UDC 544.47
DOI: 10.33184/bulletin-bsu-2025.1.7

CATALYTIC DEGRADATION OF RHODAMINE B DYE USING HYDROGEN PEROXIDE OVER CERAMIC MEMBRANE SUPPORTED BY VANADIUM (V) OXIDE LAYER

© Hein Myat Lwin*, O. V. Yarovaya, M. O. Senina

D. I Mendeleev Russian University of Chemical Technology
9 Miusskaya sq, 125047 Moscow, Russia.

**Email: heinmyatlwin2468@gmail.com*

In this paper, the catalytic degradation of Rhodamine B dye using a ceramic membrane based on α-Al_2O_3 with a V_2O_5 supported layer is described. The vanadium-supported layer was prepared using the sol-gel method. The sol $V_2O_5.1.6H_2O$ was obtained through the thermolysis of V_2O_5 with H_2O_2. The ceramic membrane with V_2O_5 supported layer was characterized using various methods including SEM, XRD, TG/DSC, and ASAP. After thermal treatment, no changes in the phase of V_2O_5 were observed on the surface of the membrane, where it appeared in the form of dendrite crystals. It was noted that the BET surface area of the supported layer decreased following thermal treatment. The degradation process of Rhodamine B dye was conducted in a batch reactor using the prepared ceramic membrane with supported layers of varying lengths. The degree of degradation of the Rhodamine B dye was assessed by measuring the optical density of the solution with a spectrophotometer. The degradation rate was analyzed using a first-order kinetic equation. It was found that increasing the length of the supported layer positively influenced the degradation rate.

Keywords: *Rhodamine B dye, V_2O_5, Catalytic degradation, H_2O_2, optical density.*

Introduction

The rapid industrialization and increasing urbanization of the past few decades have led to a significant rise in environmental pollution, particularly in water bodies. Among the various pollutants, dyes have emerged as a serious environmental concern due to their widespread use in industries such as textiles, plastics, and paper. One such dye, Rhodamine B, is a synthetic xanthene dye known for its bright fluorescent properties, making it popular in various applications. However, its presence in aquatic environments poses serious threats to human health and ecosystems because of its toxicity and potential carcinogenic effects. Consequently, the effective removal of Rhodamine B and other similar dyes from wastewater is crucial for environmental sustainability and public health [1].

Traditional methods for dye removal, including physical adsorption, coagulation-flocculation, and biological degradation, often fall short of providing efficient and cost-effective solutions. Furthermore, many of these methods can lead to secondary pollution, generating further environmental challenges. In recent years, catalytic oxidative processes have garnered significant attention as promising alternatives for water treatment, offering efficient degradation of organic pollutants through the generation of reactive radicals [2].

The quest for efficient and sustainable catalytic processes has led to significant advancements in material science, particularly in the development of support systems that enhance catalyst performance. Among these innovations, ceramic membranes have emerged as a promising substrate for supported catalysts in various catalytic degradation processes. These membranes offer unique properties, including high thermal stability, chemical resistance, and mechanical strength, making them ideal candidates for demanding industrial applications. Ceramic membranes not only improve the efficiency of catalytic reactions but also facilitate the recovery and recycling of valuable products, ultimately contributing to environmental sustainability [3].

Vanadium (V) oxide is a particularly viable candidate for such catalytic applications due to its distinctive catalytic properties, stability under varying conditions, and efficiency in promoting oxidation reactions [4]. In recent studies, researchers have successfully synthesized V_2O_5 based catalysts and showed their catalytic active activity in Rhodamine B degradation process [5–16]. However, the luck of recovery of V_2O_5 active species from the reaction medium was found in their studies. Therefore, the preparation of a reusable ceramic membrane with a supported layer of V_2O_5 and using in catalytic process become a reliable solution for the catalytic degradation of Rhodamine B.

