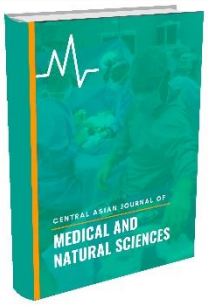
CENTRAL ASIAN JOURNAL OF MEDICAL AND NATURAL SCIENCES



Volume: 03 Issue: 03 | May-Jun 2022 ISSN: 2660-4159

http:// cajmns.centralasianstudies.org/index.php

SYNTHESIS OF MESOPOROUS SORBENTS ON THE BASIS OF AL2O3 AND THEIR TEXTURAL CHARACTERISTICS

Diyarov A.A.[1], Mukhamadiev N.Q.[1], Sayitkulov Sh.M.[1], Uzokov J.R.[1]

EMAIL: m_nurali@mail.ru

Received 20th April 2022,
Accepted 18th May 2022,
Online 28th May 2022

[1]Samarkand State University. Samarkand, Uzbekistan

ABSTRACT: The samples of mesoporous sorbent based on Al_2O_3 were synthesized using sol-gel technology. The phase composition of the samples was studied by X-ray diffractometry (XRD), the surface morphology by scanning electron microscopy methods. Also, the textural characteristics of the sorbents were studied by adsorption of benzene vapors using McBen-Bakra sensitive quartz spiral device. According to that, the specific surface area of the sorbents prepared in different temperatures (S_{BET}, m^2/g) was 400÷600 m^2/g, the volume of the pores (V_s,) 0,56÷0,82 cm^3/g, and the average diameter of the pores 4,5÷32,6 nm. On the basis of X-ray microanalysis of the sorbents, it was proved that their chemical composition corresponds to γ-Al_2O_3.

KEYWORDS: sol-gel, mesoporous sorbent, diffracrometry, specific surface, pores volume, X-ray microanalysis.

INTRODUCTION

At present, aluminum oxide and the composite materials prepared on the basis of it are widely used in various fields of industry [1-2]. In particular, the role of these materials as a carrier in catalysis, as a sorbent in the processing of oil, in the purification of wastewater, in the production of chemical sensors, in solving environmental problems, in metallurgy, in mechanical engineering, in the preparation of ceramic composite materials, and in all fields of electronics is incomparable [3-7].

Among these types of materials, mesoporous aluminum oxide and nanomaterials prepared on the basis of it are of particular importance for abovementioned areas [8-10]. In the last decade, the application areas of aluminum oxide and porous materials prepared based on it are getting wide because of their large surface area, as well as the characterization of unique physical and chemical properties due to nano-size

porosity. Therefore, the synthesis of Al_2O_3 and mesoporous composite materials with high specific surface area that can be applied in various processes of the industry is one of the actual problems [11-16].

The synthesis of Al_2O_3 and mesoporous nanomaterials prepared based on it can be carried out in several ways, both in solution and in gas phase deposition, hydrothermic processing, microwave heating, synthesis using a solid templant [17-18]. The most convenient method to synthesize pure porous aluminum oxide is sol-gel technology, which is of great importance for the simplicity, repeatability of equipment, environmental safety and cost-effectiveness of the products prepared. As well as, the method is widely used due to the introduction of monomers, polymers with different functional groups and oxides of the metals with changeable valance into the reaction system, the presence of a single solvent for all reagents and the possibility to carry out hydrolytic reactions in soft conditions in the process of sol-gel synthesis [19-22].

Therefore, in this research, the synthesis of mesoporous Al_2O_3 particles by sol-gel technology using some water-soluble crystallohydrates of aluminum, as well as cation surfactants was carried out.

