

**REPUBLIC OF AZERBAIJAN**

*On the rights of the manuscript*

**ABSTRACT**

of the dissertation for the degree of Doctor of Philosophy

**SYNTHESIS AND STUDY OF HYBRID COMPOSITE BASED  
ON BUTADIENE RUBBER AND GRAPHITE THROUGH  
OXIDATIVE CHLOROPHOSPHORYLATION**

Specialty: 2304.01 – Macromolecular chemistry

Field of science: Chemistry

Applicant: **Solmaz Bakhtiyar Aliyeva**

**Sumgait-2022**

The work was performed at th Baku State University, Department of Chemistry of High Molecular Weight Compounds

Scientific supervisors: Active member of ANAS, doctor of chemical sciences, professor  
**Abel Mammadali Maharramov**  
doctor of chemical sciences, professor  
**Rasim Mirali Alosmanov**

Official opponents: Doctor of Chemical Sciences, professor  
**Minaver Jafar Ibrahimova**  
Doctor of Chemical Sciences, docent  
**Nushaba Ismayil Gurbanova**  
Doctor of philosophy in chemistry, docent  
**Reyhan Shahmardan Hajiyeva**

Dissertation Council ED.1.28 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at the Institute of Polymer Materials of the Ministry of Science and Education of the Republic of Azerbaijan



Chairman of the  
Dissertation council:

Corresponding member of ANAS, doctor of chemical sciences, professor  
**Bakhtiyar Ajdar Mammadov**

Scientific secretary of the  
Dissertation council:

Ph.D. in chemistry, docent  
**Khayala Vagif Allahverdiyeva**

Chairman of the scientific  
seminar:

doctor of chemical sciences, professor  
**Nafaf Tofiq Kakhramanov**

## GENERAL DESCRIPTION OF WORK

**Relevance of the topic and degree of development.** Due to the high cost of production of new polymers, the preparation of polymer materials with improved performance based on existing and waste polymers has nowadays been one of the most important directions of macromolecular chemistry.

Modification of polymers is a purposeful process aimed at changing certain properties of polymers during their synthesis or as a result of additional processing of raw polymers. In this process, new properties are given to the polymer, undesirable properties are eliminated and efforts are made to maintain the existing positive properties. Depending on the nature of the processes taking place, the physical, physico-chemical, chemical and composite methods, as well as their combinations are used to modify polymers.

In recent years, there has been an increasing interest in the composite method of polymer modification based on the addition of fillers of various natures. After Andre Geim and Konstantin Novoselov's research on the synthesis of a single graphene layer was awarded the Nobel Prize in 2010, the application of graphite and its derivatives (multi-layer graphene, graphene oxide, graphene nanosheets, and functionalized graphite) as promising fillers in polymer modification has become more relevant.

Synthesis of hybrid composite (HbC) using a combination of chemical and composite methods for modification of polymers determines the relevance of the presented dissertation.

Research works based on the modification of polymers through various chemical reactions have been published in many local and foreign publications. However, currently, in the scientific literature, the studies on the modification of polymers through combination of chemical and composite methods are a minority.

**Object and subject of the research.** The objects of the study are butadiene rubber (BR), graphite, and a HbC synthesized via combination of chemical and composite modifications of BR. The subject of the research is the study of the synthesis of the HbC in the modified BR and functionalized graphite (FG) system. In addition, to confirm the homogenous structure of the synthesized HbC, its thermal,

electrical and dielectric properties were studied, and the issues of its use in the sorption of dyes and as a flame retardant were also discussed.

**Goals and objectives of the research.** The dissertation aims to develop a synthesis method and study the properties of BR and graphite-based HbC by oxidative chlorophosphorylation (OxCh) reaction. It is known that in the OxCh reaction of BR, which proceeds according to the free radical mechanism, both chemical modification and cross-linking of macromolecules take place. In the research conducted in the current dissertation, the OxCh reaction was used to functionalize the graphite to ensure the participation of the filler in the reaction and the chemical affinity between the polymer and the filler. Afterwards, the chemical modification of BR through OxCh reaction was carried out in the presence of the OxCh functionalized graphite, and a new approach was proposed for the synthesis of a HbC that meets the modern requirements of science and technology.

To achieve the goals of the dissertation, it is planned to conduct the following:

- directed functionalization of graphite by the OxCh reaction to ensure the chemical affinity of the polymer and the filler;
- study of FG by modern physical and physico-chemical methods of analysis;
- development of a HbC synthesis method based on a joint modification of BR and FG with OxCh reaction;
- study of the electrical, dielectric and thermal properties of a homogeneous HbC to confirm its synthesis;
- study of the composition and structure of the synthesized HbC employing infrared (IR) and ultraviolet-visible (UV-vis) spectroscopy, elemental analysis, scanning electron microscope (SEM), and X-ray diffraction phase analysis (XRD);
- study of the process of sorption of Acridine yellow dye (AYD) with the synthesized HbC, including the study of optimal sorption conditions, isothermal, kinetic, and thermodynamic parameters;
- testing of the synthesized HbC as a flame retardant in laboratory conditions.

**Research methods.** HbC and FG were synthesized through the OxCh reaction and a subsequent hydrolysis of the obtained modifications. The synthesized samples were analyzed using IR and UV-vis spectroscopies, XRD, SEM, thermogravimetry (TG) and differential scanning calorimetry (DSC). Electrical and dielectric properties were analyzed in an immittance measuring device at room temperature and in a wide frequency range ( $f=0.01 \cdot 10^5 \div 10 \cdot 10^5$  Hz). During the analysis of sorption properties of the samples, the initial and equilibrium concentrations of the dye solution were identified using the spectrophotometric method at a wavelength of 444 nm and on a water background.

**Conceptual issues presented for defense.**

- a new method for functionalization of graphite by OxCh reaction;
- synthesis of a new graphite-based HbC with chemical modification of BR;
- study of the synthesized HbC by methods of physical and physico-chemical analysis, study of thermal, electrical, and sorption properties.

**Scientific novelty of the research.** For the first time:

- OxCh reaction is used for the functionalization of graphite, i.e. to ensure chemical affinity between the filler and the polymer;
- HbC based on BR and FG was synthesized through OxCh reaction;
- To confirm the homogeneous structure of the HbC synthesized by the OxCh reaction based on BR and graphite, its thermal, electrical, and dielectric properties were studied;
- Sorption of AYD from model wastewater using the BR- and graphite-based HbC was studied;
- the HbC based on BR and FG was investigated as a flame retardant.

**Theoretical and practical significance of the research.**

- this approach may be important in the future in the preparation of new hybrid composites using different chemical reactions based on other polymer and layered structure fillers (carbon nitride, boron carbon nitride, natural layered silicates);

- the results and interpretations of the applied physical and physico-chemical research methods can be used in the study of other composites;
- the methods developed for the synthesis and research of the HbC may be important in the future in the preparation of polymer materials based on waste BR (a product that does not meet technical requirements and standards or an expired product) and waste graphite (used electrodes);
- the synthesized HbC can be used in the production of electrically conductive materials, in the sorption of dyes, and in the treatment of water under extreme conditions.

**Personal contribution of the author.** The author analyzed the literature data, conducted experiments related to the functionalization of graphite, synthesis and study of the properties of the HbC composite. The main role in the discussion of the research results and the preparation of scientific publications belongs to the author.

**Publications.** 9 scientific articles and 14 abstracts of reports were published on the topic of the dissertation work. Five of the articles were published in journals indexed in the Web of Science (Science Citation Index Expanded) international database.

The results of the dissertation were presented at the following international and national scientific conferences: New Carbon Nanomaterials: Ultrathin Diamond Films (Russia, 2021); XXIX Russian Youth Scientific Conference with International Participation Dedicated to the 150th Anniversary of the Periodic Table of Chemical Elements (Russia, 2019); III International Scientific Conference of Young Researchers (Azerbaijan, 2019); 14th St. Petersburg International Conference of Young Scientists (Russia, 2018); XIV Ukrainian Conference on Macromolecules (Ukraine, 2018); Current Problems of Chemistry, XII International Scientific Conference (Azerbaijan, 2018); “Naghiyev readings” Scientific Conference Dedicated to Academician Murtuza Naghiyev's 110th Anniversary (Azerbaijan, 2018); V International Bergman Conference “Physical and Chemical Analysis in Education, Science and Technology” (Russia, 2017); 6th International Conference on Ecological and Environmental Chemistry-2017 (Moldova, 2017); International

Scientific-Practical Conference on “Water Resources, Hydro-Technical Facilities and Environment” (Azerbaijan, 2017); Actual Problems of Chemistry, XI International Scientific Conference (Azerbaijan, 2017); Scientific Conference Dedicated to the 80th Anniversary of the Institute of Catalysis and Inorganic Chemistry named after M. Nagiyev (Azerbaijan, 2016); Actual Problems of Chemistry, X Republican Scientific Conference (Azerbaijan, 2016); IX International Mammadaliyev Conference on Petrochemistry (Azerbaijan, 2016).

Within the scope of the dissertation, a research work was carried out at the Department of Chemistry of High Molecular Weight Compounds at the Baku State University, Azerbaijan.

**Scope and structure of the work.** The dissertation consists of an introduction, 5 chapters, a summary of the results, and a bibliography of 284 sources. The work in total comprises 202 pages, including 33 tables, 81 images and 11 schemes.

## MAIN CONTENTS OF THE WORK

Relevance of the dissertation topic, goals and objectives of the study, methods, scientific novelty, theoretical and practical significance, and testing of the results are given in the **introduction**.

The **first chapter** of the dissertation interprets recent scientific literature data on polymer modification, graphite surface functionalization, hybrid composites, and hybrid composites used as sorbents in wastewater treatment.

The **second chapter** gives information on the methods and reagents used for the functionalization of graphite by the oxidative OxCh reaction, the synthesis and study properties of a HbC based on BR and functionalized graphite (FG), the study of the sorption processes of AYD from aqueous solutions with the HbC, and the testing of the HbC as a flame retardant.

