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Synthesis and physicochemical analysis of bimetalphthaltocyanine pigment based on bivalent metals

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In this paper, the research on the synthesis of magnesium-zinc-phthalocyanine pigment has been carried out. It has been synthesized based on phthalic anhydride, urea, zinc acetate, and magnesium acetate. The molar ratio of the initial substances is taken in the ratio of 1:4:3, and it has been synthesized with a yield of 89.5% and the reaction carried out at 225°C. The structure of this obtained pigment has been analyzed by IR spectral analysis. Based on magnesium and zinc phthalocyanine structures, it is found that the formation of phthalocyanine rings gives a peak in the region of 744.52-792.74 cm^{-1}, while the phenyl rings give a peak in the region of 975.98 cm^{-1}. Its thermal stability has been measured by thermogravimetric analysis, SEM (scanning electron microscope), EDS, and elemental analysis. According to the results of the analysis, it is confirmed that magnesium-zinc phthalocyanine has been synthesized by forming phthalocyanine rings.

Keywords: Magnesium-zinc-phthalocyanine, Phthalocyanine rings, Thermogravimetric curve, Scanning electron microscope, Photodynamic property

Over the years, phthalocyanine's simplicity and variety of structural modifications, and functional compounds with many favorable properties have become important for use in advanced technologies. In recent decades, the steady growth of several advanced technologies based on the photophysical properties of phthalocyanines has been appreciated[1].

At the moment, advanced technologies such as electrical and optical materials based on phthalocyanine pigments, solar cells, chemical sensors, and photodynamic cancer therapy are being widely developed in the world. It has recently been shown that two-dimensional structures can be created from phthalocyanine molecules to produce new gas sensors, energy converters, and catalytic membranes[2].

Metal complexes of phthalocyanines belonging to the class of organic heterocyclic compounds, functional composite materials and coatings in tribiologically active systems, and supramolecular chemistry are developing in promising fields[3].

Chemical compounds and related photophysical properties of various phthalocyanines (Pc), including organic dyes such as metalloporphyrins and metalphthalocyanines and their derivatives, other common organic materials, mixed metal complexes and clusters, fullerenes, dendrimer nanocomposites, were studied in detail. Polymer materials (organic and inorganic), inorganic semiconductors, and other nanoscopic materials with the ability to properly filter external radiation or other nanoscopic materials with useful potential are analyzed to characterize dynamically filtering materials, focusing in particular on the nonlinear optical properties of photoactive materials[4].

Surface reactions such as metalation and coordination of axial ligands in phthalocyanines are directly related to the effect of axial ligands on surface chemical bonding and magnetic properties[5]. Recently, the post-polymerization end groups of the phthalocyanine (Pc) macrocycle or the core unit of a number of dendrimers have been shown to be of some importance[6].

Porphyrins and phthalocyanines are colored compounds that are attracting a lot of attention due to their various properties in the emerging multidisciplinary field for processing in various fields of science and technology. Physico-chemical properties of different types of modified systems based on porphyrins, phthalocyanines, and related macrocycles, including important properties for the practical application of porphyrinoids[7].

Many phthalocyanines have fluorescent properties. Its manifestation largely depends on the electronic structure of the central ion. Pc complexes with electron-filled ions (for example, ZnPc, MgPc), as well as non-metal H_2Pc, exhibit fluorescence with a sufficiently high quantum yield (DF = 0.3-0.7), while ZnPc exhibits significant phosphorescence. Complexes with ions with an unfilled electron shell and a diamagnetic nature (PdPc, PtPc) exhibit very weak fluorescence (DF < 10-3), but have phosphorescence properties. Complexes with an unfilled electron shell and paramagnetic character ions (CuPc, CoPc, VOPc) usually do not luminesce (CuPc has weak phosphorescence)[8].

The type and intensity of luminescence, like other spectral properties, can be controlled by changing the dimensions of the Pc π-system, the type, position and structure of substituents, and melting conditions [9,10].

The combination of dye molecules in solutions is accompanied by constant orthic blurring, which is manifested in a decrease in the extinction coefficient, a deviation of the concentration dependence of the orthic density of solutions from the linear Lambert-Bouger-Behr law. Generally, the formation of aggregates of phthalocyanine molecules, particularly H-type, is an undesirable phenomenon for many modern applications, as it leads to non-radiative relaxation of the excited state energy. Monomerization of Pc in solutions can be achieved using surfactants[11].