EXPERIMENTAL

Materials and methods

To prepare the γ-Al_2O_3 sols in the synthesis of meseporous sorbents, $AlCl_3 \cdot 6H_2O$ crystallohydrate (purified using recrystallization >98,2%) and cetyltrimethylammonium chloride ($C_{19}H_{42}ClN$) (Jinan Xinggao Chemical Technology Co., Ltd.)., Ltd, China, purity >98,7%) as a template for the direction of mesoporous structure were used. In order to provide the hydrolysis reaction with a catalyst, as well as an alkaline environment, 0.01 M ($K_d=1{,}76 \cdot 10^{-5}$, pH=10,3) solutions of urea and NH_4OH have been used. Ethanol (purity >96,2%) was used as a solvent. During the synthesis, the solution environment was controlled using Mettler Toledo FP-20 pH meter. The synthesis process was carried out at 20°C, 30°C, 50°C and 70°C to study the affect of temperature on the specific surface size (S_{BET}, m^2/g), the volume of the pores (V, cm^3/g) and the formation of the pores with average diameter (D, nm) of the prepared sorbents. The textural characteristics of the sorbents were studied by adsorption of benzene vapors using McBen-Bakra sensitive quartz spiral device. Studying the surface morphology of the sorbents was performed using a scanning electron microscope SEM EVO MA 10 (Carl Zeiss, Germany) and the element composition by the microscope (EDS Aztec Energy Adyanted X-Act, Oxford Instruments) using additional ditector.

Synthesis of γ-Al_2O_3 sorbents

Synthesis of mesoporous γ-Al_2O_3 was carried out in the following sequence.

Initially, 1.4 gr citeltrimethylammonium chloride was dissolved in 23 ml of alcohol. Then 5 g $AlCl_3 \cdot 6H_2O$ dissolved in 20 ml of water and 0,7 g urea were added into the mixture dropwise. The resulting solution was placed in a thermostat and stirred for 30 minutes at the appropriate temperatures. Then the solution of 8 ml 0,01 M ammonia solution was added into the solution dropwise and stirred until a white suspension is formed. The formed solution turned into gel completely for 2 hours. To remove additional products from the resulting gel sample, it was washed several times with distilled water, filtered, dried in a drying oven for 8 hours at a temperature of 100°C. Then the gel sample was calcined for 5 hours at 600°C.

RESULTS AND DISCUSSION

The isoterms of sorption of benzene vapors in γ-Al_2O_3 sorbents prepared at temperatures of 20°C and 30°C are presented in Figure 1.

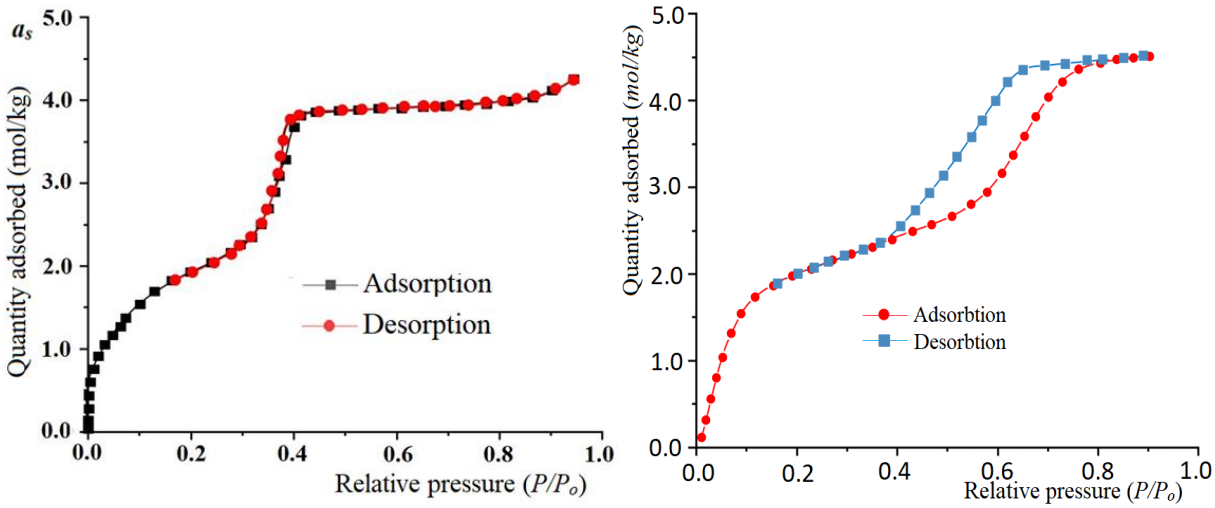


Figure 1. Adsorption isotherms of benzene vapor in the sorbents synthesized at 20°C (*a*) and 30°C (*b*)

