WATER VAPOR SORPTION AND CAPILLARY–POROUS STRUCTURE OF CHITOSAN COMPLEXES WITH Cu^{2+} & Co^{2+} IONS

Ergasheva Khusnibonu Abduqayum qizi
Institute of Polymer Chemistry and Physics, Academy of Sciences of the Republic of Uzbekistan
E-mail: khusnibonu_ea@mail.ru
Vokhidova Noira Rakhimovna
Institute of Polymer Chemistry and Physics, Academy of Sciences of the Republic of Uzbekistan
Yarkulov Axror Yuldashevich
National University of Uzbekistan named after Mirzo Ulugbek

Abstract. In this study, the water vapor sorption properties of chitosan (CS)–metal complexes with Cu^{2+} and Co^{2+} ions at different molar ratios were investigated. The samples with ratios CS: Cu^{2+}-1:0.5, CS: Cu^{2+}-1:0.25, and CS: Co^{2+}-1:0.75 exhibited higher values of monolayer capacity (a_m) and specific surface area (S_{comp}) compared to other compositions. These results indicate a more efficient formation of capillary–porous structures, thereby enhancing the sorption capacity. Considering the fungicidal and other bioactive properties of chitosan–metal complexes, these materials can be regarded as promising sorbents for agricultural applications and the development of bioactive materials.

Keywords: chitosan–metal complexes, sorption isotherms, capillary–porous structure Cu^{2+} and Co^{2+} ions, bioactive materials

Annatatsiya. Ushbu tadqiqot ishida xitozanning Cu^{2+} va Co^{2+} ionlari bilan turli nisbatlarda hosil qilingan metallokomplekslarining suv bug‘ini sorbsiyalash xossalari o‘rganildi. Olingan natijalar asosida CS:Cu^{2+}-1:0,5, CS:Cu^{2+}-1:0,25 va CS:Co^{2+} -1:0,75 mol nisbatlardagi namunalarida monoqavat sig‘imi (a_m) va solishtirma sirt yuzasi (S_{sol}) yuqori qiymatga ega ekani aniqlandi. Bu holat ularning kapillyar-g‘ovak tuzilishining boshqa nisbatlarga nisbatan yaxshi shakllanishini ko‘rsatadi va sorbsiya qobiliyatini oshiradi. Bu xitozan metallokomplekslarining fungitsid va boshqa biologik faol xossalari mavjudligi sababli, ular qishloq xo‘jaligida qo‘llash uchun muhim ilmiy va amaliy ahamiyat kasb etadi.

Kalit so‘zlar: xitozan metallokomplekslari, kapillyar-g‘ovak struktura, sorbsiya xossalar, Cu^{2+} va Co^{2+} ionlari, biologik faol materiallar

Аннотация. В данной работе исследованы изотермы сорбции водяного пара хито-зановых металлкомплексов с ионами Cu^{2+} и Co^{2+}, полученных в различных мольных соотношениях. Установлено, что образцы с соотношениями ХЗ:Cu^{2+}-1:0,5, ХЗ:Cu^{2+}-1:0,25 и ХЗ:Co^{2+}-1:0,75) обладают более высокими значениями мономолекулярной ёмкости ($a_м$) и удельной поверхности ($S_{срав}$). Это свидетельствует о более эффективном

ISSN 3030-3907

формировании капиллярно–пористой структуры, что приводит к повышению сорбционной способности. С учётом фунгицидных и других биологически активных свойств хито-зановых металлкомплексов, данные материалы могут рассматриваться как перспективные сорбенты для применения в сельском хозяйстве и в области биоактивных материалов.

Ключевые слова: хитозановые металлкомплексы, сорбционные изотермы, капиллярно–пористая структура, ионы Cu^{2+} и Co^{2+}, биологически активные материалы

Introduction

Chitosan is one of the unique biopolymers with high sorption activity among natural polysaccharides. The amine and hydroxyl groups in its molecule are capable of protonation and coordination bonding, forming stable complexes with heavy metal ions. In this regard, chitosan complexes with Cu^{2+} and Co^{2+} ions serve as critical model systems for studying sorption processes. Analysis of water vapor sorption isotherms in such metallopolymer complexes serves to reveal the laws of formation of the capillary-pore structure. As a result, not only is the behavior of chitosan-based sorbents at the molecular level clarified, but also their application possibilities are expanded. These studies are of urgent scientific and practical importance in areas such as water purification, gas and vapor separation, membrane technologies, and the development of bioactive coatings.