Examination of the samples and study of their various properties were carried out in IR (Varian 3600) and UV-vis (SPECORD 210 Plus) spectrophotometers, XRD diffractometer (Bruker “D2 Phaser” and “D8 Advance”), scanning electron microscope (SEM) equipped

with energy-dispersive X-ray spectrometer (EDS), immittance meter (RLC meter E7-20), and derivatograph (Netzsch STA 449 F3 Jupiter).

Filler functionalization is important to ensure the chemical affinity of polymers and inorganic components in the synthesis of hybrid composites<sup>17\*</sup>. The **third chapter** describes the functionalization of graphite by the OxCh reaction under various conditions, the study of the synthesized samples using XRD, IR and UV-vis spectroscopy and SEM-EDS, and the study of thermal, electrical and dielectric properties, as well as the probable mechanism of functionalization.

Functionalization of graphite through the OxCh reaction was performed under three different conditions: 1) by heating the mixture consisting of graphite and  $\text{PCl}_3$  at a temperature of  $65^\circ\text{C}$  in the presence of oxygen; 2) without heating the mixture of graphite and  $\text{PCl}_3$  in the presence of oxygen in  $\text{CCl}_4$  medium; 3) by heating the mixture of graphite and  $\text{PCl}_3$  at a temperature of  $65^\circ\text{C}$  in  $\text{CCl}_4$  medium in the presence of oxygen. The functionalized graphite (FG) samples, synthesized by hydrolysis of chlorophosphorylated graphite specimens obtained in the abovementioned conditions, were named FG1, FG2, and FG3, respectively<sup>5,16\*</sup>.

Figure 1 shows the XRD patterns of samples of pristine graphite and FG. According to XRD data of graphite, the used graphite has a hexagonal phase with crystal parameters  $P63mc$ ,  $a=2.456$ ,  $c=6.696 \text{ \AA}$ <sup>a</sup>.

In Figure 2, the (002) diffraction peaks are given separately. As can be seen, the (002) diffraction peaks for graphite are symmetrical, while the corresponding peaks for FG1, FG2, and FG3 are very broad and asymmetric. This is due to the chemical destruction of the elementary layers of graphite during functionalization and the formation of phosphorus-containing acidic groups in the newly formed active centers. In addition, the (002) diffraction peaks of FG1, FG2, and FG3 shifted towards lower  $2\theta$  values, which indicates an increase in the graphite interlayer distance as a result of functionalization.

The high intensity of the (002) diffraction peak of graphite ( $I_{\text{Graphite}}=307411$ ) indicates a high degree of graphite crystallization. A

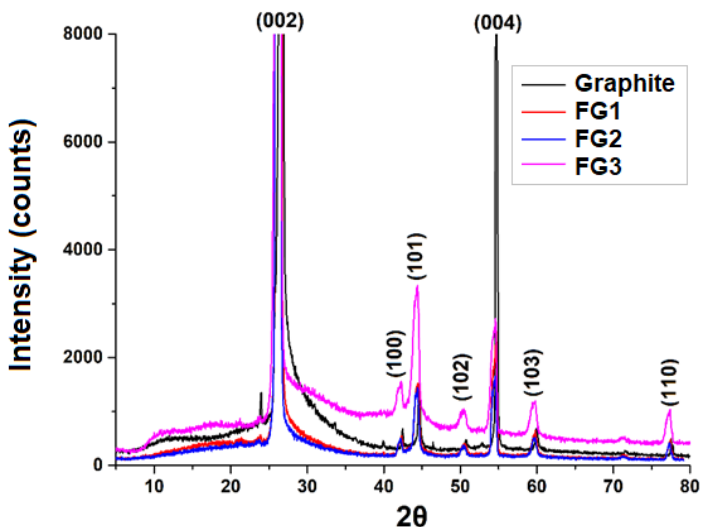
---

\* number in the list of the published scientific manuscripts

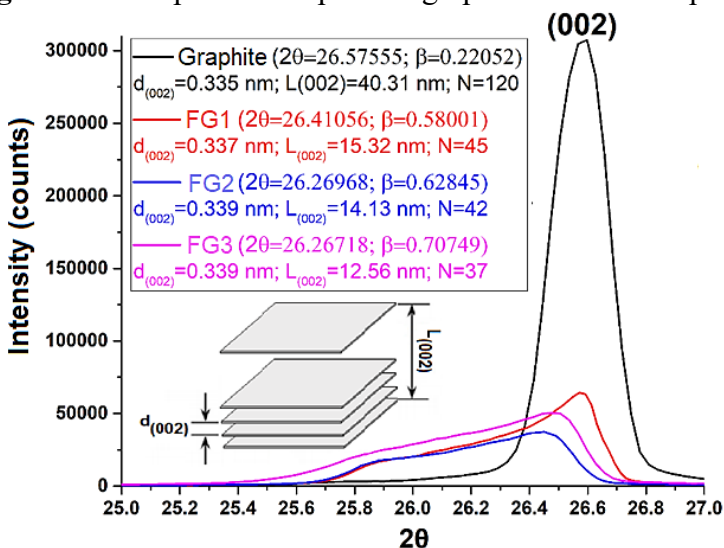
<sup>a</sup>Wyckoff R.W.G. Crystal structures-Volume 1 / R.W.G.Wyckoff. -New York:Interscience Publishers, -1963. -260 p.



sharp decrease in the intensity of the (002) diffraction peak of FG1, FG2, and FG3 ( $I_{FG1}=64360$ ;  $I_{FG2}=37470$ ;  $I_{FG3}=50335$ , respectively) is associated with a decrease in the degree of graphite crystallization as a result of functionalization.



**Figure 1.** XRD patterns of pristine graphite and FG samples



**Figure 2.** (002) diffraction peak of graphite, FG1, FG2, and FG3  
As can be seen, the (002) diffraction peaks for graphite are symmetric, while the corresponding peaks for FG1, FG2, and FG3 are

very broad and asymmetric. This is due to the chemical disintegration of graphite elementary layers during functionalization and the formation of phosphorus-containing acid groups in the newly formed active centers. In addition, the (002) diffraction peaks of FG1, FG2, and FG3 shifted to smaller values of  $2\theta$ , indicating that the interlayer distance of graphite increased as a result of the functionalization. The high intensity of the diffraction peak of graphite (002) ( $I_{\text{Graphite}}=307411$ ) indicates that the degree of initial graphite crystallization is high. The sharp decrease in the intensity of the (002) diffraction peak of FG1, FG2, and FG3 ( $I_{\text{FG1}}=64360$ ;  $I_{\text{FG2}}=37470$ ;  $I_{\text{FG3}}=50335$ , respectively) is related to the decrease in the degree of graphite crystallization as a result of functionalization.

According to the parameters  $\theta$  and  $\beta$  of the (002) diffraction peaks for graphite and FG samples, the interlayer distance between graphene layers ( $d_{(002)}$ , nm) was calculated using Bragg's formula (1), the thickness was calculated using the Debye-Scherrer formula ( $L_{(002)}$ , nm) (2), while formula (3) was used to calculate the average number of graphene layers:

$$\lambda=2d_{(002)}\sin\theta \quad (1) \quad L_{(002)}=\frac{0.98\lambda}{\beta_{(002)}\cos\theta} \quad (2) \quad N=\frac{L_{(002)}}{d_{(002)}} \quad (3)$$

where  $\lambda$  is the X-ray wavelength ( $\lambda=0.15406$  nm for Cu K $\alpha$  X-rays),  $\beta$  is the full width at half maximum (FWHM) of the (002) diffraction peak and  $\theta$  is the diffraction angle.

According to the results (Figure 2), the functionalization caused both an increase in the distance between the graphene layers and the breaking of Van der Waals bonds. Consequently, FG samples synthesized under different conditions are composed of fewer graphene layers (compared to pristine graphite)<sup>16,22\*</sup>.

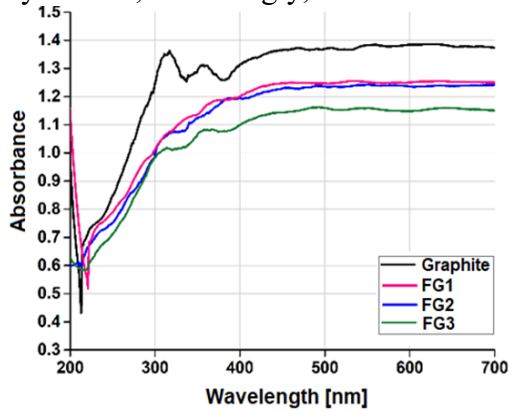
The results of spectroscopy of the UV-vis spectrum of pristine graphite and FG samples are shown in Figure 3. As can be seen, the absorption peaks of  $\pi$ - $\pi^*$  transitions in the UV range (200-400 nm) are observed in the spectra of all samples.

The absorption coefficients of FG1, FG2 and FG3 are smaller than that of pristine graphite, because their crystal sizes are smaller than

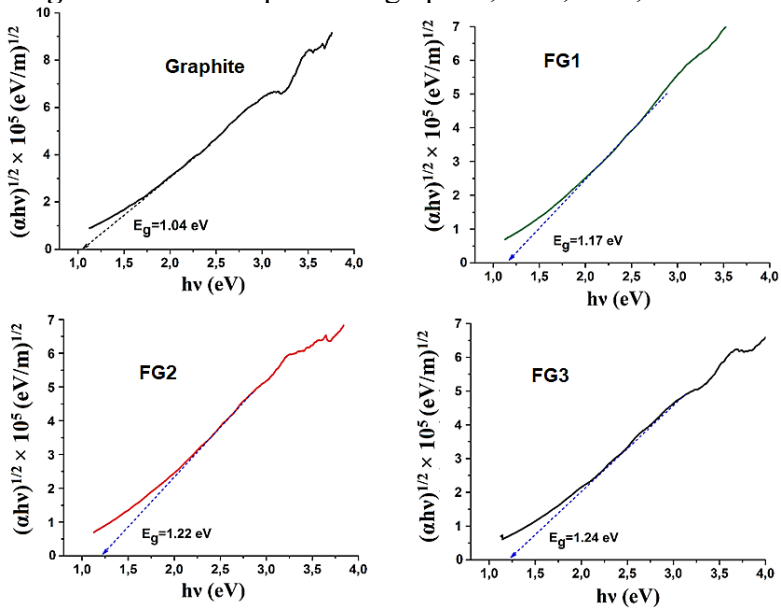
---

\* number in the list of the published scientific manuscripts

those of pristine graphite (Figure 3). Because a relatively larger size of the crystal reduces the ability to reflect the incident photon from the surface of the crystal and, accordingly, increases the absorption<sup>b,16\*</sup>.