In the sorbent prepared at 20°C, adsorption isotherms of benzene vapor showed a sharp increase in the amount of adsorption in the range from zero to p/p_s=0,2 and remained unchanged when p/p_s=0,8 (Figure 1-*a*). This indicates that the main part of the sorbent pores prepared at 20°C is micropores. The obtained sorption isoterm belongs to Type I according to the IUPAC classification, it was found that the total part of the pores consists of 72-80% micropores.

In the sorbent prepared at 30°C (picture 1-*b*), the adsorption isotherms of benzene vapor showed a sharp increase in the amount of adsorption in the range from zero to p/p_s=0,4 and approaching the saturation pressure at p/p_s=0,9. It was also observed that the relative pressure value in the range p/p_s=0,4÷0,8 the adsorption and desorption lines form a hysteresis loop due to capillary condensation. In addition, the sorbent sample prepared at 30°C consists of mesopores, and the adsorption isoterm belongs to type IV according to the IUPAC classification.

The adsorption isoterms of benzene vapor in the sorbents prepared at 50°C and 70°C showed that samples consist of larger mesopores (Figure 2).

The adsorption isotherm in γ-Al_2O_3 sorbent prepared at 50°C shows that the area of the hysteresis loop formed due to capillary condensation was large and they moved to the side of the large value of the relative pressure. It was determined that the hysteresis occurs in the range of the relative pressure p/p_s=0,6÷0,8 (Figure 2-*a*).

In γ-Al_2O_3 sorbent prepared at 70°C, it was observed that the formation of hysteresis loop corresponds to the areas of relative pressure p/p_s=0,6÷0,75. This is evidenced by the fact that the main percentage of total pores in the sorbents prepared at 50°C and 70°C corresponds to mesopores [23-24].

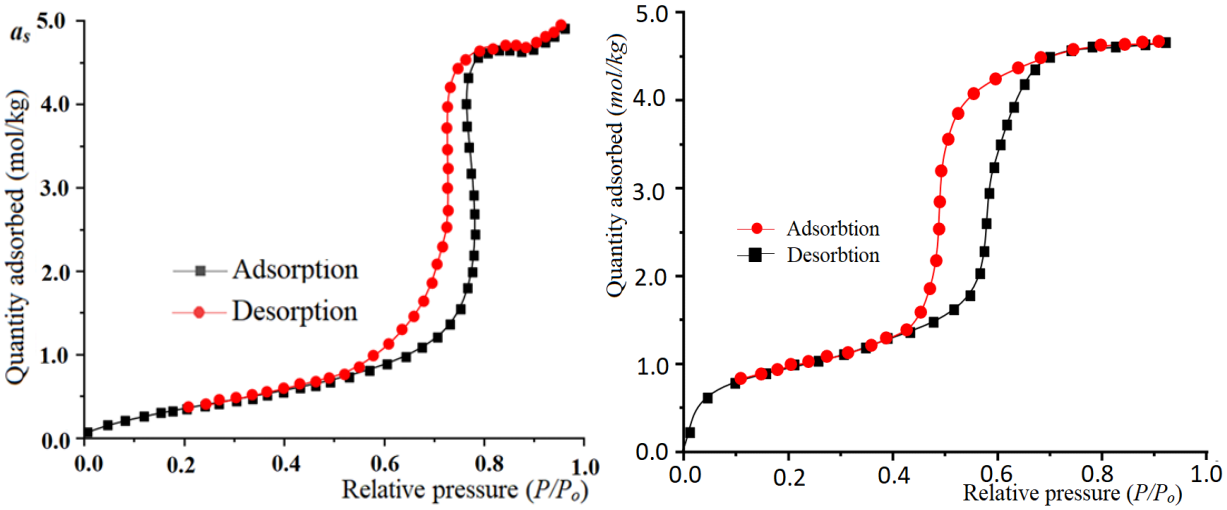


Figure 2. Benzene vapor adsorption isoterms in sorbents synthesized at 50 °C (*a*) and 70 °C (*b*)

Using the values obtained on the basis of adsorption isotherms, the saturation of the mesopores and the specific surface of the sorbents (S_{BET}, m^2/g) on the basis of BET isotherm models, the average diameter of the pores (D, nm), the monolayer capacity of the sorbents (a_m mol/kg) and saturation adsorption (a_s, mol/kg) were calculated (Table 1).