REVIEW

The interaction of chitosan with metal ions is associated with the chemical sorption of nanoparticles on its surface. It has been proven that the sorption process of metal ions occurs in the macromolecular spaces of chitosan [1-3]. The sorption properties of complexes of chitosan with metals show that Chitosan-Me^{2+} has higher sorption properties than Chitosan-Me^{0} [4-7].

The sorption capacity of polymer metal complexes (PMCs) based on CS is better in samples with a high chitosan content. In complexes formed by CS and Metal (II) (Me^{2+}), the volume of PMC increases with an increase in the amount of Me^{2+}. At the same time, the absorption activity of Me^{2+} contributes to the rise in chitosan sorption. The sorption capacity of PMCs also depends on the size of the particles in the complexes. That is, it is said that the smaller the particle size, the smaller the sorption capacity. In particular, it has been found that nano-sized complexes of PMCs have low sorption properties [8].

Chitosan-metal complexes have been widely studied in wastewater treatment. In this study, the factors affecting the adsorption capacity of chitosan-metal complex adsorbents, including various metals, various metal salts, and the degree of crosslinking, were investigated [9]. The results showed that the chitosan-Fe(III) complex prepared using sulfate salts exhibited the best adsorption efficiency

ISSN 3030-3907

(100%) for various dyes within a very short time (10 min), with a maximum adsorption capacity of 349.22 mg/g. The anion of the metal salt used in the preparation played an essential role in enhancing the adsorption capacity of the chitosan-metal complex. SO42− ions not only interacted with the amine group of the chitosan polymer but also could facilitate the chelation of metal ions with the chitosan polymer during the synthesis process, and the pH value and ionic environment sensitivity were analyzed for the chitosan-metal complex. These factors affecting the adsorption of chitosan-metal complexes can not only help optimize their use but also aid in designing new chitosan-metal-based complexes [10].

The anionic pollutant adsorption efficiency of β-type chitosan from squid of the *Loligo genus* is clearly enhanced when chelated with metal ions. The β-structured chitosan-Fe(III) and Al(III) complexes exhibited adsorption capacities of 621.45 mg g-1 and 144.53 mg g-1 for acid red 73 dye and fluoride ions, respectively, according to the adapted Langmuir-Freundlich model; and more than 173.03 mg g-1 for Cr(VI) according to the Freundlich model. These values are much higher than those observed for α-structured chitosan-metal complexes. The polymer chains of β-chitosan are arranged in parallel with relatively weak intermolecular forces, which allows them to chelate metal ions easily. If the electrostatic attraction of the –NH3+ β groups is weak, the chelated metal ions in the chitosan-metal complex can effectively adsorb anionic pollutants. This study [11] provides more detailed information on β-chitosan-based adsorbents for application in the adsorption and removal of anionic pollutants.

Literature analysis reveals that chitosan and its various derivatives have been found to exhibit optimal conditions for use as environmentally safe, biodegradable biosorbents for different metal ions in wastewater. However, the water vapor sorption properties of these metal complexes have been insufficiently studied. In our research, the aim was to examine the water vapor sorption properties of metal complexes of chitosan with Cu^{2+} and Co^{2+} ions in different ratios, as well as their capillary-pore structures. Metal complexes of chitosan with Cu^{2+} and Co^{2+} ions are of considerable interest in agriculture due to their fungicidal and other biologically active properties.

RESEARCH METHODOLOGY

For the research work, Bombyx mori chitosan (molecular weight 134 kDa, deacetylation degree 87%), copper(II) chloride ($CuCl_2 \cdot 2H_2O$, purity: ≥99%, Shanghai Macklin Biochemical Co., Ltd. China), cobalt(II) chloride ($CoCl_2 \cdot 6H_2O$, purity: ≥98%, Aladdin Reagent Co., Ltd. China) salts were used, synthesized in laboratory conditions from chitin isolated from the silkworm cocoon.