Materials and Methods

The following reagents were used in the work: vanadium (V) oxide, “analytical grade”; hydrogen peroxide H_2O_2, “special purity grade”. The supported carriers used were porous tubular ceramic membranes based on α-Al_2O_3 (85%) with an internal diameter of 6.5 mm with a wall thickness of 1.5 mm, obtained using technology developed at the Department of Chemical Technology of Ceramics and Refractories of the D. I. Mendeleev Russian University of Chemical Technologies (MRUCT). Their detailed characteristics are given in *table* 1.

Sol-gel method was selected for preparing membrane with catalytic supported layer of V_2O_5. $V_2O_5.1.6H_2O$ sol (0.5 wt. %) was prepared according to the previous study [17]. To obtain a V_2O_5 sol, the thermolysis of V_2O_5 powders in hydrogen peroxide solutions was carried out. A solution of hydrogen peroxide (H_2O_2) was added to a round-bottom flask containing

0.5 gram of V_2O_5 powder in the mole ratio [1]:[30] and stirred until a homogeneous yellow mass was formed. Then the required amount of water was added and heated to boil. After boiling for 5 minutes, the color changes from yellow to orange and after 3 minutes turns into dark red resulting $V_2O_5.nH_2O$ sol. The supported layer was obtained by using synthesized $V_2O_5.nH_2O$ sol (0.5 wt. %) by filtration of the dispersion medium through the outer layer of ceramic membrane using a laboratory vacuum pump as in the previous work [18]. Schematically, the process of producing membranes with a supported layer was as follows. First, the tubular membrane was closed at one end with a rubber cap and the other end of the membrane tube was left open, then the open end of the tube was connected to a plastic hose. Next, one end of the tubular substrate was sealed, and a vacuum pump was connected to the plastic hose through a Bunsen flask. The ceramic membrane was immersed vertically in the sol and a fixed volume of sol was passed through the substrate under the action of a vacuum pump. In this case, partial fixation of particles occurs on the surface of aluminum oxide grains forming the layer on the outer layer of ceramic membrane. According to this procedure, the outer surface of the ceramic membrane was coated with supported $V_2O_5.1.6H_2O$ layers of varying lengths, each with a theoretically calculated maximum allowable thickness of 45 micrometers according to the work [18] to ensure optimal adhesion. After drying the applied layer, the sample was subjected to thermal treatment at 650 °C for 60 minutes. Thermal treatment temperature was chosen at the melting point of supported V_2O_5 layer according to TG/DSC analysis (*fig*. 3).

Morphology of the supported layer was analyzed by scanning electron microscope (SEM) JEOL 1610LV (JEOL, Japan) MRUCT. The crystallographic structure of the samples was established using powder X-ray diffraction analysis (XRD, with Cu-Ka radiation). Absorption spectra of aqueous solutions methylene blue were recorded on a brand spectrophotometer LEKI SS2110UV in plastic or quartz cuvettes with an absorbing layer thickness of 10 mm in the wavelength range of 450–650 nm. Surface properties and pore structure of the supported V_2O_5 nanostructures were studied by ASAP 2020 MP (Micrometrics Instrument Corp., USA) MRUCT. Thermal analysis of the samples was carried out using a TG-DSC study on a Netzsch synchronous thermal analysis unit STA 449F1 Jupiter®. The concentration of V_2O_5 was determine by oxidimetric titration method according to the literature [19].

The degradation of Rhodamine B was carried out in a batch reactor. The membranes were immersed in a dye solution; hydrogen peroxide was added in mole ratio $[C_{28}H_{31}ClN_2O_3]:[H_2O_2] = [1]:[10]$ and stirred until the solution depreciated. The initial concentration of Rhodamine B ($C_{28}H_{31}ClN_2O_3$) was 0.25 mmol/liter. A sample of the solution was taken every 30 minute and the absorption spectrum was analyzed on a spectrophotometer. The degree of decolorization was calculated at maximum wavelength of 554 nm using the following equation:

$$D = \frac{A_0 - A_t}{A_0} x100, \tag{1}$$

where: A_o – optical density at time t = 0 minutes, A_t – optical density at time t.