Macrocyclic phthalocyanine ligands are obtained with ions of most elements of the periodic table. At the same time, despite the very rigid structure of the macrocycle, the radius of the central ion can vary widely from 50 to 150 nm. Such adaptation occurs due to the distortion of the plane of the ligand[12]. For example, metal-free H_2Pc, as well as metal complexes of Pc (Cu^{+2}, Zn^{+2}, Ni^{+2}, Co^{+2}, *etc.*) have a planar structure with an ionic radius of about 70 nm. Complexes with some oxidation state metals (eg, $FeCl_2Pc$, $Ge(OH)_2Pc$) and additional axial ligands are perpendicular to the macrocycle plane. A deviation of the central ionic radius from the optimal value to a smaller or larger side leads to the appearance of conformational stresses due to the approach or distance of the isoindole nitrogen atoms. In some cases, non-planar coordination of two ions located on opposite sides of the macrocycle (for example, Tl_2Pc) can also coordinate one ion with two phthalocyanine molecules ($LuPc_2$, $ZrPc_2$) [13].

Material and Methods

In this research work, compounds s phthalic anhydride, urea, zinc acetate and magnesium acetate were used. All chemical reagents were purchased as "chemically pure" from "Merit Chemicals" company.

IR-analysis

The structure of this obtained complex compound was determined by IR-spectroscopy (Fure spectrometer manufactured in Japan. IR spectroscopic studies were carried out in the powder method on a SHIMADZU infrared Foure spectrometer (range 4000-600 cm^{-1}, dimensions 4 cm^{-1}).

The simultaneous TG-DTA study.

The DTG-60 equipment from Shimadzu was used to obtain results from thermogravimetric (TG) and differential thermal analysis (DTA). The tested sample was initially held at 30°C in an argon atmosphere with a flow rate of 100 mL/min for 10 min, followed by heating at a rate of 10°C/min.

SEM and EDS analysis

Surface morphology and microstructure studies of the samples was carried out using a scanning electron microscope SEM - EVO MA 10 (Carl Zeiss, made in Germany).

Experimental Section

Synthesis bimetall phthaltocyanine pigment.

Mix phthalic anhydride, urea, zinc acetate, magnesium acetate and catalyst in a special container (Table 1). The resulting mixture is kept in oven at 225°C for one hour. As a result of the reaction, gases and phthalimide begin to separate, which are unwanted substances that affect the production of pure products. Therefore, we install the exhaust pipe on the top of the furnace and immerse the hose connected to the pipe in a container of water, so that the exhaust gas does not affect the reaction and is safe. As a result, a green porous non-solid substance is formed in the container. The resulting substance was cooled to 100°C and mixed with 20 mL of concentrated (90%) sulfuric acid, resulting in a dark green solution. The resulting solution is cooled to 50°C and mixed with boiling water. The solution

Table 1 — Effect of mass ratio of $Mg(CH_3COO)_2$ and $Zn(CH_3CO_2)_2*2H_2O$ and temperature on pigment yield obtained for magnesium-zinc phthalocyanine

S. No.	$Mg(CH_3COO)_2$:$Zn(CH_3CO_2)_2*2H_2O$	Temp. (T, °C)	ω (%)	S.No.	$Mg(CH_3COO)_2$:Zn $(CH_3CO_2)_2*2H_2O$	Temp. (T, °C)	ω (%)
1	1,1:1	200	65,4	10	1:2,6	200	69,3
2		225	85,2	11		225	87,9
3		250	73,1	12		250	78,1
4	1:1,2	200	66,3	13	1:4,3	200	79,6
5		225	86,7	14		225	89,5
6		250	75,2	15		250	79,3
7	1:1,8	200	67,1	16	1:5	200	73,3
8		225	87,4	17		225	89,5
9		250	76,3	18		250	78,4

melts and a green precipitate is formed, the pale green liquid that separates is carefully poured into another container and disposed of. Distilled water is added to the precipitate and it is filtered using a vacuum pump in a Buchner funnel. The green filtrate is zinc-magnesium phthalocyanine, which is dried in an oven at 105°C for two hours. Dried magnesium-zinc-phthalocyanine is crushed in a mortar and sieved in Table 1.

From the obtained results, it was found that when the ratio of starting reagents for synthesis of Mg-ZnPc pigment is 1:4.3 and the temperature is 225°C, the yield is equal to 89.5%. These results are favorable conditions for the synthesis of Zn-MgPc (Fig. 1).