**Figure 3.** UV-vis spectra of graphite, FG1, FG2, and FG3



**Figure 4.** Tauc plots of pristine graphite, FG1, FG2 and FG3

<sup>b</sup> Khalaf, M.K. Influence of nanocrystalline size on optical band gap in CdSe thin films prepared by dc sputtering / M.K.Khalaf, B.A.M.Alhilli, A.I.Khudiar [et al.] // Photonics and Nanostructures-Fundamentals and Applications, -2016. Vol.18, - p.59-66.

\* number in the list of the published scientific manuscripts

Based on the results of UV-vis spectroscopy, the optical band gap was calculated using the Tauc formula (Figure 4). An increase in the optical band gap in the graphite→FG1→FG2→FG3 direction is associated with a decrease in the crystal size of the samples in the same direction<sup>16\*</sup>.

*The probable mechanism of graphite functionalization.* To explain the functionalization of graphite by various reactions, it is usually considered as a diene, dienophile, or polyaromatic hydrocarbon<sup>17\*</sup>. In this study, when graphite was functionalized by the OxCh reaction, it was considered as 1,3-alkadiene. The OxCh reaction of 1,3-alkadienes begins with the action of chlorine radicals (chlorine radicals are formed as a result of the reaction of oxygen with PCl<sub>3</sub>) on the double bond. This reaction leads to the migration of the double bond and the formation of a compound containing chlorine atoms (-Cl) in the 1st position and functional groups of phosphonyl dichloride (-P(O)Cl<sub>2</sub>) in the 4th position<sup>c</sup>. Similar to the OxCh reaction of 1,3-butadiene, as a result of the OxCh reaction of graphite, the phosphochlorinated graphite with the -Cl and -P(O)Cl<sub>2</sub> functional groups are formed. Afterwards, FG with -P(O)(OH)<sub>2</sub> and -Cl groups are synthesized through hydrolysis of the phosphochlorinated graphite. To confirm the presence of -P(O)(OH)<sub>2</sub> functional groups, in contrast to graphite, the main focus in the IR spectrum of FG samples is aimed at observing new absorption bands at frequencies of -2900-2800 cm<sup>-1</sup> (stretching vibrations of -PO-H groups)<sup>d</sup> and 1250-1150 cm<sup>-1</sup> (valence vibrations of the P=O groups in the hydrogen bond)<sup>16\*</sup>.

According to the results of XRD, IR and UV-vis spectroscopy, it was established that FG consisting of <100 graphene layers and containing -P(O)OH<sub>2</sub> groups on their edge surfaces are synthesized from the OxCh reaction of graphite in all three conditions. The FG2 synthesis process was chosen as the optimal condition for the functionalization of graphite by the OxCh reaction, and further studies were carried out based on FG2.

---

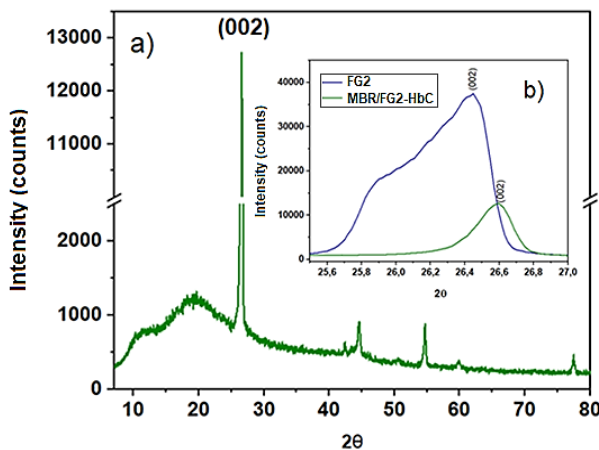
\* number in the list of the published scientific manuscripts

<sup>c</sup> Dogadina, A.V., Ionin, B.I., Petrov, A.A. 1,3-Alkadiene-phosphonates // Soviet Scientific Reviews/ Section B, -1990. Vol.15, - p.1-55.

<sup>d</sup> Ghafuri, H., Talebi, M. Water-soluble phosphated graphene: preparation, characterization, catalytic reactivity, and adsorption property // Ind. Eng. Chem. Res., -2016. Vol. 55, №11, - p.2970-2982

The **fourth chapter** is devoted to the study of a HbC (modified butadiene rubber (MBR)/FG2-HbC) synthesized based on the joint modification of BR with FG2 by the OxCh reaction by instrumental methods of analysis, as well as the study of thermal, electrical and dielectric properties.

Figure 5 shows the results of XRD studies of MBR/FG2-HbC. In the diffraction spectrum of MBR/FG2-HbC, diffraction peaks, corresponding to the amorphous phase, are observed in the direction of angles smaller than  $2\theta=25.32^\circ$  relative to the polymer, which is the organic component of the composite. As shown in Figure 5(b), (002) diffraction reflection of MBR/FG2-HbC has less intensity than that of FG2. This may be due to a further decrease in the number of graphene layers and homogeneous dispersion of FG2 in the polymer matrix as a result of the fact that FG2 can again undergo the OxCh reaction. The shift of the (002) peak towards larger values of  $2\theta$  can be associated with the penetration of polymer macromolecules into the intergallery of FG2 and the formation of a regular and close-packed structure by wandering around the FG2<sup>16\*</sup>.

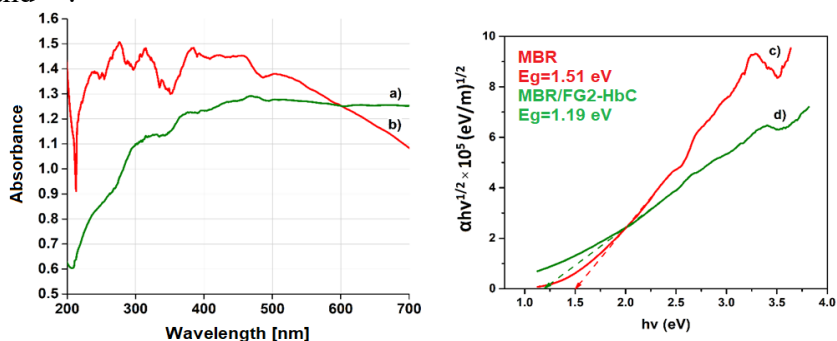


**Figure 5.** XRD diffractograms of MBR/FG2-HbC (a) and comparison of enlarged patterns of (002) diffraction reflections of FG2 and MBR/FG2-HbC at  $2\theta = 25.5\text{--}27.0^\circ$  (b)

UV-vis absorption measurements of the MBR/FG2-HbC and MBR were carried out to investigate the optical bandgap of the samples. As

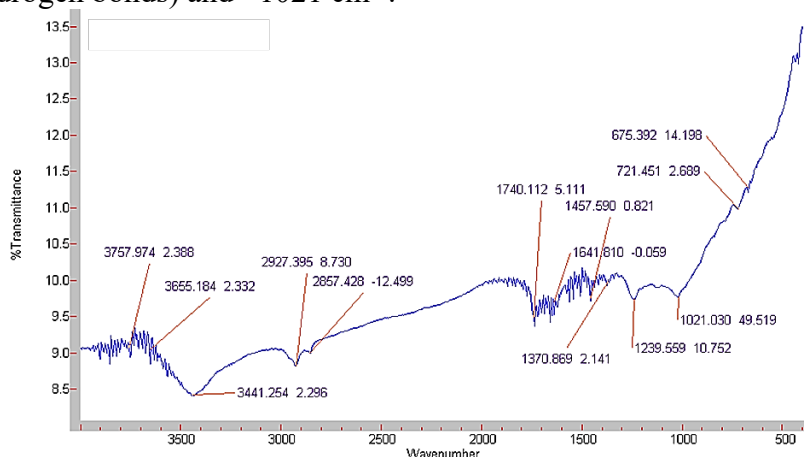
\* number in the list of the published scientific manuscripts

can be seen from Figure 6, the optical band gap of MBR/FG2-HbC (d) is smaller than that of MBR (c). This shows that the additional levels formed inside the band gap upon the addition of FG2 facilitate the transportation of electrons from the valence band to the conduction band<sup>16\*</sup>.



**Figure 6.** UV-vis spectra: MBR/FG2-HbC (a) and MBR (b) and Tauc plots: MBR (c) and MBR/FG2-HbC (d)

In the IR spectrum of the MBR/FG2-HbC (Figure 7), the main focus was on absorption bands observed at  $\sim 3441\text{ cm}^{-1}$  (stretching vibrations of -OH groups),  $\sim 2927$  and  $\sim 2857\text{ cm}^{-1}$  (stretching vibrations of -P-OH groups),  $\sim 1641\text{ cm}^{-1}$  (stretching vibrations of C=C bonds in FG2 graphene layers),  $\sim 1239\text{ cm}^{-1}$  (stretching vibrations of P=O bonds in hydrogen bonds) and  $\sim 1021\text{ cm}^{-1}$ .

