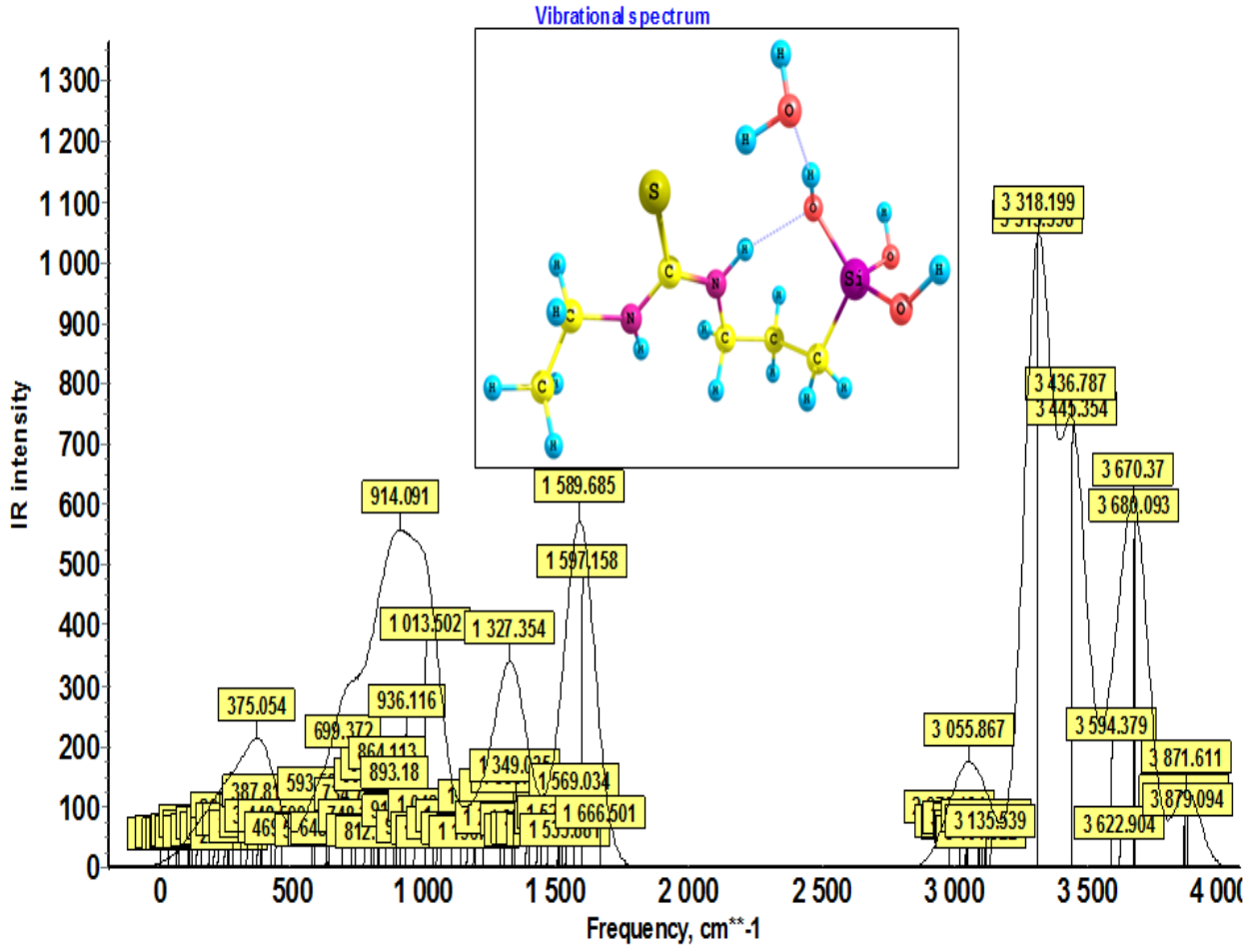


Fig. 2. IR vibration spectrum of the fragment functionalized with thiourea group in the presence of the water molecule

TABLE 2

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

Conclusion

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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