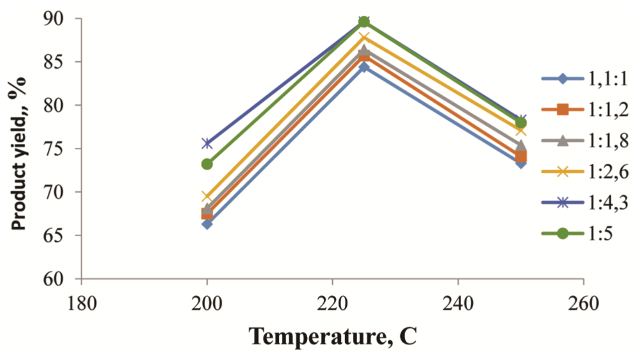


Fig. 1 — Graphic representation of the influence of the mass ratio of $Mg(CH_3COO)_2$ and $Zn(CH_3CO_2)_2*2H_2O$ and temperature on the yield of pigments obtained for magnesium-zinc phthalocyanine.

Results and Discussion

IR analysis

The structural analysis of magnesium-zinc-retaining phthalocyanine pigment was confirmed by the IR analysis (Fig. 2).

According to Fig. 2 the formation of phthalocyanine rings in magnesium-zinc phthalocyanine is seen in the absorption region of 744.52-792.74 cm^{-1}, the formation of benzene rings in the region of 975.98 cm^{-1}, the formation of the S-N $^{+}$ isoindole plane is seen in the absorption region of 1141.86 cm^{-1}, pyrrole rings appear in the absorption region of 1307.74 cm^{-1}, pyrrole nitrogen atoms appear in the absorption region of 1386.82 cm^{-1}, isoindole appears in the absorption region of 1467.83 cm^{-1}, -N= appears in the absorption region of 1604.77 cm^{-1}. Based on the IR analysis, it was determined that the approximate formula for the synthesis of magnesium-zinc-preserving phthalocyanine complex is as follows[14].

Based on the above-mentioned formula, the change of pigment yield with respect to temperature

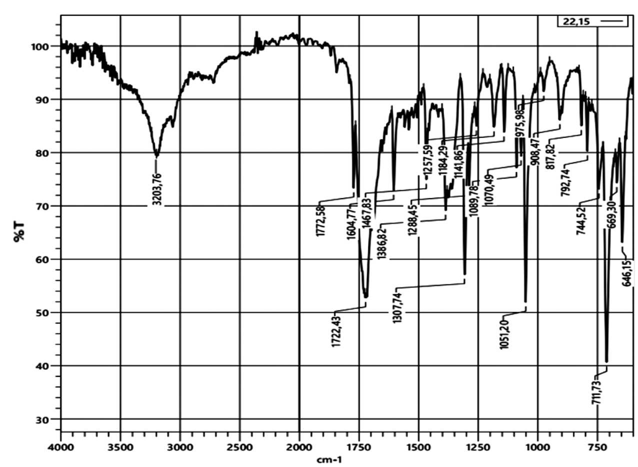


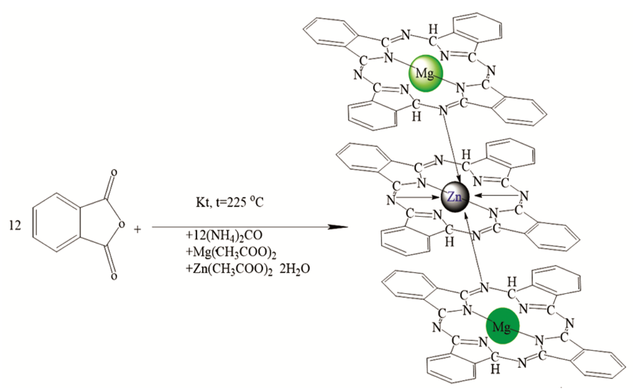
Fig. 2 — IR spectrum of magnesium-zinc-retaining phthalocyanine pigment

was studied (Scheme 1). It was found that the best temperature for the synthesis of magnesium-zinc-retaining phthalocyanine pigment is 225°C. Based on the experiments conducted, magnesium-zinc phthalocyanine pigment gives the highest result at

225°C. It was observed that one of the main characteristics is that the intensity of the pigment is better than that obtained at low temperature[15].