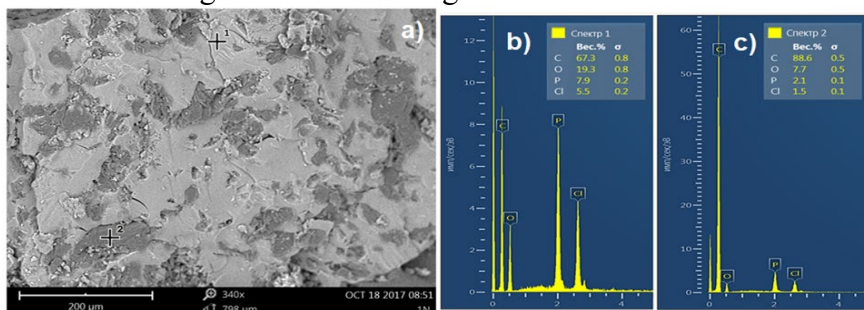


**Figure 7.** IR spectrum of MBR/FG2-HbC

\* number in the list of the published scientific manuscripts

The absorption band at  $\sim 1021\text{ cm}^{-1}$  corresponding to the C-O-P bonds indicates that the  $-\text{P}(\text{O})(\text{OH})_2$  groups of MBR/FG2-HbC are attached to the main chain via oxygen (Figure 7).

According to the SEM micrograph of MBR/FG2-HbC, the hybrid composite consists of two heterogeneous media evenly distributed among themselves, as brighter (region 1) and darker (region 2) regions were observed in the SEM micrographs (Figure 8 (a)). In the brighter region, the dispersion medium is MBR, the dispersed phase is FG2. In the darker region, the dispersion medium is FG2, the dispersed phase is MBR. In the SEM micrograph of MBR/FG2-HbC, the gap between brighter and darker regions is not observed, which shows a good adhesion between the components. The elements of carbon, oxygen, phosphorus and chlorine were identified in the darker and brighter regions according to EDS analyses. The results show that the amount of elements in lighter and darker regions are different.



**Figure 8.** SEM micrograph of MBR/FG2-HbC (a); EDS spectra of brighter (b) and darker (c) regions

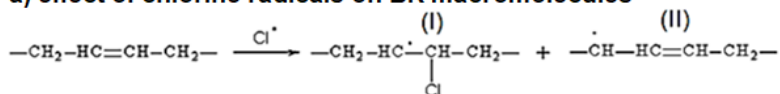
To study the synthesis mechanism of MBR/FG2-HbC, the probable reactions between substances in the reaction medium (BR, FG2,  $\text{PCl}_3$ , and  $\text{O}_2$ ) were considered:

*Scheme 1(a)* – OxCh reaction of BR takes place by a free radical mechanism. It begins as a result of the influence of atomic chlorine radicals, formed due to the reaction of  $\text{PCl}_3$  and  $\text{O}_2$ , on butadiene rubber macromolecules, resulting in the formation of chlorine-containing (I) and free (II) macroradicals<sup>f</sup>;

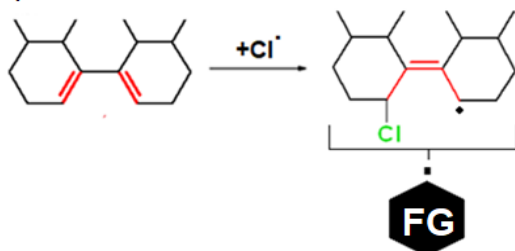
<sup>f</sup> Alosmanov, R.M. Divinil kauçukunun oksidləşmə xlorfosforlaşma reaksiyasının və alınan modifikatlarla sərbəsiya proseslərinin qanunauyğunluqları: / kimya elmləri doktoru dis. / -Bakı, 2013. - 304 s.

*Scheme 1(b)* – it is probable that in the joint OxCh reaction of BR and FG2, the active centers on the edge surfaces of the graphene layers of FG2 may be affected again by chlorine radicals<sup>16\*</sup>;

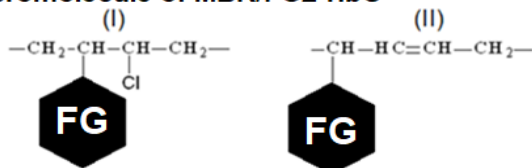
**a) effect of chlorine radicals on BR macromolecules**



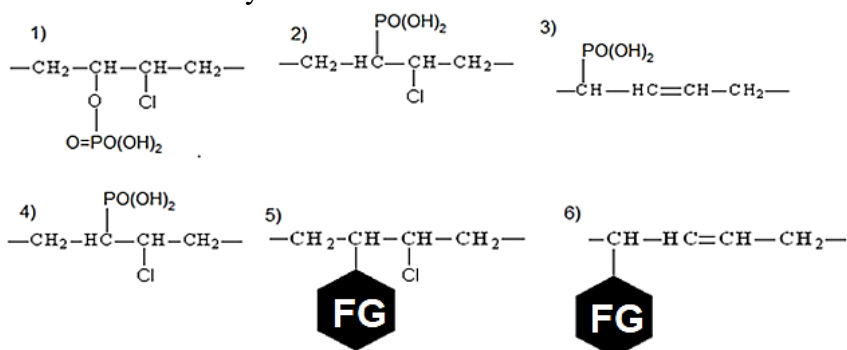
**b) Effect of chlorine radicals on unreacted edge surfaces of FG2**



**c) Macromolecule of MBR/FG2-HbC**



**Scheme 1.** Schematic representation of a probable mechanism for the synthesis of MBR/FG2-HbC



**Figure 9.** Constituent units of MBR/FG2-HbC

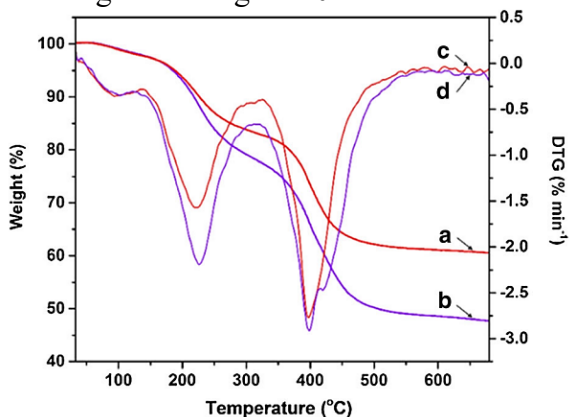
*Scheme 1(c)* – during the synthesis of MBR/FG2-HbC, chlorine-containing macroradicals (I), shown in Scheme 1(a), or free macroradicals (II) can react with the radicals shown in Scheme 1(b).

\* number in the list of the published scientific manuscripts



As a result, macromolecules with constitutional units shown in Scheme 1(c) can be formed<sup>16\*</sup>. MBR/FG2-HbC synthesized after the hydrolysis reaction of the obtained product can be composed of the constituent units shown in Figure 9.

The results obtained from the study of the thermal properties of MBR/FG2-HbC are given in Figure 10.



**Figure 10.** TG thermograms of MBR/FG2-HbC (a) and MBR (b); DTG thermograms of MBR/FG2-HbC (c) and MBR (d)

The comparison of the TG thermograms of MBR/FG2-HbC (a) and MBR (b) shows that the thermal stability of the polymer increased with the addition of FG2 to the polymer (Figure 10). Thus, MBR loses 52.3% of its mass, and MBR/FG2-HbC loses 39.5% of its mass when heated from 33°C to 680°C in an argon atmosphere. The low mass loss of MBR/FG2-HbC may be related to the formation of a homogeneous structure between FG2 and the polymer matrix<sup>16\*</sup>.

Based on the differential thermogravimetry (DTG) thermograms shown in Figure 10, it can be said that the thermal decomposition of MBR/FG2-HbC (c) and MBR (d) occurs in three steps. The first step of mass loss of MBR/FG2-HbC is the desorption of physisorbed water (33-139°C); the second step is the thermal condensation and decomposition of phosphonic and phosphate functional groups (139-325°C); and the third step occurs due to elimination of side groups from the polymer chain and random depolymerization (325-680°C)<sup>16\*</sup>.

\* number in the list of the published scientific manuscripts

The glass transition ( $T_g$ ), melting ( $T_m$ ) and crystallization temperature ( $T_c$ ) parameters of MBR and MBR/FG2-HbC were identified by the DSC method (Table 1). The  $T_g$  value of MBR/FG2-HbC is less than that of MBR, and this may be because FG2 can play the role of a plasticizer in the polymer matrix. MBR/FG2-HbC can also be more hygroscopic than MBR due to a large number of functional groups, because the mass loss of MBR/FG2-HbC (2.27%) was greater than that of MBR (1.81%) in the first step of thermal decomposition, related to the desorption of physically adsorbed water<sup>16\*</sup>. Based on the values of  $T_m$  and  $T_c$  parameters, the addition of FG2 to the polymer matrix almost does not affect the  $T_m$  and  $T_c$  temperatures.

Table 1. Parameters obtained from the DSC thermogram

Sample	$T_g$ (°C)	$T_c$ (°C)	$T_m$ (°C)
MBR	212.3	231.7	400.6
MBR/FG2-HbC	186.6	229.0	400.3

To study the electrical properties of the synthesized samples, thin films of MBR, MBR/FG2-HbC and a mechanical mixture of MBR and FG2 were prepared using polyvinyl alcohol (PVA). Accordingly, the films are named PVA+MBR, PVA+MBR/FG2-HbC and PVA+MBR and FG2 (mechanically mixed). The electrical resistance ( $R$ , Ohm) of the films was determined at values of the frequency of  $f=0.01 \cdot 10^5 \div 10 \cdot 10^5$  Hz at room temperature, their resistivity was calculated by the formula (4), and then their electrical conductivity was determined by the formula (5):

$$\rho = \frac{R \times A}{d} \quad (4) \qquad \sigma = \frac{1}{\rho} \quad (5)$$

where  $A$  is the electrode area ( $m^2$ ),  $d$  is the sample thickness (m), and  $\sigma$  is electrical conductivity ( $Ohm \cdot m$ )<sup>-1</sup>.