Synthesis of Chitosan Metallocomplexes

ISSN 3030-3907

To synthesize CS-Cu^{2+} and CS-Co^{2+} metallocomplexes of *Bombyx mori* chitosan, a 1 M solution of chitosan in 2% acetic acid was initially prepared. The chitosan solution was adjusted to pH 6 with intensive stirring using a 1 M NaOH solution. 1 M solutions of Cu^{2+} and Co^{2+} salts selected as precursors were also prepared and added to the chitosan solution in the required amount, corresponding to the known molar ratios of chitosan-Me^{2+}. The synthesis was carried out in the molar ratios of CS:Cu^{2+}-1:0.25; 1:0.75; 1:0.5; 1:0.33 and CS:Co^{2+}-1:0.75; 1:0.5; 1:0.33. The precipitate formed as a result of the reaction was collected using ethyl alcohol, and the precipitate was then separated using a centrifuge. The resulting precipitate was dried in a freeze dryer at -50 ºC.

Methodology for studying the sorption isotherms of chitosan metallocomplexes in water vapor: A high-vacuum sorption device was used to study the thermodynamic and sorption properties. The change in the sample mass during the sorption process was determined using a quartz spring MAK-BEN balance with a sensitivity of 2-4 mg/mm. The temperature in the sorption cells was maintained with an accuracy of 25±0.1 °C [12-14]. Measurements were carried out using a KM-8 cathetometer at pressures ranging from 10^ (-3) to 10^ (-4) Pa. Water vapor sorption isotherms were obtained for Bombyx mori chitin, chitosan, and metallocomplexes based on them in the ratios of CS/Cu^{2+} and CS/Co^{2+} at 298 K, with ratios of 1:0.75, 1:0.5, 1:0.33, and 1:0.25 mol.

The parameters of the capillary-pore structure of the samples were calculated based on the sorption isotherms using the BET method (Brunauer-Emmet-Teller) [15].

Discussion and results

3.1. Water vapor sorption isotherms of Bombyx mori chitosan and its CS-Cu^{2+} and CS-Co^{2+} metallocomplexes at 298 K

The water vapor sorption isotherms of Bombyx mori chitin and chitosan at 298 K are S-shaped, and this shows that the water vapor sorption property of chitosan is almost two (2) times higher than that of chitin. We can see that the water vapor sorption isotherms of CS/Cu^{2+} metal complexes obtained at different ratios exhibit distinct water vapor sorption properties compared to the original chitosan (Figure 1). In this case, as the amount of copper(II) ion increases in the formation of metal complexes with the original chitosan, the sorption property also increases accordingly. It was found that when the amount of copper (II) ion is (CS: Cu^{2+}-1:0.25 mol ratio), its sorption property is higher than that of the original chitosan (Figure 1a, line 1). The reason is that this metallocomplex interacts more effectively with the solvent. It can be said that in a metallocomplex that follows the isotherm, there is no dense arrangement of macromolecules from the mixed components, which in turn leads to improved water sorption.

ISSN 3030-3907

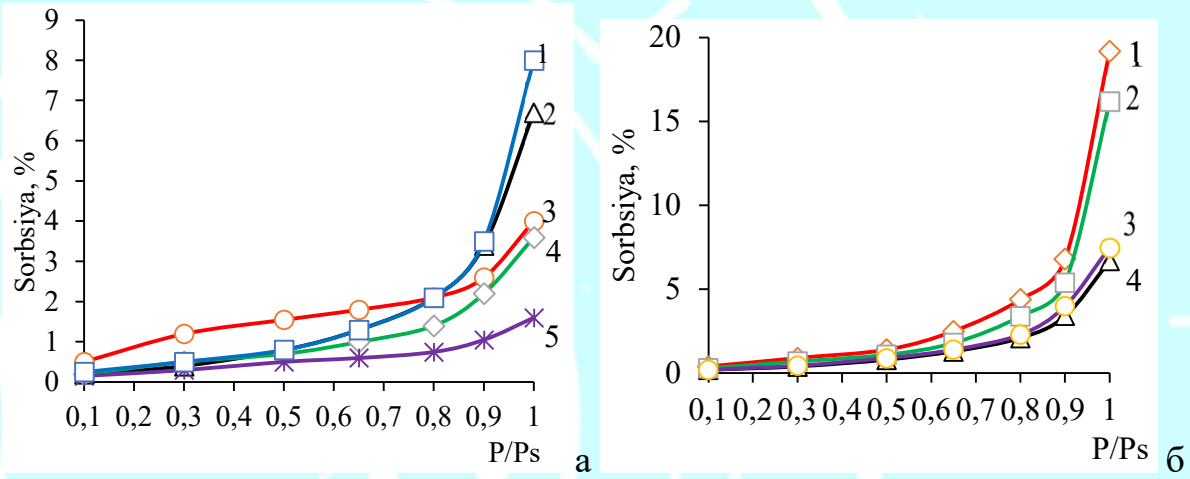


Figure 1. Water vapor sorption isotherm of the metallocomplex CS:Cu^{2+} 1:0.25 (a-1); Chitosan (a-2); 1:0.75 (a-3); 1:0.5 (a-4); 1:0.33 (a-5) and CS:Co^{2+} 1:0.75 (b-1); 1:0.5 (b-2); 1:0.33 (b-3) Chitosan (b-4) at 298 K

