

Cationic organic dyes adsorption on few-layer graphene produced by self-propagating high-temperature synthesis

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ABSTRACT The effectiveness of carbon nanomaterials in purifying water from organic dyes has been proven over the previous decade. However, the problem of industrial application of carbon nanomaterials has not yet been solved. This is primarily due to the high cost and low productivity of carbon nanomaterials synthesis methods. This article presents the thermodynamic and kinetic data of rhodamine 6G and methylene blue adsorption on few-layer graphene. Few-layer graphene was obtained by self-propagating high-temperature synthesis from cellulose. It is a promising method which is inexpensive and easy to scale. It was found that the studied few-layer graphene has a high adsorption capacity for both dyes, and the obtained values of adsorption capacity are higher than most of the studied carbon materials, such as carbon nanotubes or activated carbon. The most common adsorption models were used to describe the thermodynamics of the process. The kinetics of the process are described by a pseudo-second-order equation, which is quite common in graphene materials. The proposed adsorption mechanism is based on hydrophobic interaction between adsorbent and adsorbate with the formation of H- π and π - π bonds.

KEYWORDS Few-layer graphene, graphene, SHS, adsorption, rhodamine 6G, methylene blue.

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1. Introduction

Organic dyes are widely used in the textile, paper, and cosmetics industries. Dyes make it possible to achieve stable coloring of most materials and their production is constantly increasing. Organic dyes are classified according to their structure. Most of them are bulky molecules containing aromatic groups and heteroatoms. However, organic dyes are dangerous to the environment and humans, even in extremely low concentrations [1]. The effect of dyes on organisms is still at the research stage due to the synthesis of new dyes [2]. That's why, one of the problem of industries using dyes is to treat their wastewater.

One of the most common methods of purifying water from organic dyes is adsorption due to its fairly simple and relatively cheap implementation method. Various carbon materials can be adsorbents, such as activated carbon [3], carbon black [4], highly dispersed graphite [5], carbon nanotubes [6], as well as natural materials – sawdust [7]. However, industry development led to an increase in the volume of wastewater, and treatment cannot be carried out with proper efficiency using classical adsorbents. Therefore, the adsorption properties of new materials are actively studied including nanomaterials. For these purposes, graphene and its derivatives can be used. It has been shown that graphene-based materials can act as an effective adsorbent for many substances, for example, dyes [8,9], gases [10,11], aromatic solvents [12], and metal ions [13]. One of the characteristics of graphene nanostructures is the number of layers, which can also influence on adsorption efficiency. However, there is currently no consensus in the literature regarding the detailed influence of the number of layers in graphene-based materials on their adsorption efficiency. The theoretical value of the specific surface area of single-layer graphene is 2600 m²/g and by increasing the number of layers the specific surface area will decrease. It should also be noted that in addition to the specific surface area, attention should be paid to the pore volume, type and degree of surface functionalization. The use of graphene materials for adsorption purposes is still limited by the high cost and low productivity of synthesis methods [14,15]. The complexity of the synthesis of carbon nanomaterials may cast doubt on their use as adsorbents. Thus, for the real use of carbon nanomaterials in adsorption

processes, in addition to increasing the adsorption capacity, it is also necessary to look for more accessible methods of synthesis.

In our previous works, it was shown that few-layer graphene obtained by self-propagating high-temperature synthesis [16] is an effective adsorbent for purifying water from radionuclides [17] and mycotoxins [18]. We have also previously shown that FLG obtained by the SHS method from a mixture of cellulose and ammonium nitrate in a mass ratio of 1/1 is capable for adsorption of rhodamine 6G [19]. In this work, we selected the optimal composition of the mixture for FLG synthesis by the SHS method for the effective adsorption of organic dyes – rhodamine 6G (Rh6G) and methylene blue (MB). Rh6G and, in particular, MB are fairly common objects in the study of organic dye adsorption. They are also cationic and suitable for objects with oxygen-containing groups. The main difference between these dyes can be considered their geometry and size, which will be discussed below. Self-propagating high-temperature synthesis can be used for obtaining few-layer graphene from wastes and products containing carbohydrates - cellulose, lignin, starch, etc., which is utilized for processing waste from the pulp and paper industry. The productivity of the method in laboratory is 500 g/hour, while the low cost of the product is due to cheap reagents and the simplicity of the synthesis process.

2. Experimental part

2.1. FLG synthesis

Few-layer graphene (FLG) was synthesized by self-propagating high-temperature synthesis from cellulose (99.9 %, Sigma-Aldrich, no. 9004-34-6) according to [16]. A mixture of cellulose and ammonium nitrate was added to a steel reactor in a mass ratio of 30/70, respectively. The mixture was heated to 250 °C, at which point the decomposition of ammonium nitrate began, and the reaction started. After the end of the exothermic reaction, the product was washed with demineralized water and isopropyl alcohol and then dried in air at 120 °C. Dried FLG was homogenized in a drum mill for 20 min (BPR 50/1).

2.1.1. Annealing in vacuum. To investigate the adsorption mechanism, FLG was annealed in vacuum. 1 g FLG was placed in a vacuum oven (VTSh-K52-250, Octan), after which the atmosphere was pumped out to a pressure of $6.6 \cdot 10^{-3}$ Pa. Then, the furnace was heated to 1100 °C at a heating rate of 15 °C/min, the sample was annealed at 1100 °C for 2 hours.