Table 1

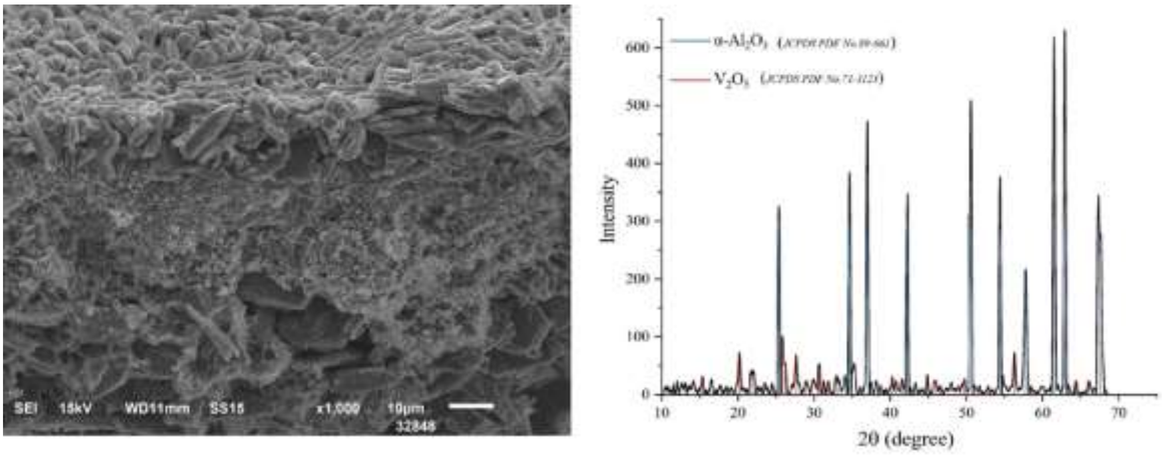
Main characteristics of porous tubular ceramic membranes based on α-Al_2O_3

№	Characteristics	Value
1	Internal diameter, mm	6.5
2	Wall thickness, mm	1.5
3	Pore radius, µm	0.8
4	Open porosity, %	45 ± 3
5	Most probable particle size, µm	15
6	Specific surface area, m^2/g	0.3

Results and Discussion

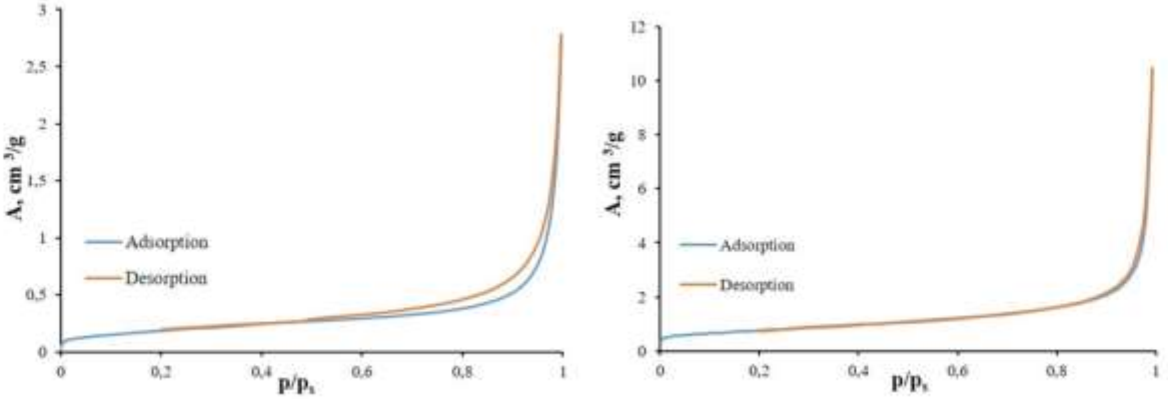
To assess the morphology of the supported layer, the substrate surfaces were analyzed using SEM micrographs. Before heat treatment, $V_2O_5.1.6H_2O$ layers were represented by overlapping nanosheets with a thickness of about 25 nm without infiltration of the layer into the pores of the membrane. After heat treatment at 650 °C, dendrites of V_2O_5 crystals formed. (fig. 1 (a)). The XRD patterns of the supported layer on the ceramic membrane after thermal treatment at 650 °C are shown in *fig*. 1 (b). It was proven by X-ray phase analysis that after heat treatment temperature of 650 °C, all of the water molecules were removed and the oxidation state of V_2O_5 did not change according to the V-O phase diagram [20].