Table 1. Texture characteristics of γ-Al_2O_3 sample prepared at different temperatures

Synthesis temperature	S_{BET}, m^2/g	a_m, mol/kg	a_s, mol/kg	D, nm
20°C	684,6±100	2,6±0,2	6,2±0,8	1,8±0,05
30°C	613,2±100	1,2±0,1	5,7±0,5	6,8±0,42
50°C	541,3±100	1,75±0,6	5,2±0,2	12,3±0,23
70°C	410,6±100	2,6±0,2	1,2±0,8	32,4±0,05

On the basis of the data at the table it was determined that the specific surface area of the sorbents prepared at 20°C to be higher 1,2 times than that of the sorbents prepared at 30°C, 1.26 times higher than that of the sorbents prepared at 50°C, 1,66 times higher than that of the sorbents prepared at 70°C. Also, with the increase in temperature in the synthesis process, an increase in the average diameter of the sorbents by 1,8÷32,4 nm was observed [25].

As well as, based on the values obtained from benzene vapor adsorption, the saturation adsorption volumes of the sorbents (V_s), the volume of the micropores (W_0), the volume of the mesopores (W_{mes}) were determined (Table 2).

Table 2. The volume of the pores based on γ-Al_2O_3 sorbents prepared at different temperatures and their distribution on the surface

Synthesis temperature	Micropores	Mesopores	General pores
	$W_0 \cdot 10^3$, cm^3/g	$W_{mes} \cdot 10^3$, cm^3/g	$V_s \cdot 10^3$, cm^3/g
20°C	0,324 ± 0,05	1,052 ± 0,06	1,376 ± 0,10
30°C	0,302 ± 0,01	0,911± 0,04	1.213 ± 0,24
50°C	0,182 ± 0,04	0,872 ± 0,08	1,054 ± 0,15
70°C	0,324 ± 0,05	1,052 ± 0,06	1,376 ± 0,10

It can be seen from the table that the volume of the pores increases with the increase in the temperature during the synthesis process.

The study of surface morphology of the sorbents using SEM confirmed that the textural characteristics of the sorbents correspond to the above values (Figure 3).

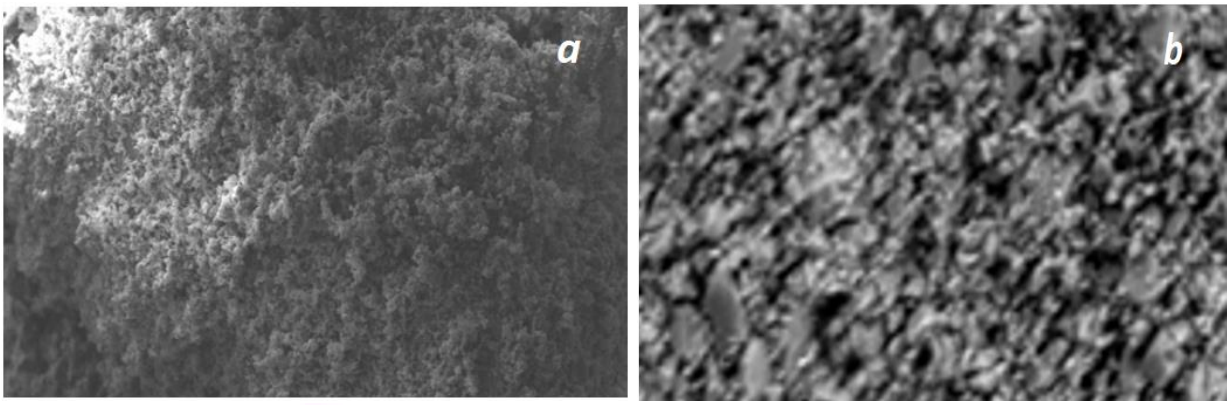


Figure 3. SEM image of the sorbents prepared at 20°C and 30°C

It can be seen from the figure that with the increase in temperature, the size of the particles and the average diameter of the pores are enlarged [26].