Thermogravimetric analysis (TGA) analysis

For the thermal analysis of the magnesium-zinc phthalocyanine (Mg-ZnPc) pigment sample, 1.80 mg of substance was taken. The thermal analysis process



Scheme 1 — Magnesium-zinc preservative phthalocyanine pigment extraction reaction

was studied in the temperature range of 200-600°C. The obtained results show that the derivatogram of magnesium-zinc-retaining phthalocyanine (Mg-ZnPc) pigment is presented, which consists of 2 curves. Thermogravimetric analysis curve (TGA) analysis (Curve 1) shows that the TGA curve of magnesium-zinc-retaining phthalocyanine (Mg-ZnPc) pigment mainly takes place in the 3 intensively decomposing temperature range. The 1st decomposition interval corresponds to the temperature of 22.48-153.67°C, the secondd decomposition interval corresponds to the temperature of 153.67-258.68°C, and the 3rd decomposition interval corresponds to the temperature of 258.68-653.94°C (Fig. 3).

Analysis shows that the core mass loss occurs in the the second line between 153.67-258.68°C, where 72.863% of the core mass is lost. The first decomposition takes place at 22.48-153.67°C, during which 4.273% of the mass is lost. The third- decomposition takes place at 258.68-653.94°C, during which 24.251% of the mass is lost[15,16] (Table 2).

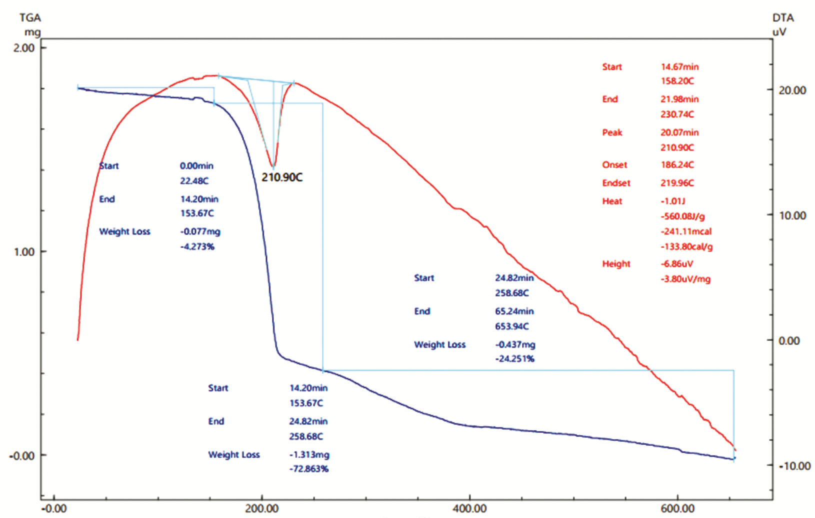


Fig. 3 — Thermogravimetric (TGA) and Differential Thermal Analysis (DTA) of Magnesium-Zinc Retaining Phthalocyanine Pigment.

Table 2 — Effect of temperature on the weight loss of a magnesium-zinc-retaining phthalocyanine pigment sample

S.No.	Dw (1.80)	1/T	dw/dt	Mg	Minutes	T°+K
1	1.76	0.0026	0.005	0.04	7.96	373
2	1.40	0.0021	0.022	0.4	17.95	473
3	0.35	0.0017	0.051	1.45	27.96	573
4	0.14	0.0014	0.043	1.66	37.96	673
5	0.10	0.0012	0.035	1.7	47.95	773
6	0.03	0.0011	0.030	1.77	57.95	873
7	0.007	0.0010	0.019	1.79	63.21	926

Table 3 — Results of thermal-oxidation analysis of magnesium-zinc-retaining phthalocyanine pigment sample

S. No.	dw (1.80)	Ln (W_1/W_2)	1/T *10^{-3}
1	1.76	0.022	2.6
2	1.40	0.251	2.1
3	0.35	1.637	1.7
4	0.14	2.554	1.4
5	0.10	2.891	1.2
6	0.03	4.098	1.1
7	0.007	5.572	1.0