The N_2 gas adsorption/desorption isotherms of supported layer $V_2O_5.1.6H_2O$ before thermal treatment and V_2O_5 supported layer after thermal treatment at 650 °C were also studied. To study them, the sol was dried at room temperature on a glass plate to form a xerogel. Thermal treatment of xerogel was also carried out under the same thermal procedure conditions as for the membrane with supported layer. These isotherms (*fig*. 2 (a, b)) show a type IV curve with a hysteresis loop of H3-type based on the IUPAC classification. The hysteresis loop above $P/P_0 = 0.4$ suggests the presence of mesoporous structures. BET surface area of the $V_2O_5.1.6H_2O$ xerogel is 0.6861 m^2g^{-1} and of V_2O_5 nanoparticles (after thermal treatment at 700 °C) is 0.5456 m^2g^{-1}. It shows that specific surface area of nanoparticles after thermal treatment has decreased.



(a) (b)

Fig. 1. (a) SEM micrographs and (b) XRD patterns of the supported V_2O_5 layer after thermal treatment at 650 °C.



(a) (b)

Fig. 2. (a) N_2 adsorption-desorption isotherm of $V_2O_5.1.6H_2O$ xerogel and (**b**) V_2O_5 powder after thermal treatment at 650 °C.

The TG/DSC curve of the membrane with the applied layer of $V_2O_5.1.6H_2O$ is shown in *fig.* 3. At the initial stage of heating, the DSC curve shows an endothermic thermal effect “a” -0.1221 J/g accompanied by a mass loss of 0.04%. This effect begins at 355.6 °C, has a peak at 360.9 °C and ends at 372.8 °C. With further heating from 375 to 640 °C, no thermal effects are found on the DSC curve, and with increase in temperature after this stage, a thermal effect “b” is observed, associated with the melting of the vanadium compound. It has a value of -1.351 J/g, begins at 646.9 °C, has a peak at 660.6 °C and ends at 667.7 °C. The effect is accompanied by a mass loss of 0.03%. The total mass loss was 0.07%. Upon cooling, an effect “c” is detected, associated with the crystallization process. The effect begins at 581.7 °C, peaks at 570.1 ºC, and ends at 547.6 °C. There were no thermal effects detected upon further cooling.

Catalytic degradation of Rhodamine B was carried out at different length of supported layer (V1-V5) using the oxidizing agent H_2O_2. The calculated amount of V_2O_5 loaded depending on the length of the supported layer is shown in *tab.* 2. As it is shown in *fig.* 4 (a), the optical density of Rhodamine B decreases with time, and the maximum adsorption wavelength of Rhodamine B is observed at 554 nm. So, to compare the effect of length of the supported layer (effect of mass loading) and determine the time dependence of optical density D, the value of optical density D at 554 nm was chosen. According to *fig.* 4 (b), it is observed that increasing the mass of the catalyst has a positive effect on the degradation of Rhodamine B and the optical density is clearly decreased with time.

On the basis of data shown in *fig.* 4 (b), the degree of discoloration was calculated using equation (1), and a graph of the degree of decolorization versus time was plotted as shown in *fig.* 5 (a). The reaction kinetic was calculated using the $\ln A_t/A_o$ – time graph (*fig.* 5 (b)). The conversion of methylene blue after 3 h of reaction and the kinetic rate of the reaction results calculated from the first order rate equation are shown in *tab.* 2. Vanadium 5V loaded membranes removed 85.54% of Rhodamine B in 3 hours of catalytic reaction.