It was determined that the electrical conductivity of PVA+MBR/FG2-HbC is higher than that of PVA+MBR at all values of the frequency. Thus, for PVA+MBR/FG2-HbC, the electrical conductivity at the lowest value of the frequency ( $0.01 \cdot 10^5$  Hz) is  $1.19 \cdot 10^{-6}$  ( $Ohm \cdot m$ )<sup>-1</sup> and at the highest value ( $10 \cdot 10^5$  Hz) it is equal to

---

\* number in the list of the published scientific manuscripts

$2.27 \cdot 10^{-3} \text{ (Ohm}\cdot\text{m)}^{-1}$ . These results for PVA+MBR/FG2-HbC are higher than the electrical conductivity identified for PVA+MBR. The electrical conductivity identified for PVA+MBR is equal to  $5.4 \cdot 10^{-7} \text{ (Ohm}\cdot\text{m)}^{-1}$  at  $0.01 \cdot 10^5 \text{ Hz}$  and to  $1.04 \cdot 10^{-3} \text{ (Ohm}\cdot\text{m)}^{-1}$  at  $10 \cdot 10^5 \text{ Hz}$ . The improvement of electrical properties indicates that FG2, which is an electrically conductive component, forms a conduction pathway in the hybrid composite (Figure 8(a)).

In hybrid composites, the observation of improved properties, as opposed to a simple mixture of components, usually indicates a positive synergistic effect. The electrical conductivity of PVA+MBR and FG2 (mechanical mixing) film is less than the electrical conductivity of PVA+MBR/FG2-HbC and PVA+MBR in the interval of frequency of  $0.01 \cdot 10^5 \div 10 \cdot 10^5 \text{ Hz}$ . For PVA+MBR and FG2 (mechanical mixing) film, the electrical conductivity at the lowest value of the frequency ( $0.01 \cdot 10^5 \text{ Hz}$ ) is equal to  $4.5 \cdot 10^{-7} \text{ (Om}\cdot\text{m)}^{-1}$  and at the highest value ( $10 \cdot 10^5 \text{ Hz}$ ) is equal to  $7.1 \cdot 10^{-4} \text{ (Om}\cdot\text{m)}^{-1}$ . These results indicate that the mechanically mixed FG2 and MBR components have almost no effect on the electrical conductivity of the PVA film.

In the **fifth chapter**, the sorption of AYD from aqueous solutions with MBR/FG2-HbC was studied, and also MBR/FG2-HbC was tested as a flame retardant.

The concentration of AYD in the solution was determined using a calibration curve based on the values of absorbance at a wavelength of 444 nm. The sorption capacity at equilibrium ( $Q_e$ , mg/g) and removal percentage (R, %) of the samples were calculated using the following formulas:

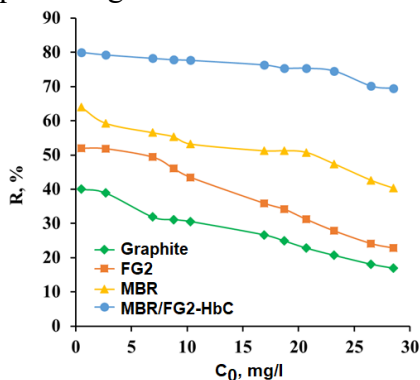
$$Q_e = \frac{(C_0 - C_e) \times V}{m} \quad (6) \quad R(\%) = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (7)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of AYD (mg/l),  $V$  is the volume of dye solution (l), and  $m$  is the amount of sorbent (g).

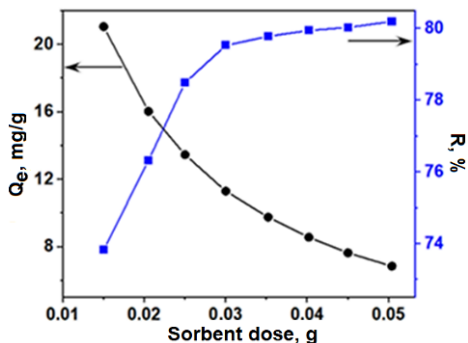
The sorption of AYD with an initial concentration of  $0.5 \div 28.5 \text{ mg/l}$  with graphite, FG2, MBR and MBR/FG2-HbC was carried out under static conditions for 24 hours, and based on the obtained results, the effect of the dye's initial concentration on sorption was studied. With

an increase in the initial concentration of AYD from 0.5 mg/l to 28.5 mg/l, the removal percentage decreases from 40% to 16.9% for graphite, from 52% to 22.8% for FG2, from 64% to 40.4% for MBR and from 80% to 69.5% for MBR/FG2-HbC (Figure 11). This indicates that the initial concentration plays an important role in the sorption of AYD by all samples.

To study the effect of the amount of HbC on sorption, the sorption of the dye was carried out under static conditions for 24 hours from an AYD solution (pH=6.8) with an initial concentration of 28.7 mg/l (0.015 l) using MBR/FG2-HbC samples in range 0.015÷0.050 g. According to the results, when the amount of MBR/FG2-HbC is increased from 0.015 g to 0.05 g, the value of the  $Q_e$  parameter decreases from 21.05 mg/g to 5.68 mg/g (Figure 12). This indicates a decrease in the total sorption surface available as a result of overlapping or merging of the sorption centers on the surface of the composite with the increase in the amount of MBR/FG2-HbC. On the other hand, with an increase in the amount of MBR/FG2-HbC from 0.015 g to 0.03 g, the removal percentage increases from 73.82% to 79.53%. A further increase in the amount of the composite from 0.03 g to 0.05 g does not significantly affect the change in the removal percentage<sup>21\*</sup>.



**Figure 11.** Effect of initial concentration of AYD on sorption

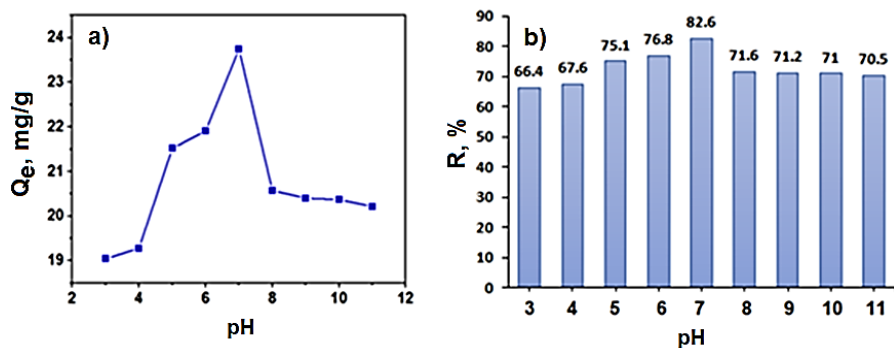


**Figure 12.** Effect of amount of MBR/FG2-HbC on sorption

\* number in the list of the published scientific manuscripts

The effect of temperature and sorption time on sorption was studied at temperatures of 298 K, 308 K and 323 K under the following conditions:  $C_0=28.7$  mg/l;  $V=0.05$  l;  $m=0.05$  g;  $pH=6.8$ ; stirring speed=100 rpm and  $t=180$  min. Based on the obtained results, the  $Q_e$  parameter value for MBR/FG2-HbC was 23.851 mg/g at  $T=298$  K, 24.313 mg/g at  $T=308$  K and 24.514 mg/g at  $T=323$  K in 180 minutes. The sorption percentage of MBR/FG2-HbC also increased with the increasing temperature and reached values of  $R=84.2\%$  at  $T=298$  K,  $R=85.9\%$  at  $T=308$  K and  $R=86.6\%$  at  $T=323$  K. Equilibrium was observed at 298 K temperature for 55 min, at 308 K temperature for 45 min and 323 K temperature for 35 min. Thus, with an increase in the temperature, equilibrium is established in the system faster<sup>21\*</sup>.

The influence of pH on sorption was studied ( $pH=3\div 11$ ;  $C_0=28.7$  mg/l;  $V=0.015$  l;  $m=0.015$  g) and the obtained results were explained considering the chemical structure of the composite and the AYD. As can be seen, the  $Q_e$  parameter increased with the increase of pH from 3 to 6 (Figure 13). At pH 7, it was at the maximum: 23.7 mg/g. With the increase of pH from 8 to 11, the value of the  $Q_e$  parameter decreased.



**Figure 13.** The influence of pH on sorption

This result can be explained as follows:

– In the pH range of 2 to 8, the AYD exists in solution as a cation (the protonated nitrogen atom is in the heterocycle)<sup>g</sup>;

\* number in the list of the published scientific manuscripts

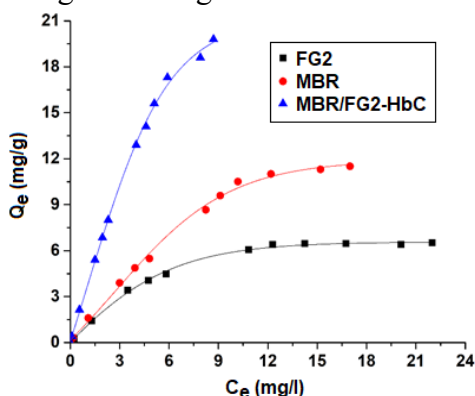
<sup>g</sup> Vlasova, N., Golovkova, L., Stukalina, N. Adsorption complexes of acridine diaminderivatives on silica surface // Colloid Journal, -2012. Vol.74, - p.25-34

– MBR/FG2-HbC has phosphonic ( $-\text{PO}(\text{OH})_2$ ) and phosphate ( $-\text{OPO}(\text{OH})_2$ ) acid groups. In moderately acidic media, the negative charges of the oxygen-containing functional groups are neutralized by protonation. As a result, the sorption of positively charged MBR/FG2-HbC dye molecules under these conditions can be hindered. The sorption occurring at pH values of 3 to 6 can be explained by the formation of hydrogen bonds between the composite and the AYD;

– A decrease in the value of the  $Q_e$  parameter with an increase in pH from 8 to 11 indicates that sorption occurs not only due to electrostatic forces but also as a result of other physical interactions. Also, at pH above 8, a decrease in protonation of the HbC surface in basic environments, as well as non-occurrence of protonation both in amino groups and in the nitrogen atom of the AYD heterocycle – which in turn cause a lack of electrostatic interaction and hydrogen bonding between the composite and AYD – result in a low sorption. In addition, at pH=8-11, an excess of  $\text{NH}_4^+$  ions in the media (formed during the dissociation of  $\text{NH}_4\text{OH}$  and  $\text{CH}_3\text{COONH}_4$  buffer solutions in water) can interfere with sorption by interacting with the negatively charged surface of the composite;

– Under neutral conditions (pH=7), both electrostatic interaction and hydrogen bonding may occur between the composite's partially negatively charged/neutral surface and positively charged dye molecules.