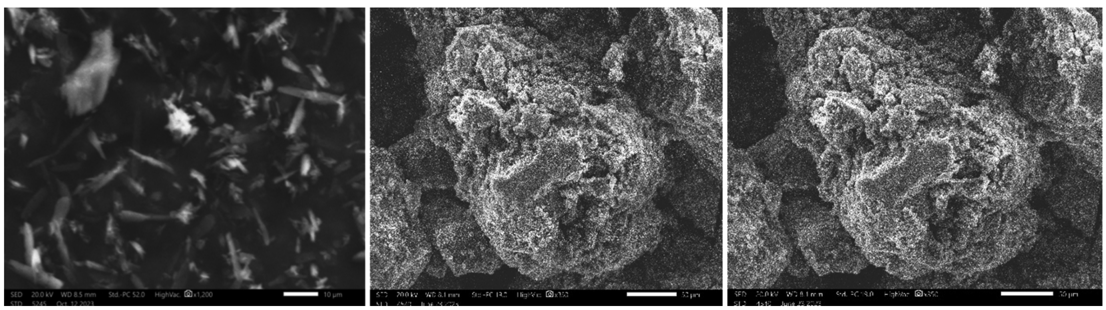


Fig. 4 — Electron microscope image of magnesium zinc phthalocyanine pigment (Mg-ZnPc) surface magnified 1200 times.

Activation energy values for this process are shown for a sample of magnesium-zinc-retaining phthalo cyanine pigment (Table 3).

Thus, based on the experimental data obtained on the kinetics of processes in the temperature range from 295.48 to 962.94 K, the characteristics of the thermal-oxidative degradation of the XX brand sample were studied.

The mass loss of the studied magnesium-zinc (Mg-ZnPc)-retaining phthalocyanine pigment due to temperature exposure over time is associated with various processes: decomposition begins with the observation of an increase in mass due to primary oxidation, and secondly, decomposition occurs with the release of volatile substances contained in the magnesium-zinc-retaining phthalocyanine pigment. occurs, and the decomposition of other substances accelerates as the temperature increases. In this case, it can be determined that magnesium-zinc phthalocyanine is actually synthesized by forming phthalocyanine rings[17].

SEM analysis

Scanning electron microscope analyses were performed under high vacuum. Microanalysis of chemical elements f pigments was carried out in the same device, studied in fields with an accelerating voltage of 20 keV and a current of 1 nA.

The image of the obtained magnesium-zinc-preserving phthalocyanine pigment is given in the scanning electron micrograph (Fig. 4). It can be seen in the picture that the initial substances were in a completely dispersed state.

The image, magnified 1200 times, provides information on the composition and structure of the near-surface layers. At the same time, it can be seen from the 1200 times magnified images that the porosity of the pigment crystals is high and the absence of additives increases the intensity of the pigment[18-20].

EDS analysis

Also, taking into account the photodynamic property of the obtained pigment, its good color absorption indicates that it can be used as a paint pigment (Fig. 5a and Fig. 5b).

The elemental analysis of our synthesized magnesium-zinc phthalocyanine pigment (Mg-ZnPc) in SEM shows that it contains all the elements contained in the magnesium-zinc phthalocyanine complex. This means that a magnesium-zinc-retaining phthalocyanine complex is formed.

It was proved that the synthesized green magnesium-zinc-preserving phthalocyanine pigment should comply with the requirements of the GOST 6220-76 standard and the sample approved in the prescribed manner (Table 4).