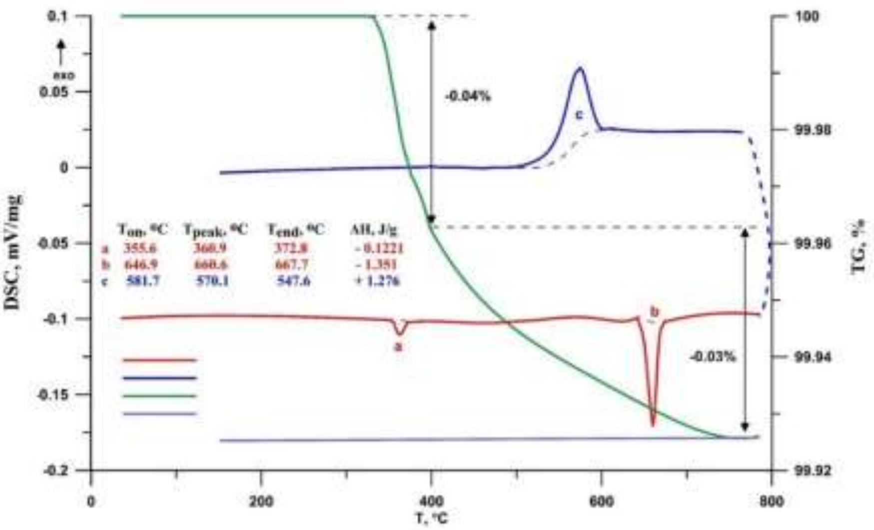
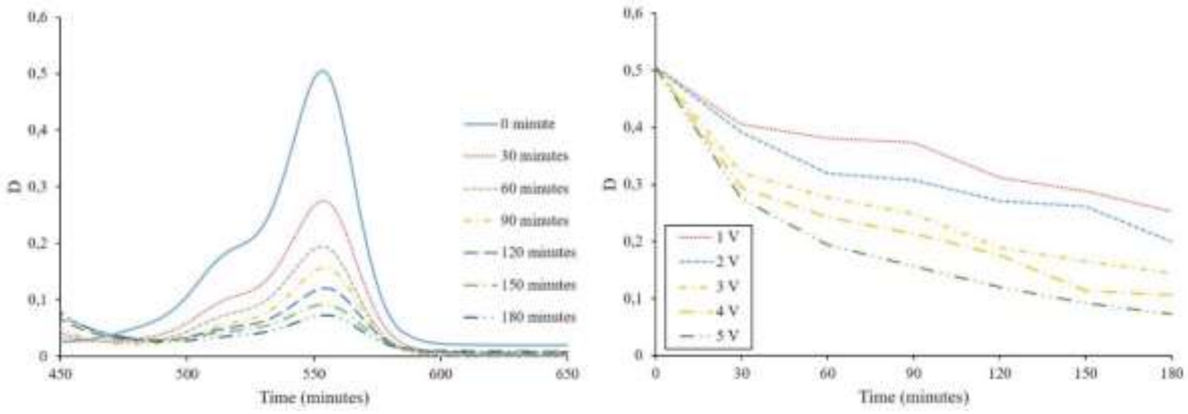
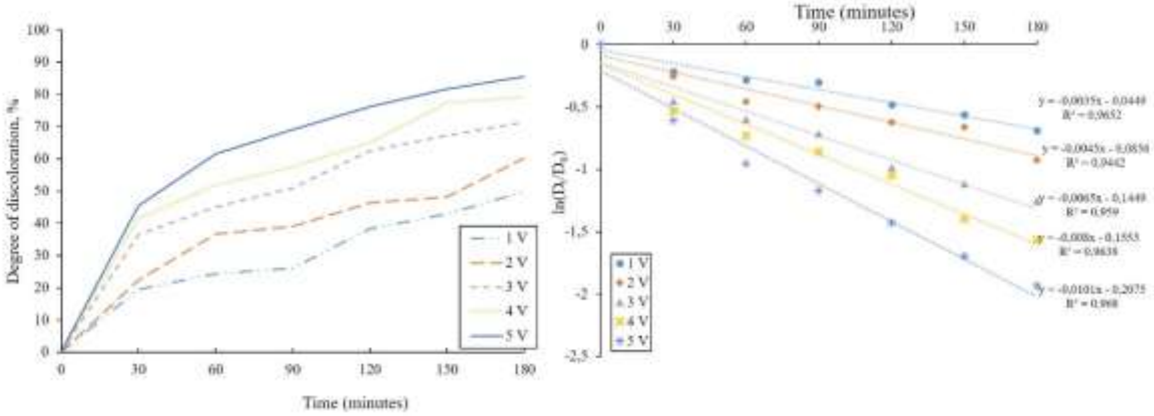


Fig. 3. TG/DSC curve of membrane with vanadium supported layer.