Experimental isotherms of sorption of AYD with FG2, MBR, and MBR/FG2-HbC are given in Figure 14.



**Figure 14.** Isotherms of AYD sorption

As can be seen (Figure 14), the observed isotherms belong to the L-type isotherms according to the Giles classification. Sorption isotherms show that all samples have a limited number of active centers, and at a certain concentration, the active centers are relatively saturated. From the obtained results, it was also known that FG2 has improved sorption properties compared to graphite, and MBR/FG2-HbC has improved sorption properties compared to its predecessors, that is MBR and FG2<sup>21\*</sup>.

The sorption isotherm was processed according to the two-parameter Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) models and the three-parameter Sips model. The calculated values of the parameters of these models are given in Table 2.

The Langmuir isotherm model describes better the sorption of AYD by FG2 than by MBR and MBR/FG2-HbC. This indicates that the surface of FG2 is more homogeneous than the surface of MBR and MBR/FG2-HbC. Also, the value of the calculated  $R_L$  parameter for all samples is greater than 0 and less than 1, indicating that FG2, MBR, and MBR/FG2-HbC are favorable for the sorption of AYD. The small correlation coefficient ( $R^2=0.95$ ) of the Langmuir isotherm model for MBR and MBR/FG2-HbC shows that this model is not sufficient to fully explain the sorption of AYD by MBR and MBR/FG2-HbC.

The Freundlich isotherm model better describes the sorption of AYD by MBR and MBR/FG2-HbC rather than by FG2 (Table 2). The fact that the value of the  $1/n$  parameter is less than 1 for all samples indicates that FG2, MBR, and MBR/FG2-HbC are suitable sorbents for AYD. The  $K_F$  parameter value is higher for MBR/FG2-HbC (3.491 mg/g) than for MBR (1.455 mg/g). This result shows that the addition of FG2 to the polymer increases the roughness of the material surface and increases the surface area, and thus MBR/FG2-HbC has more active centers for the sorption of AYD.

For FG2, MBR and MBR/FG2-HbC, the value of the  $E$  parameter calculated from the D-R isotherm model is less than 8 kJ/mol (1.581 kJ/mol, 1.581 kJ/mol, and 2.236 kJ/mol, respectively), and this indicates that physical processes prevail in the sorption of AYD by the mentioned samples. However, the small values of the correlation

---

\* number in the list of the published scientific manuscripts

coefficient indicate that this model is not suitable for the comprehensive explanation of sorption processes (Table 2)<sup>8\*</sup>.

**Table 2.** Isotherm constants of sorption of AYD

Parameter	FG2	MBR	MBR/FG2-HbC
“Langmuir”			
$Q_{\max}$	8.7	21.3	47.8
$Q_{\max}$ (experimental)	6.51	11.5	19.8
$K_L$	0.17	0.08	0.09
$R_L$	0.92÷0.17	0.96÷0.30	0.96÷0.28
$R^2$	0.98	0.95	0.95
“Freundlich”			
1/n	0.699	0.812	0.887
n	1.431	1.232	1.127
$K_F$ , mg/q	1.032	1.455	3.491
$R^2$	0.94	0.99	0.99
D-R			
$Q_{D-R}$	5.077	7.309	11.591
$K_{D-R}$	2·10 <sup>-7</sup>	2·10 <sup>-7</sup>	1·10 <sup>-7</sup>
E, kJ/mol	1.581	1.581	2.236
$R^2$	0.86	0.78	0.81
“Sips”			
$Q_S$	7.3	14.5	27.8
$a_S$	0.15	0.07	0.14
1/ $n_S$	1.42	1.47	1.33
$n_S$	0.70	0.68	0.75
$R^2$	0.99	0.98	0.99

The sorption of AYD by all samples was well described by the Sips isotherm model (Table 2). The calculated  $Q_S$  values for FG2, MBR and MBR/FG2-HbC are close to the experimental results and smaller than the  $Q_{\max}$  value calculated from the Langmuir isotherm model. The fact that the correlation coefficients of the Sips isotherm model are greater than the correlation coefficients of the Langmuir isotherm model indicates that the sorption capacity values obtained from the

\* number in the list of the published scientific manuscripts



Sips equation are more realistic than that of the Langmuir equation. As the value of  $a_s$  parameters calculated from the Sips isotherm model of sorption of AYD with FG2, MBR and MBR/FG2-HbC come closer to 0, this model becomes the Freundlich equation.

The kinetics of sorption of AYD by MBR/FG2-HbC was studied using the pseudo-first and pseudo-second-order kinetic models. As can be seen from the parameters calculated by applying these kinetic models (Table 3), the correlation coefficients ( $R^2$ ) calculated for the pseudo-second-order kinetic model are high, and the values of the  $Q_e$  parameter calculated from the pseudo-second-order kinetic model are relatively close to the  $Q_e$  (experimental) results.

**Table 3.** Kinetic parameters of AYD sorption

T, K	$Q_e$ (exp.)	pseudo-first order			pseudo-second order		
		$k_1$	$Q_e$	$R^2$	$k_2$	$Q_e$	$R^2$
298	23.803	0.054	22.4	0.88	0.002	28.902	0.98
308	24.246	0.0431	6.8	0.84	0.009	25.510	0.99
323	24.505	0.0428	2.8	0.93	0.038	24.691	1

The better description of the sorption of AYD by MBR/FG2-HbC with the pseudo-second-order kinetic model indicates that chemical processes take place between the sorbate and the composite during the sorption<sup>21\*</sup>.

The thermodynamic parameters  $\Delta H^\circ$  and  $\Delta S^\circ$  of the sorption of AYD by MBR/FG2-HbC were calculated from the dependence of  $\ln K_d$  and  $1/T$  using formula (8), and the  $\Delta G^\circ$  parameter was calculated using formula (9):

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (8) \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (9)$$

where  $K_d$  is the distribution coefficient ( $l/q$ ) and is calculated by the formula  $K_d = Q_e/C_e$ ,  $R$  is the universal gas constant (8.314 J/mol·K) and  $T$  is the temperature (K).

Based on the obtained results,  $\Delta G^\circ$  had negative values in the temperature range 298K-323K, which indicates to the possibility and spontaneity of sorption (Table 4).

The change of the  $\Delta G^\circ$  parameter from -4.196 kJ/mol to -5.041 kJ/mol with temperature increase indicates that the sorption process is

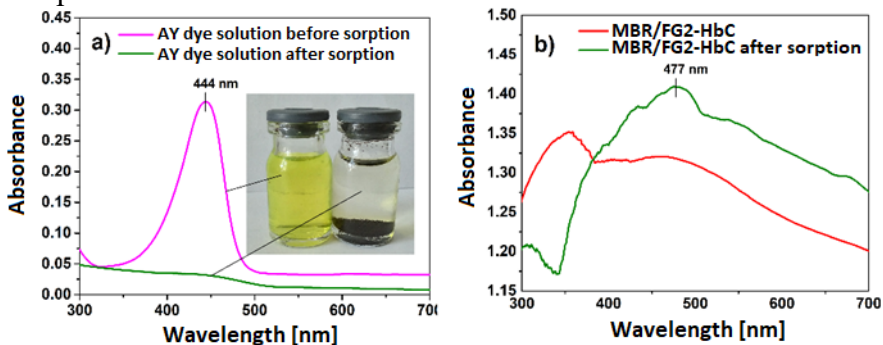
\* number in the list of the published scientific manuscripts

more spontaneous at relatively high temperatures. A positive value of the  $\Delta S^\circ$  parameter (+33.78 J/mol·K) indicates to an increase in randomness at the solid/solution boundary due to sorption and subsequent desorption<sup>21\*</sup>.

**Table 4.** Parameters  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  of sorption

T (K)	$K_d$	$\Delta S^\circ$ (J/mol·K)	$\Delta H^\circ$ (kJ/mol)	$R^2$	$\Delta G^\circ$ (kJ/mol)
298	5.34	+33.78	+5.87	0.91	-4.196
308	6.08				-4.534
323	6.45				-5.041

The UV-vis spectra of MBR/FG2-HbC before and after AYD sorption are shown in Figure 15. The absorption peaks corresponding to AYD shifted to a longer wavelength and were observed at 477 nm instead of 444 nm on the surface of MBR/FG2-HbC. This phenomenon is related to the formation of electrostatic interactions between cationic dye molecules and phosphorous acid groups of the composite<sup>21\*</sup>.