The results of the elemental analysis obtained from separate areas of the surface showed that the mesoporous alumina sorbent composition consists only of Al and O and has no additional components. It was found that the element content of the sorbents consists of 31.8±0.2% Al, 67,3±0,6% O in mass.

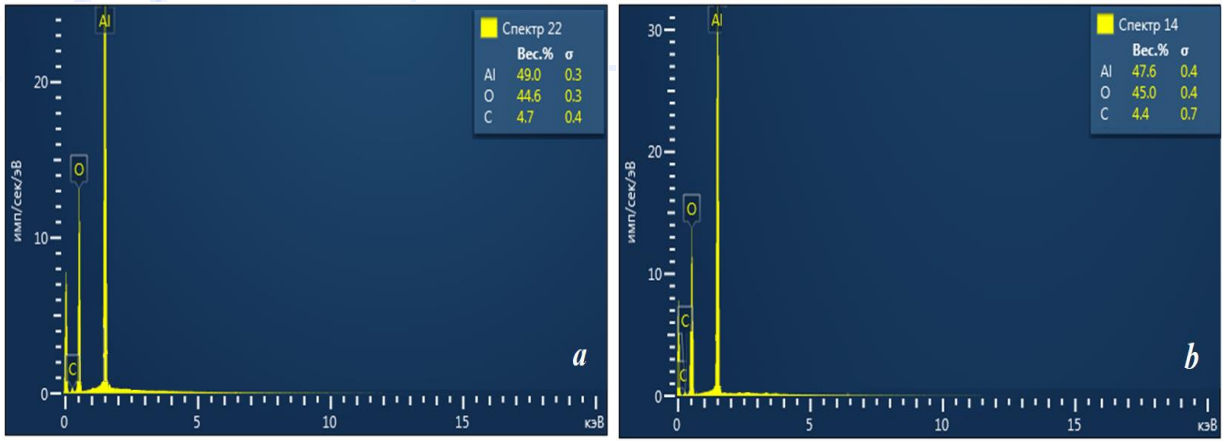


Figure 4. EDS images of mesoporous γ-Al_2O_3 sorbent prepared at 20°C (*a*) and 50° C (*b*)

The phase composition of the sorbents was studied by Pananalytical Empyran X-ray diffractometer (XRD). To obtain diffractograms by XRD, CuKa-radiation (b-filter, Cu, current mode 1.5406 A° and the voltage applied to the tube is 30 mA and 30 kV, respectively) and the detector at a constant rotation speed of 4 degrees/min with a step of 0.02° (compatibility ω/2 θ) was applied. The scanning angle was changed from 0^0 to 90^0. The obtained X-ray diffractograms are shown in Figure 5.