The sorption isotherms of CS/Co^{2+} metal complexes showed that the sorption properties of the metal complexes increase with the increase in the content of cobalt(II) ions in CS.

When comparing the water vapor sorption isotherms of CS/Cu^{2+} and CS/Co^{2+} metal complexes, it was found that the sorption properties of CS/Co^{2+} metal complexes are higher. The reason for this is considered to be the size of the chitosan and metal ions, the radius of the metal, i.e., the activity, as well as the crystalline or amorphous nature of the substances formed during the synthesis of metal complexes [3,5,8]. In general, the initial part of all isotherms is characteristic of rigid chain non-densely packed polymers, which is because the physical adsorption of sorbate on non-densely packed parts of the polymer is accompanied by the simultaneous deposition of the polymer in sorbate.

This form of sorption isotherms is characteristic of glassy polymers that are immiscible with the solvent. Depending on the location of the isotherm curves, it is possible to estimate the interaction of macromolecules of different chemical nature. All the obtained isotherms belong to types 2 and 3 of the classification of physical sorption forms, as proposed by S. Brunauer, L. Deming, U. Deming, and E. Teller. It is known that there is a VI type of isotherms. They are interpreted differently depending on the adsorbent-adsorbate and adsorbate-adsorbate interactions. Type I of the isotherm refers to monomolecular adsorption, that is, the Langmuir isotherm, while types II and III refer to polymolecular adsorption. In this case, in type II of the isotherm, the adsorbent-adsorbate interaction is more pronounced, and in type III, the adsorbate-adsorbate interaction is stronger.

It is known that the sorption capacity of various adsorbents depends to a large extent on their crystalline, amorphous, capillary-pore structure and molecular arrangement of macromolecules. The analysis of these parameters is carried out

ISSN 3030-3907

using various adsorption models, including the Freundlich, Langmuir, Dubinin-Radushkevich, Brunauer-Emmett-Teller (BET), and Aranovich models. The sorption parameters of metal complexes of chitosan with Cu^{2+} and Co^{2+} ions in different ratios in water vapor were analyzed based on the Brunauer-Emmett-Teller sorption model.

3.2. Analysis of water vapor sorption isotherms of CS-Cu^{2+} and CS-Co^{2+} metallocomplexes at 298 K using the Brunauer-Emmet-Teller (BET) sorption model

In the BET model, the van der Waals force is the primary driving force of physical adsorption. In general, according to the BET theory, the adsorbate molecules adsorbed on the adsorbent are interpreted as complexes consisting of chains of individual molecules. The capillary-pore structures of the studied samples were calculated using the polymolecular theory of adsorption, the BET theory, based on their sorption in water vapor (Fig. 2).