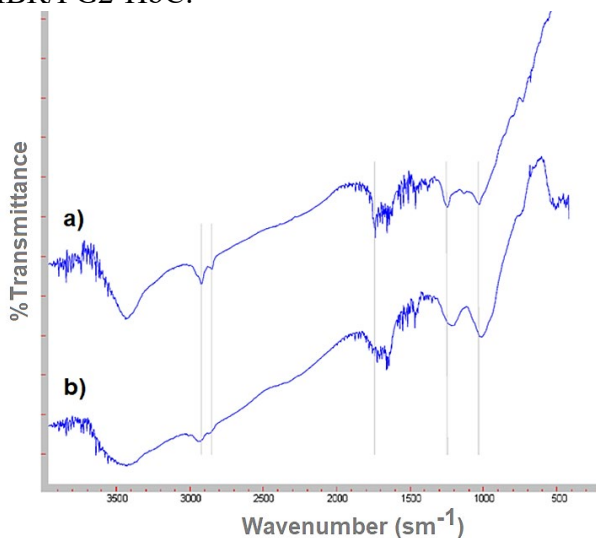


**Figure 15.** UV-vis spectra before and after sorption: AYD solution (a); MBR/FG2-HbC (b)

Figure 16 shows the IR spectra of MBR/FG2-HbC before and after sorption. As can be seen, the same absorption bands at the same frequencies were observed in the IR-spectrum of MBR/FG2-HbC before and after the sorption, but after the sorption, the intensity of absorption bands at  $\sim 2927\text{ cm}^{-1}$ ,  $\sim 2857\text{ cm}^{-1}$  and  $\sim 1740\text{ cm}^{-1}$  frequencies decreased. This may be due to the formation of a large

\* number in the list of the published scientific manuscripts

AYD molecule coating on the surface of MBR/FG2-HbC as a result of the sorption and thus the dye molecules covering the functional groups of MBR/FG2-HbC.



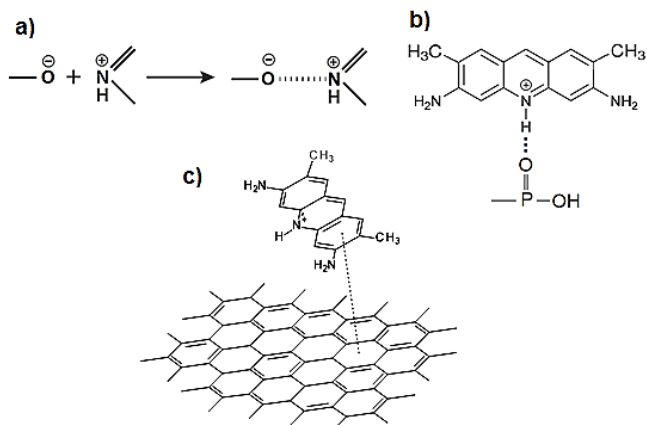
**Figure 16.** IR spectra of MBR/FG2-HbC before (a) and after (b) sorption

Absorption bands at frequencies of  $\sim 1239\text{ cm}^{-1}$  and  $\sim 1021\text{ cm}^{-1}$  observed in the IR spectrum of MBR/FG2-HbC before the sorption were shifted to lower frequencies ( $\sim 1186\text{ cm}^{-1}$  and  $\sim 995\text{ cm}^{-1}$ , respectively). This may be due to the formation of an electrostatic interaction force between the protonated nitrogen atom of AYD located in the heterocycle and the phosphorus-containing functional groups of MBR/FG2-HbC<sup>21\*</sup>.

When explaining the mechanism of sorption of AYD using MBR/FG2-HbC, the following interactions should be taken into account (Figure 17): a) electrostatic interaction between negatively charged phosphorous functional groups of MBR/FG2-HbC and positively charged AYD molecules; b) hydrogen bonds; c)  $\pi$ - $\pi$  interactions between aromatic rings of AYD and aromatic rings in graphene layers of the inorganic component (FG2) of MBR/FG2-HbC.

---

\* number in the list of the published scientific manuscripts



**Figure 17.** Schematic representation of the sorption mechanism of AYD using MBR/FG2-HbC

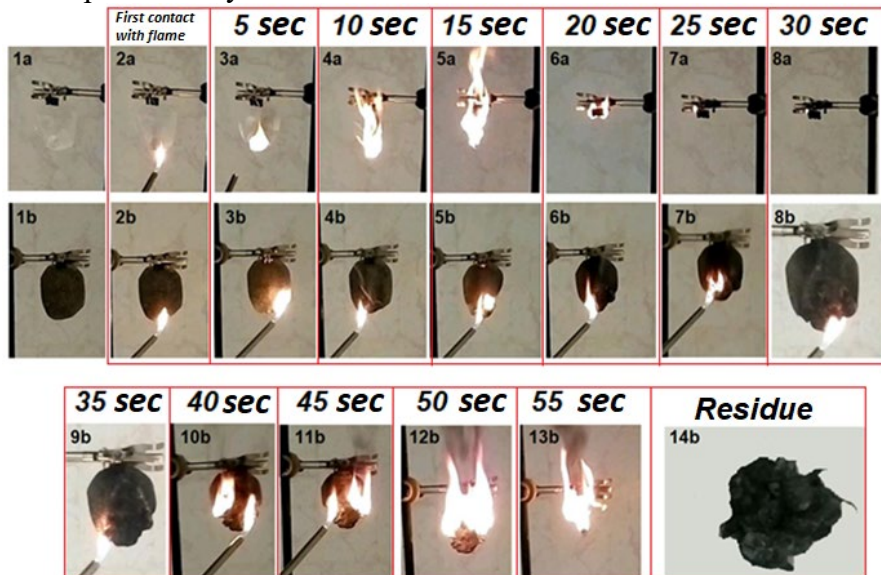
Based on the abovementioned, it can be said that AYD can be connected with graphite only by  $\pi$ - $\pi$  interactions due to polyaromatic rings in graphene layers, and with FG2 by hydrogen bonds and electrostatic interactions – in addition to  $\pi$ - $\pi$  interactions – due to phosphonic acid groups. Since MBR and MBR/FG2-HbC have the same functional groups (phosphonic and phosphate), the sorption of AYD with these samples occurs due to both hydrogen bonding and electrostatic interactions. As the sorption of AYD by MBR/FG2-HbC additionally involved  $\pi$ - $\pi$  interactions, this sample had a higher sorption capacity (Table 2).

Figure 18 shows the experimental work carried out for testing MBR/FG2-HbC as a flame retardant. Time-dependent combustion of PVA without additive and MBR/FG2-HbC-added PVA (PVA+MBR/FG2-HbC) films in the open air were compared. Figure 18 (1a) shows the PVA film and (2a) shows the first flame contact of the PVA film, Figure 18 (1b) shows the PVA+MBR/FG2-HbC film, and (2b) shows the first flame contact of the PVA+MBR/FG2-HbC film.

After the PVA film ignited, the flame source was removed and the burning of the film was observed at a certain time interval.

As can be seen from Figure 18 (2b)-(13b), the flame source was not removed during the combustion of the PVA+MBR/FG2-HbC film. Because, unlike pure PVA film, the burning of PVA+MBR/FG2-HbC

film stops when the flame source is removed. After 45 seconds, the flame source was removed and the burning of the PVA+MBR/FG2-HbC film continued for 10 seconds. PVA+MBR/FG2-HbC film remains as a residue after burning, unlike PVA which retains the shape of the previous layer after combustion.



**Figure 18.** Comparison of flammability of PVA+MBR/FG2-HbC and PVA film

In MBR/FG2-HbC the functionalization of graphite, which is a heat-conducting filler, and ensuring the chemical affinity of the polymer matrix led to an improvement in the thermal conductivity and fire-retardant properties of the material. Also, the water molecules released during the dehydration of the MBR/FG2-HbC functional groups and the chlorine atoms contained in it slow down the combustion of the material<sup>23\*</sup>.

## RESULTS

1. For the first time, graphite was functionalized by the OxCh reaction under different conditions, the obtained products were characterized using instrumental analysis methods, and a probable mechanism of the functionalization reaction was developed. The

\* number in the list of the published scientific manuscripts

results of the conducted research allowed us to determine that the functionalization changes the crystal lattice parameters and morphology of graphite and the presence of phosphonic acid groups in FG.

2. Differences in the crystal lattice parameters and morphologies of pristine graphite and FG, as well as the phosphonic functional groups contained in FG result in different thermal, electrical, dielectric and sorption properties of pristine graphite and FG.

3. Chemical modification of BR with FG2 was carried out through the OxCh reaction and a method for synthesis of HbC (MBR/FG2-HbC) was developed. MBR/FG2-HbC was systematically characterized using instrumental analysis methods, and the homogeneous structure of MBR/FG2-HbC was identified based on the results obtained from the study of its thermal, electrical, dielectric and sorption properties. Thus, MBR/FG2-HbC showed better electrical, dielectric, thermal and sorption properties compared to the components (FG2 and MBR) of which it is composed.

4. The sorption capacity of MBR/FG2-HbC against AYD was studied and the effect of factors, such as the initial concentration of the dye solution, temperature and sorption time, the dosage of the composite and pH of the medium on the sorption process were analyzed. According to the results, when the initial concentration of the dye solution increased from 0.5 mg/l to 28.5 mg/l, the removal percentage decreased from 80% to 69.5%, and the maximum sorption capacity was observed in the amount of 0.015 g of the composite and at pH 7. The sorption capacity increased with the increase of temperature and the equilibrium state was reached in 55 minutes at 298 K temperature, in 45 minutes at 308 K temperature, and in 35 minutes at 323 K temperature.

5. The sorption isotherm was studied using various two- and three-parameter mathematical isotherm models. It was determined that the sorption of AYD by MBR/FG2-HbC does not correspond to ideal monomolecular sorption, and the role of active centers of different natures is greater in sorption.

6. The sorption kinetics was investigated and it was found that the process is better described using the pseudo-second-order kinetic

model and that the dye molecules diffuse both on the surface and inside of MBR/FG2-HbC. The effect of temperature on the rate of sorption was studied and it was found that the process is chemical in nature.

7. As a result of thermodynamic studies, it was identified that the sorption of AYD by MBR/FG2-HbC is endothermic, occurs spontaneously, and randomness increases at the solid/solution boundary.

8. Based on the results of IR- and UV-vis spectroscopy studies, as well as taking into account the structure of AYD and the HbC, and the experimental results of sorption, it was deduced that the sorption of AYD by MBR/FG2-HbC occurs simultaneously with the participation of electrostatic interactions,  $\pi$ - $\pi$  interactions and hydrogen bonding.