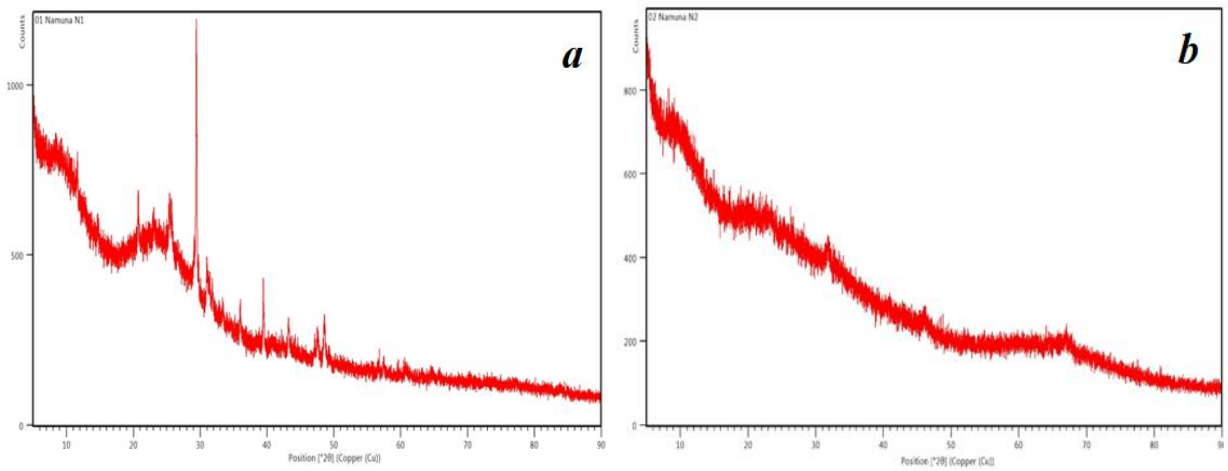


Figure 5. X-ray diffractograms of the sorbents prepared at 30°C (*a*) and 50°C (*b*)

It can be seen from the figures that the main part of the sorbents prepared at different temperatures is amorphous phases.

CONCLUSIONS

The sorbent samples were synthesized on the basis of mesoporous aluminum oxide at different temperatures using sol-gel technology. The influence of the temperature on the formation of textural characteristics of the sorbents, including the specific surface area of the sorbents, the average diameter and volume of the pores was studied. According to that, it was noted that the average diameter of the pores of the sorbent is D=1,8÷32,4 nm, the size of the surface is S_{BET}=410,6÷684,6 m^2/g, the average volume of the pores is V_s=0,205÷0,412 cm^3/g. Also, the isoterms obtained from benzene vapor adsorption on the sorbents prepared at 20°C belong to Type I according to the IUPAC classification, and represent single-layer adsorption at micropores, the isoterms obtained at 30°C, 50°C and 70°C belong to type IV and represent polymolecular adsorption.

REFERENCES:

[1]. Yaqoob A. A. et al. Role of nanomaterials in the treatment of wastewater: a review //Water. – 2020. – T. 12. – №. 2. – C. 495.

[2]. Nturanabo F., Masu L., Kirabira J. B. Novel applications of aluminium metal matrix composites //Aluminium Alloys and Composites. – 2019.

[3]. Khodakarami M., Bagheri M. Recent advances in synthesis and application of polymer nanocomposites for water and wastewater treatment //Journal of Cleaner Production. – 2021. – T. 296. – C. 126404.

[4]. He Y. He, J., Wang L., Yu Z., Zhang H., Liu Y., Lei,B.Synthesis of double carbon dots co-doped mesoporous Al2O3 for ratiometric fluorescent determination of oxygen //Sensors and Actuators B: Chemical. – 2017. – T. 251. – C. 918-926.

[5]. Wu Z., Q., Feng D., Webley P. A., Zhao D. Ordered mesoporous crystalline γ-Al2O3 with variable architecture and porosity from a single hard template //Journal of the American Chemical Society.