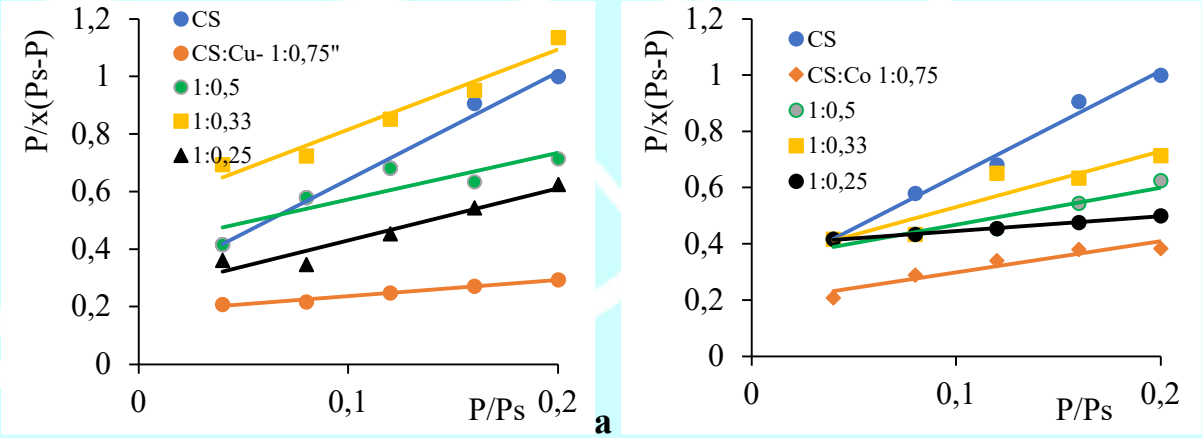


Figure 2. Water vapor sorption isotherm in the BET equation coordinates of CS-Cu^{2+} and CS-Co^{2+} samples at 298 K

The BET theory, which satisfies the basic criteria, is widely used in scientific research and practical calculations. Therefore, it is necessary to pay special attention to its inherent limitations: it does not take into account the energy diversity of the surface, and the BET theory cannot be applied to the high-pressure range (excluding capillary condensation) P_i/P_i^0 >0.3; therefore, it is only applicable to the range 0,05< P_i/P_i^0 >0.3. Additionally, the BET theory, which is based on the concept of condensation, is only used to describe the adsorption of vapors; therefore, it does not apply to the adsorption of gases. The structural adsorption parameters of the adsorbents were determined based on the polymolecular BET theory of adsorption with water vapor, based on the monolayer capacity am, the specific surface area Ssol, and the maximum quantitative values S_{comp} of the sorbed substance (at P_i/P_i^0=1), and the total volume sum of the pores Wo and the pore radius rk were determined (Table 1).

ISSN 3030-3907

Table 1.

Water surface parameters calculated from the BET equation from the water vapor sorption isotherm of CS-Cu^{2+} and CS: Co^{2+} samples at 298 K

BET parameters	a_m, g/g	S_{BET}, m^2/g	W_0 sm^3/g	r_k, Å	K_{BET}	R^2
CS	0,24	8,77	0,067	151,50	14,89	0,980
CS:Cu^{2+} 1:0,75	1,34	47,13	0,04	16,97	4,14	0,98
CS:Cu^{2+} 1:0,5	0,49	17,26	0,036	41,71	4,96	0,77
CS:Cu^{2+} 1:0,33	0,43	15,14	0,016	99,02	6,16	0,92
CS:Cu^{2+} 1:0,25	0,48	17,1	0,08	93,52	8,21	0,92
CS:Co^{2+} 1:0,75	0,77	27,09	0,192	141,7	6,9	0,907
CS:Co^{2+} 1:0,5	0,6	21,26	0,162	153,29	4,9	0,901
CS: Co^{2+} 1:0,33	0,43	15,14	0,075	99,02	6,99	0,85
CS:Co^{2+} 1:0,33	1,09	38,44	0,064	33,29	2,32	0,99

As we know, the phenomenon of polymolecular adsorption is explained by M. Polanyi's theory, in which the volume of the potential area on the surface of the adsorbent plays a crucial role in the adsorption process. Polanyi's theory explains the phenomenon of adsorption, specifically in cases of pure physical adsorption and macroporous adsorbents. According to the results of water sorption studies presented in Table 1, it was found that the highest values of monolayer capacity and specific surface area in chitosan-metal complexes are observed for CS:Cu^{2+} -1:0.5, CS:Cu^{2+}-1:0.75, and CS: Co^{2+}-1:0.25. It can be concluded that the monolayers in the samples CS:Cu^{2+}-1:0,5, CS:Cu^{2+}-1:0,25, and CS:Co^{2+}-1:0,75 represent a capillary-porous structure with a significant value compared to the capacity am and the specific surface area S_{comp} [5,8,13] -equilibrium constant (K_{BET}) of polymolecular adsorption. If K_{BET} >1, the vapor is far from saturation; if KBET = 1, the BET equation for polymolecular adsorption is converted into the Langmuir monomolecular equation, and it is considered that, as a result of adsorption, the adsorbent surface forms a monomolecular layer with the adsorbate molecules. All values of the correlation coefficients are greater than $R^2 > 0.70$.