9. For testing of MBR/FG2-HbC as a flame retardant, the burning time of its film (PVA+MBR/FG2-HbC), prepared using PVA, was compared with the corresponding parameters of a pure PVA film. It was found that the PVA film ignited completely and burned out within 20 seconds after the flame source was removed. The PVA+MBR/FG2-HbC film was exposed to a constant flame source for 45 seconds and the burning faded 10 seconds after the flame source was removed.

### **Main results of the dissertation were published in the following scientific manuscripts:**

1. Aliyeva, S.B. Graphite intercalated compound / S.B.Aliyeva, E.M.Aliyev, R.M.Alosmanov, A.M.Maharramov, A.A.Azizov, I.A.Bunyatzadeh, G.M.Eyvazova, A.Aghamaliyev // Azərbaycan Kimya Jurnalı, -2016. №4, - p.24-28
2. Əliyeva, S.B., Əzizov, A.Ə., Alosmanov, R.M., Bünyadzadə, İ.A. Butadien kauçuku və qrafit əsaslı polimer hibrid kompozit material // Kimyanın aktual problemləri, X Respublika Elmi Konfransı, -Bakı, - 4-5 may, -2016, -s.5
3. Aliyeva, S., Azizov, A., Alosmanov, R., Buniyatzadeh, I. Polybutadiene rubber-graphite hybrid composite as an adsorbent for removal of oil products from water // Neft kimyası üzrə IX Beynəlxalq Məmmədəliyev Konfransı, -Bakı, -4-5 oktyabr, -2016, -p.202

4. Əliyeva, S.B. Qrafit interkalyasiya edilmiş birləşmə / S.B.Əliyeva, A.M.Məhərrəmov, A.Ə.Əzizov, R.M.Alosmanov, İ.A.Bünyadzadə // M.Nağıyev adına Kataliz və Qeyri-üzvi Kimya İnstitutunun 80 illik yubileyinə həsr olunmuş elmi konfrans, -Bakı, -15-16 noyabr, -2016, -s.82-83.
5. Aliyeva, S. Synthesis of o-phenylenediamine functionalized graphite / S.Aliyeva, E.Aliyev, A.Maharramov, R.Alosmanov, A.Azizov, I.Buniyatzadeh, G.Eyvazova, Z.Aghamaliyev // Fullerenes, Nanotubes and Carbon Nanostructures, -2017. Vol. 25(5), - p.306-311
6. Əliyeva, S.B. Oksidləşdirici mühitdə xlorfosforlaşdırma reaksiyası ilə qrafit səthinin modifikasiyası / R.M.Alosmanov, İ.A.Bünyadzadə, Q.M.Eyvazova, İ.R.Əmiraslanov, A.A.Əzizov, A.M.Məhərrəmov // Bakı Universitetinin xəbərləri. Təbiət elmləri seriyası, -2017. №2, -s.18-23
7. Aliyeva, S.B. Carbon materials as adsorbents for Removal of crystal violet dye from aqueous solutions / S.B.Aliyeva, A.M.Maharramov, A.A.Azizov, R.M.Alosmanov, I.A.Buniyatzadeh // Su ehtiyatları, hidrotexniki qurğular və ətraf mühit mövzusunda beynəlxalq elmi-praktiki konfrans, -Bakı, -15-16 mart, -2017, -s.106-108.
8. Aliyeva, S. Application of phosphorus-functionalized carbon material for removal of crystal violet dye from the wastewater / S.Aliyeva, A.Maharramov, A.Azizov, R.Alosmanov, I.Buniyatzadeh, O.Balayeva // Ecological and environmental chemistry-2017, The 6th international conference, -Chisinau, Republic of Moldova, -2-3 March, -2017, -p.59
9. Əliyeva, S.B. Oksidləşdirici xlorfosforlaşma reaksiyası ilə sintez edilmiş kompozitin Rentgen difraksiya metodu ilə tədqiqi / S.B.Əliyeva, R.M.Alosmanov, İ.A.Bünyadzadə, A.Ə.Əzizov, A.M.Məhərrəmov // Kimyanın aktual problemləri, XI Beynəlxalq Elmi Konfransı, -Bakı, -3-4 may, -2017, -s.60.
10. Алиева, С.Б. Гибридный композит на основе поверхностно-модифицированного графита и бутадиенового каучука / С.Б.Алиева, Р.М.Алосманов, И.А.Буниятзаде, Г.М.Эйвазова, А.А.Азизов, А.М. Магеррамов, Балаева О.О. // V Международная Бергмановская конференция «Физико-химический анализ в



образовании, науке и технике, -Махачкала, -27-28 сентября, -2017, -с.94-96.

**11.** Əliyeva S.B. Əsas su çirkləndiricilərinin xarakterizə edilməsi və hibrid polimer kompozitlərin tullantı sularının təmizlənməsində adsorbent kimi tətbiqi (ədəbiyyat icmalı) // Su problemləri: elm və texnologiyalar, -2018, Vol.2(12), -p.104-111.

**12.** Aliyeva, S.B. Effect of hybrid composite dosage on efficiency of acridine yellow dye removal / S.B.Aliyeva, R.M.Alosmanov, I.A.Buniyatzadeh A.A.Azizov, A.M.Maharramov // Kimyanın aktual problemləri, XII Beynəlxalq Elmi Konfransı, -Bakı, -3-4 may, -2018, -p.161.

**13.** Əliyeva, S.B. Səthi modifikasiya edilmiş qrafit və polimer əsaslı hibrid kompozitlə akrinin sarı boyaq maddəsinin sorbsiyasının kinetik və termodinamiki qanunauyğunluqları / S.B.Əliyeva, R.M.Alosmanov İ.A.Bünyadzadə, Q.M.Eyvazova, A.Ə.Əzizov, A.M.Məhərrəmov // Akademik Murtuza Nağıyevin 110 illiyinə həsr olunmuş “Nağıyev qıraətləri” elmi konfransı, -Bakı, -30-31 oktyabr, -2018, -s.156.

**14.** Aliyeva, S.B. Desorption studies of Acridine yellow dye from polymer hybrid composite by different desorbing agents / S.B.Aliyeva, R.M.Alosmanov, I.A.Buniyatzadeh A.A.Azizov, A.M.Maharramov // XIV Ukrainian conference on macromolecules, -Kyiv, Ukraine, -15-18 october, -2018, -p.9-10.

**15.** Aliyeva, S.B. Intraparticle diffusion process during acridine yellow dye adsorption onto polymer hybrid composite / S.B.Aliyeva, R.M.Alosmanov, I.A.Buniyatzadeh A.A.Azizov, A.M.Maharramov // 14th International Saint Petersburg conference of young scientists – Saint Petersburg, Russia, -12-14 november, -2018, -p.161.

**16.** Aliyeva, S. Functionalized graphene nanoplatelets/modified polybutadiene hybrid composite / S.Aliyeva, R.Alosmanov, I.Buniyatzadeh, G.Eyvazova, A.Azizov, A.Maharramov // Colloid and Polymer Science, -2019. Vol. 297, -p.1529-1540

**17.** Aliyeva, S. Recent developments in edge-selective functionalization of surface of graphite and derivatives – a review / S.Aliyeva, R.Alosmanov, I.Buniyatzadeh, A.Azizov, A.Maharramov // Soft Materials, -2019. Vol.17(4), -p.448-466

- 18.** Əliyeva, S.B. Hibrid kompozitlər-ədəbiyyat icmalı // Pedaqoji Universitetin Xəbərləri. Riyaziyyat və təbiət elmləri seriyası, -2019. C.67, №4, -s.69-78
- 19.** Əliyeva, S.B. Səthi funksionallaşdırılmış qrafit və polivinil spirti əsaslı təbəqənin dielektrik xassələrinin tədqiqi / S.B.Əliyeva, R.M.Alosmanov, İ.A.Bünyadzadə, Q.M.Eyvazova, A.Ə.Əzizov // Gənc Tədqiqatçıların III Beynəlxalq Elmi Konfransı, -Bakı, -29-30 aprel, -2019, -s.136-137.
- 20.** Aliyeva, S.B. A comparative study of sorption of acridine yellow dye from aqueous solutions on graphite and modified graphite / S.B.Aliyeva, R.M.Alosmanov, I.A.Buniyatzadeh A.A.Azizov, A.M.Maharramov // XXIX Российская молодежная научная конференция с международным участием, посвященной 150-летию Периодической таблицы химических элементов, - Екатеринбург, Россия, -23-26 апрель, -2019, -с.162.
- 21.** Aliyeva, S. Adsorption of acridine yellow G from aqueous solutions using functionalized graphene nanoplatelets/modified polybutadiene hybrid composite // Journal of the Chinese Chemical Society, -2020. Vol.67(11), - p.2071-2081
- 22.** Aliyeva, S. X-ray powder diffraction analysis of graphite modified by oxidative chlorphosphorylation reaction under different conditions // New Carbon Nanomaterials: Ultrathin Diamond Films, - Moscow, Russia, -6-9 december, -2021, -p.11-12.
- 23.** Aliyeva, S., Alosmanov, R. Fire-retardant properties of functionalised graphene nanoplatelets/modified polybutadiene hybrid composite material: a technical note // Journal of Rubber Research, - 2022. Vol.25, -p.19-26.

The defense will be held on 21th October 2022 at 10<sup>00</sup> a.m at the meeting of the Dissertation council ED 1.28 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at the Institute of Polymer Materials of the Ministry of Science and Education of the Republic of Azerbaijan.

Address : 124 S.Vurgun str., Sumgait, Azerbaijan Republic, AZ 5004

The dissertation is accessible at the Institute of Polymer Materials Library

Electronic versions of the dissertation and its abstract are available on the official website (amea-pmi.az) of the Institute of Polymer Materials of the Ministry of Science and Education of the Republic of Azerbaijan.

Abstract was sent to the required addresses on 16 September 2022.

Signed for print: **06.09.2022**  
Paper format: **A5 60x90 1/16**  
Volume: **39431 characters**  
Number of hard copies: **30**