– 2010. – Т. 132. – №. 34. – С. 12042-12050.
[6]. Fayomi O. S. I., Babaremu K. O., Akande I. G. Impact of Al-Composites in the Manufacturing Industry: A Neccessity //International Journal of Civil Engineering and Technology. – 2019. – Т. 10. – №. 3.
[7]. Szczęśniak B. Babaremu K. O., Akande I. G. Mechanochemical synthesis of highly porous materials //Materials Horizons. – 2020. – Т. 7. – №. 6. – С. 1457-1473.
[8]. Xifre-Perez Mesoporous alumina as a biomaterial for biomedical applications //Open Material Sciences. – 2015. – Т. 2. – №. 1. – С. 13-32.
[9]. Naik B., Ghosh N. N. A review on chemical methodologies for preparation of mesoporous silica and alumina based materials //Recent patents on nanotechnology. – 2009. – Т. 3. – №. 3. – С. 213-224.
[10]. Griffin, Sharoon, "Natural nanoparticles: a particular matter inspired by nature." Antioxidants 7.1 (2017): 3.
[11]. Wei, Jing, "Ordered mesoporous alumina with ultra-large pores as an efficient absorbent for selective bioenrichment." Chemistry of Materials 29.5 (2017): 2211-2217.
[12]. Wu, Y. S., Ma, J., Li, M. C., & Hu, F. (2013). Synthesis of γ-Al2O3 with high surface area and large pore volume by reverse precipitation-azeotropic distillation method. Chemical Research in Chinese Universities, 29(2), 206-209.
[13]. Wu, Yu-sheng, Jiao Ma, Ming-chun Li, and Fang Hu. "Synthesis of γ-Al2O3 with high surface area and large pore volume by reverse precipitation-azeotropic distillation method." Chemical Research in Chinese Universities 29, no. 2 (2013): 206-209.
[14]. Said, S., S. Mikhail, and M. Riad. "Recent processes for the production of alumina nano-particles." Materials Science for Energy Technologies 3 (2020): 344-363.
[15]. Sayed, E., Haj-Ahmad, R., Ruparelia, K., Arshad, M. S., Chang, M. W., & Ahmad, Z. (2017). Porous inorganic drug delivery systems—a review. Aaps Pharmscitech, 18(5), 1507-1525.
[16]. Toberer, E.S. and Seshadri, R., 2006. Template-free routes to porous inorganic materials. Chemical communications, (30), pp.3159-3165.
[17]. Ghanizadeh, S., Bao, X., Vaidhyanathan, B., & Binner, J. (2014). Synthesis of nano α-alumina powders using hydrothermal and precipitation routes: a comparative study. Ceramics International, 40(1), 1311-1319.
[18]. Yang, Yanping, Kunming Pan, Shizhong Wei, Wuhui Li, Liujie Xu, Jiwen Li, Fangnao Xiao et al. "Hydrothermal synthesis and adsorption property of porous spherical Al2O3 nanoparticles." Materials Research Express 6, no. 7 (2019): 075023.
[19]. Gaweł, Bartłomiej, Kamila Gaweł, and Gisle Øye. "Sol-gel synthesis of non-silica monolithic materials." Materials 3.4 (2010): 2815-2833.
[20]. Moein, Mohammad Mahdi, Abbi Abdel-Rehim, and Mohamed Abdel-Rehim. "Recent applications of molecularly imprinted sol-gel methodology in sample preparation." Molecules 24, no. 16 (2019): 2889.
[21]. Feinle, Andrea, Michael S. Elsaesser, and Nicola Huesing. "Sol–gel synthesis of monolithic

materials with hierarchical porosity." Chemical Society Reviews 45, no. 12 (2016): 3377-3399.
[22]. Colleoni, Claudio. "Sol-gel synthesis and hybrid thin film deposition for innovative textile finishing. Study, characterization and environmental impact evaluation." (2012).
[23]. Uzokov J. R., Mukhamadiev N. K. Sorption characteristics of mesoporous composite SiO2· TiO2 // Central asian journal of medical and natural sciences. – 2021. – V. 2. – №. 5. – P. 494-498.
[24]. Uzokov J.R., Mukhamadiev N.K. Synthesis of mesopore SiO2 · xZrO2 nanocomposite sorbents and their texture characteristics // Scientific bulletin of Samarkand State University-2021. Special issue. Sol-gel 2020 International Conference set of materials -2021.-V. №. 4. – P. 32-33.
[25]. Uzokov J.R., Muhamadiyev N.K. Synthesis of nanosorbents for chromatography from tetraethoxysilane and metal oxides // Proceedings of the international scientific-practical conference "Achievements, problems and prospects of complex innovative development of the Zarafshan oasis" Navoiy-2019. P. – 366-368.
[26]. Uzokov J.R., Mukhamadiev N.K. Sorption Characteristics of the mesoporous sorbents based on tetraethoxysilane and titanium oxide //European journal of molecular and clinical medicine. – 2020. – V. 7.– №. 7. – P. 656-660