(a) (b)

Fig. 4. (a) the optical density of Rhodamine B as a function of time during catalytic degradation process (5V) and (b) comparison of the dependence of the optical density of Rhodamione B as a function of time at different length of supported layer (λ = 554 nm).



(a) (b)

Fig. 5. (a) comparison of the dependence of the degree of decolorization of Rhodamine B as a function of time at different catalyst loading (λ = 554 nm) and (b) dependence of the logarithm of the optical density of the dye on time during catalytic degradation process.

The amount of V_2O_5 dissolving during the catalytic process was determined by oxidimetric titration method according to the method described in [19]. The amount of V_2O leaching from the surface of the membrane obtained by this titration method during catalytic degradation process the is 2.63 mass %.

Table 2

Effect of catalyst mass loaded on change in methylene blue conversion and reaction rate constant during the catalytic reaction

№	Length of membrane, cm	Mass of V_2O_5 layer, mg/cm^2 x 10^{-3}	Mass of V_2O_5 layer, mg/cm^2 x 10^{-3}	Rate constant min^{-1} x 10^3
1V	5	9.0	49.85	3.5
2V	10	18	60.30	4.5
3V	15	27	67.25	6.5
4V	20	36	79.06	8.0
5V	25	45	85.54	10.1

Conclusion

In this paper the photocatalytic degradation of Rhodamine B over reusable ceramic membrane with V_2O_5 supported layer was successfully carried out. With the help of the diagnostic techniques (SEM, XRD, ASAP, TG/DSC) the supported layer of V_2O_5 was analyzed. The reaction rate calculated according to first order equation shows that the length of supported layer (the mass of the catalyst loaded) has a positive effect on it; and the degrading efficiency is 85%.