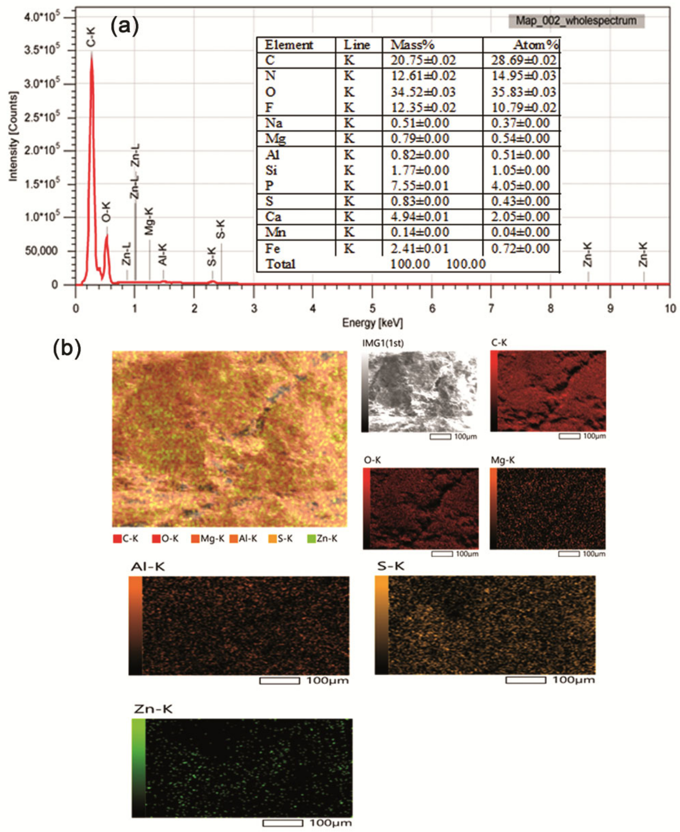


Fig. 5 — (a) EDS element map and (b) EDS results of magnesium zinc phthalocyanine pigment (Mg-ZnPc).

Table 4 — Comparison of synthesized magnesium-zinc-retaining phthalocyanine pigment according to GOST 6220-76

S. No.	The name of the indicators	Indicator standard		Mg - ZnPc
		High grade	The first variety	
1	Coloring power (concentration),%	100	100	100
2	Purity of colors	Suitable		Suitable
3	The mass percentage of water and volatile substances, %, is not much	0,4	1,5	0,3
4	The mass fraction of the residue after wet sieving, %, is not much	0,1	0,8	0,1
5	The mass fraction of the residue after dry sieving, %, is not much	0	0,5	0
6	The mass percentage of water-soluble substances, %, is not much	0,1	1,0	0,1
7	Water extract reaction (pN)	5,5-7,0	5,5-7,0	6,7
8	Fluidity of printing inks, mm	Suitable		Suitable
9	Dispersion, mm: for polyvinyl chloride printing inks	Suitable		Suitable
10	Migration resistance: in polyvinyl chloride in rubber in a nitrocellulose coating	Do not migrate		Do not migrate
11	Reagents, binders, plasticizers, light and weather resistance	Fits standard pattern		Suitable

Conclusion

(i). Phthalocyanine pigment synthesized based on $Mg(CH_3COO)_2$ and $Zn(CH_3CO_2)_2*2H_2O$ has been found to have the same properties as other phthalocyanines reported in the literature while studying the IR spectrum analysis.

(ii). The analysis of the thermogravimetric curve shows that the TGA curve mainly passes through the temperature range of three intensive mass losses, the first- intensive decomposition takes place in the range of 22.48-153.67°C in which 13.11% of the main mass is lost. The second- intensive decomposition takes place at 153.67-258.68°C, during which 10.511% of the mass is lost. The third intense decomposition takes place at 258.68-653.94°C, during which 39.53% of the mass is lost.

(iii). The curve shows the thermal stability of magnesium-zinc-retaining phthalocyanine pigment. In this case, it can be determined that the magnesium-zinc-containing phthalocyanine is synthesized by forming phthalocyanine rings. The presence of all the elements in the magnesium-zinc phthalocyanine pigment in the elemental analysis in the scanning electron microscope means that it is actually (Mg-ZnPc) formed. In the synthesis of phthalocyanine pigment based on $Mg(CH_3COO)_2$ and $Zn(CH_3CO_2)_2*2H_2O$, when the optimum temperature is 225°C, the yield of pigment is 89.5% and it meets the standard requirements of GOST 6220-76 for the production of this green pigment. indicates that it can be recommended.

Overall, the comprehensive studies in this research herald the magnesium zinc-phthalocyanine pigment (Mg-ZnPc).

Supplementary Information

Supplementary information is available in the website http://nopr.niscpr.res.in/handle/123456789/58776.

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Disclosure statement

The authors declare no conflict of interest.

Conflicts of Interest: None.

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- No animal studies are present in the manuscript (Only if the author did not use laboratory animal in his/her research).
- No human studies are present in the manuscript (Authors who did not present manuscripts reporting studies involving human participants, human data or human tissue).
- All authors agreed with participation in research and publication of the results.
- Ethical Clearance: The project was approved by the local ethical committee at Termez State University and Termez Institute of Engineering and Technology.

Authors' Contribution Statement

Mirzaeva F.Dzh: data curation and formal analysis. Turaev Kh.Kh: investigation, methodology, and original draft. Umbarov I.A: review and editing. Dzhalilov A.T: review and editing. Fayziev J.B: review and editing. Nomozov A.K: conceptualization, writing (original draft), and supervision. All authors have read and agreed to the published version of the manuscript.

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