CONCLUSION AND SUGGESTIONS

The water vapor sorption properties of Bombyx mori chitosan and its metal complexes (CS-Cu^{2+} and CS-Co^{2+}) formed in different ratios with copper(II) and cobalt(II) metal ions belonging to the valence d-element family (II) were studied, and sorption isotherms were obtained. As a result of the studies, samples synthesized in the molar ratios of CS:Cu^{2+}-1:0.5, CS:Cu^{2+}-1:0.25, and CS:Co^{2+}-1:0.75 exhibited high values of monolayer capacity (a_m) and specific surface area

ISSN 3030-3907

(S_{comp}). These results confirm that a well-formed capillary-pore structure characterizes these metal complexes. As a result, their sorption properties are further enhanced, indicating that they can be effectively utilized in future adsorption processes, catalytic systems, and the development of biologically active composite materials.

LIST OF REFERENCES USED

1. Vokhidova, N. R., & Rashidova, S. Sh. (2016). Polimer–metallic systems of chitosan *Bombyx mori*. Monograph. Tashkent: Fan, pp. 9–10.
2. Rashidova, S. Sh. (2012). Nanopolysaccharides: synthesis, structure, properties. Fiziko-khimiya polimerov: sintez, svoystva i primenenie, (18), 129–134.
3. Vokhidova, N.R., Yunusov, M.Yu., Kareva, N.D., Milusheva, R. Yu., & Rashidova, S. Sh. (2010). Sorption properties of chitosan-metal complexes from Bombyx mori. Republican Conference of Young Scientists, Tashkent, 57–58.
4. Vokhidova, N.R., Abdurasulov, A.T., & Rashidova, S.Sh. (2018). Development of an Optimal Technology for Obtaining Chitosan Bombyx mori Complexes with Copper (II) Ions. Ufimskie Izvestiya Nauchnogo Tsentra RAN, Seriya Biologiya, Biokhimiya i Genetika, 3(2), 39–40.
5. Vokhidova, N. R., & Rashidova, S. Sh. (2016). Metal complexes of chitosan Bombyx mori with Co^{2+}, Cu^{2+} ions, and features of their formation. Nano Science and Nano Technology: An Indian Journal, 10(2), 67–72.
6. Suvorova, A.I., Safronov, A.P., & Melnikova, O.L. (2002). Thermodynamic compatibility of starch and sodium carboxymethylcellulose. Vysokomolekulyarnye Soedineniya, 44(A)(1), 98–103.
7. Suvorova, A. I., Safronov, A. P., & Melnikova, O. L. (2000). Enthalpies of interaction of cellulose derivatives with starch. Vysokomolekulyarnye Soedineniya, 42(5), 822–827.
8. Vokhidova, N. R. (2016). Synthesis, properties, and applications of chitosan *Bombyx mori* metal complexes and chitosan-stabilized d-metal nanoparticles (Doctoral dissertation). Tashkent, pp. 70–72.
9. Sadia, R., Chensi, S., Jing, Y., Jianshe, L., & Jing, L. (2017). Preparation and properties of chitosan–metal complex: Factors influencing adsorption capacity for dyes in aqueous solution. Journal of Environmental Sciences. https://doi.org/10.1016/j.jes.2017.04.033
10. Benavente, M. (2010). Adsorption of metallic ions onto chitosan: Equilibrium and kinetic studies (Licentiate thesis). KTH Royal Institute of Technology, Sweden.
11. Ma, C., Li, F., Wang, C., He, M., Shen, C., Sand, W., & Liu, Y. (2018). Tuning the Adsorption Behavior of β-Structure Chitosan by Metal Binding. Environmental Chemistry. https://doi.org/10.1071/EN18070

ISSN 3030-3907

12. Keltsev, N.V. (1984). Fundamentals of the adsorption technique. Moscow: Khimiya.
13. Ergasheva, H.A., Yarkulov, A.Yu., Umarov, B.S., Vokhidova, N.R., & Akbarov, H.I. (2021). Sorption of water vapor by chitosan complexes with copper and cobalt ions. Proceedings of the International Scientific-Practical Conference "Topical Problems of Chemical Technology Sciences", Tashkent, pp. 485.
14. Hutson, N. D., & Yang, R. T. (2000). Adsorption. Journal of Colloid and Interface Science, 189.
15. Siderius, D.W., Evans, J.D., Iacomi, P., Vanduyfhuys, L., Van Speybroeck, V., Bon, V., & Kaskel, S. (2025). Best-Practice Reporting for Adsorption Data of Porous Materials. Angewandte Chemie International Edition. https://doi.org/10.1002/anie.202513606

ISSN 3030-3907