REFERENCES

1. Baldev E., Mubarak Ali D., Ilavarasi A. Degradation of synthetic dye, Rhodamine B to environmentally non-toxic products using microalgae // Colloids and Surfaces B: Biointerfaces. 2013. Vol. 105. P. 207–214.
2. Katheresan V., Kansedo J., Lau S. Y. Efficiency of various recent wastewater dye removal methods: A review // Journal of Environmental Chemical Engineering. 2018. Vol. 6. No. 4. P. 4676–4697.
3. Weihua Qing, Fang Liu, Hong Yao. Functional catalytic membrane development: A review of catalyst coating techniques // Advances in Colloid and Interface Science. 2020. Vol. 282. Art. 102207.
4. Chiranjivi L., Nuggehalli M. R. Vanadium Oxides: Synthesis, Properties, and Applications // Semiconductors, Springer, Cham. 2019. P. 127–218.
5. Rafique M., Hamza M., Tahir M. B. Facile hydrothermal synthesis of highly efficient and visible light-driven Ni-doped V_2O_5 photocatalyst for degradation of Rhodamine B dye // J Mater Sci: Mater Electron. 2020. Vol. 31. P. 12913–12925.
6. Yusuf T. L., Orimolade B. O., Masekela D. The application of photoelectrocatalysis in the degradation of rhodamine B in aqueous solutions: a review // RSC Adv. 2022. Vol. 12. P. 26176–26191.
7. Sohaimi K. S. A., Jaafar J., Othman M. H. D. A novel approach of photo-charging and dark-discharging mechanisms by using V_2O_5/g-C_3N_4 photocatalysts for ciprofloxacin degradation // Applied Catalysis B: Environment and Energy. 2024. Vol. 357. Art. 124233.
8. Yongtao Xue, Mohammadreza K., Xiaobin Yu. Novel CuO/$Cu_2(V_2O_7)$/V_2O_5 composite membrane as an efficient catalyst for the activation of persulfate toward ciprofloxacin degradation // Chemical Engineering Journal. 2023. Vol. 455. A140201.
9. Pankaj S. Ch., Kuldeep K., Kirtiman S. Fast decolorization of rhodamine-B dye using novel V_2O_5-rGO photocatalyst under solar irradiation // Synthetic Metals. 2022. Vol. 283. Art. 116981.
10. Sze-Mun Lam, Man-Kit Choong, Jin-Chung Sin. Construction of delaminated $Ti3C_2$ MXene/$NiFe_2O_4$/V_2O_5 ternary composites for expeditious pollutant degradation and bactericidal property // Journal of Environmental Chemical Engineering. 2022. Vol. 10. Art. 108284.
11. Jenifer A., Suno Sastri M. L., Sriram S. Photocatalytic dye degradation of V_2O_5 Nanoparticles: An experimental and DFT analysis // Optik. 2021. Vol. 243. Art. 167148.
12. Mekala R., Ramamoorthy C. Photocatalytic activities of CTAB assisted ZrO_2, V_2O_5, and ZrO_2-V_2O_5 composite by precipitation process and their studies on structural, morphological and optical properties // Chemical Physics Impact. 2023. Vol. 7. Art. 100273.
13. Bharali L., Kalita J., Dhar S. S. Fabrication of hydroxyapatite based ternary nanocomposite for photocatalytic degradation of Rhodamine B dye // Interactions. 2024. Vol. 245. P. 300.
14. Haribaaskar K., Yoganand K. S. Photocatalytic Degradation of Dye with Surface Engineering of Zr-Doped V_2O_5 Photocatalyst // BioNanoSci. 2024. Vol. 14. P. 571–580.
15. Missaoui K., Ouertani R., Jbira E. Morphological influence of $BiVO_4$ nanostructures on peroxymonosulfate activation for highly efficient catalytic degradation of rhodamine B // Environ Sci Pollut Res. 2021. Vol. 28. P. 52236–52246.
16. Remila A., Shally V., Parvathiraja C. Exploration of Photoactive Cd^{2+} Substitutions on V_2O_5 Nanoparticles and Their Catalytic Potential Against the Toxic Dye // Iran J Sci. 2024. Vol. 49(1).
17. Hein M. L., Yarovaya O. V. Colloidal chemical properties of the sol $V_2O_5.nH_2O$ // Nanosystems: physics, chemistry, mathematics. 2024. Vol. 15. No. 4. P. 487–497.
18. Hein M. L., Yarovaya O. V. Development of a method for obtaining V_2O_5 dispersions for obtaining deposited layers on the outer surface of tubular membranes based on Al_2O_3 // Advances in Chemistry and Chemical Technol. 2022. Vol. 13. P. 132–134. (In Russian Language).
19. Bakhvalov A. V. Adaptation of the method for determining vanadium (V) compounds for the analysis of alkaline electrolyte of electrolysis units // Problems of modern science and education. 2004. Vol. 6. P. 17–21.
20. Wriedt H. A. The O-V (Oxygen-Vanadium) System. Bull // Alloy Phase Diagrams. 1989. Vol. 10. P. 271−277.

Received 13.12.2024.

About the authors

Hein MYAT LWIN
D. I Mendeleev Russian University
of Chemical Technology, Russia.
PhD student of the Department
of Colloidal Chemistry.
Email: heinmyatlwin2468@gmail.com
ORCID: https://orcid.org/0009-0000-6975-2380

YAROVAYA Oksana Viktorovna
D. I. Mendeleev Russian University
of Chemical Technology, Russia.
Associate Professor of the Department
of Colloidal Chemistry.
Email: iarovaia.o.v@muctr.ru
ORCID: https://orcid.org/0000-0001-8661-3235
Web of Science ResearcherID: O-3629-2016

SENINA Marina Olegovna
D. I. Mendeleev Russian University of Chemical Technology, Russia.
Associate Professor, Department of Chemical Technology
of Ceramics and Refractories.
Email: senina.m.o@muctr.ru.