2.2. Characterization of FLG

Images of the samples were obtained by scanning electron spectroscopy (SEM) using a Mira-3M scanning electron microscope (TESCAN). To obtain SEM images, a sample of FLG was applied to double-sided electrically conductive carbon tape 8 mm wide (TED PELLA, INC.). X-ray phase analysis was carried out on a Rigaku SmartLab 3 X-ray diffractometer ($\text{CuK}\alpha$, wavelength $\lambda = 0.154051$ nm). The particle sizes of FLG were determined by laser diffraction using Mastersizer 2000 (Malvern Instruments). For measurements, a 50 mg sample was used, which was dispersed in 50 ml of deionized water by stirring for 1 minute. FTIR spectra of FLG were obtained using an Infracum FT-08 spectrometer (Lumex-Marketing LLC). Raman spectra of FLG were obtained using a “Ntegra Spectra” (NT-MDT). Zeta potential measurements were performed using a Zetasizer Nano ZS (Malvern Instruments). pH- measurement was carried out using a laboratory ion meter I-160 (Antech). To determine the specific surface area of FLG samples, we used the ASAP 2020MP automated system (Micromeritics), designed to measure the characteristics of the adsorption capacity by the volumetric method using various gases. The studies were carried out using the method of low-temperature nitrogen adsorption (77 K).

2.3. Adsorption of organic dyes

Rh6G analytical grade “GK Interhim” and MB analytical grade “GK Interhim” were used. To study the adsorption capacity of FLG towards organic dyes, standard solutions of Rh6G with a concentration of 100 mg/dm³ and MB with a concentration of 1 g/dm³ were prepared in demineralized water. All other solutions were obtained by dilution standard solutions. The adsorption study was carried out in 250 cm³ flat-bottomed flasks. An organic dye with a known concentration and FLG was added to the flask after that the mixture was kept under the studied conditions on an S-3.02 20M auto-shaker (ELMI). FLG was separated from solution by centrifugation at 4000 rpm for 10 min. The equilibrium concentration of organic dye solutions was determined by absorbance at 520 nm and 660 nm for Rh6G and MB, respectively, using a UV-1800 ECOVIEW spectrophotometer (Shanghai Mapada Instruments Co., Ltd.). The specific adsorption capacity q_e was calculated using equation (1).

$$q_e = \frac{C_0 - C_e}{m} \times V, \quad (1)$$

where C_0 is the concentration of the dye before adsorption (mg/dm³), C_e is the concentration of the dye after adsorption (mg/dm³), m is the mass of FLG (g), V is the volume of the solution (dm³).

2.4. Effect of pH

The effect of pH on adsorption was studied from 3 to 11 pH in a 100 cm³ solution of Rh6G and MB with concentrations of 40 mg/dm³ and 200 mg/dm³ respectively, and 50 mg of FLG. HNO₃ (70 %, Sigma-Aldrich, no. 7697-37-2), diluted with demineralized water to 1 %, and NaOH (98 %, Sigma-Aldrich, no. 1310-73-2) in the form of 1 were added to vary pH of the solution.

2.5. Effect of temperature

To study the thermodynamics of adsorption, 50 mg of FLG was added to 100 cm³ of an organic dye solution with initial concentrations from 5 to 100 mg/dm³ and from 5 to 800 mg/dm³ for Rh6G and MB respectively, at temperatures of 293 and 333 K. Temperature was controlled by water thermostat.

2.6. Adsorption kinetics

The kinetic of adsorption was carried out using a solution 40 mg/dm³ and 800 mg/dm³ of Rh6G and MB, respectively, and 50 mg of FLG. The contact time was varied from 10 to 1350 min (24 h) on an S-3.02 20M autoshaker (ELMI).

3. Results and discussion

3.1. FLG structure

Using SEM method, it was shown that the particles of FLG obtained by self-propagating high-temperature synthesis are plates with torn edges (Fig. 1A). Using the EDX-analysis, it was found that FLG contains nitrogen (5 %) and oxygen (10 %) atoms on the surface due to the synthesis technique. X-ray diffraction studies were carried out to estimate the number of layers in FLG (Fig. 1B). Using the Scherrer equation, the crystallite size was determined (12.1 Å). Based on the data on the width of the 002 peak at half maximum and in conjunction with data on the interplanar distance (4.07 Å), it was established that the number of layers in the FLG does not exceed 3 [20]. The X-ray image also contains low-intensity broad peaks (10 °2θ, 44 °2θ) that are the result of software processing.

The Raman spectrum (Fig. 1C) contains three characteristic bands of graphite materials: D – 1380 cm⁻¹, G – 1601 cm⁻¹ and 2D – 2834 cm⁻¹. The obtained Raman spectrum is similar for graphene oxide and reduced graphene oxide [21, 22]. The presence of the D-band indicates various defects in the aromatic structure - vacancies, sp³-hybridized carbon atoms, and incorporation of oxygen atoms into the aromatic structure. The G-band characterizes planar vibrations of sp²-hybridized carbon atoms. The D+G band should also be present in the 2D-band area, but it is not detected. These bands characterize structural electronic defects [23, 24]. However, as was shown in [25], the synthesized FLG does not contain Stone-Wales defects, unlike graphene nanostructures synthesized using alternative methods.

The FTIR spectrum of FLG (Fig. 1D) contains bands at 1170 cm⁻¹, 1540 cm⁻¹, 2360 cm⁻¹, 2850 cm⁻¹, 2934 cm⁻¹ and 2966 cm⁻¹. The band at 1170 cm⁻¹ corresponds to the vibration of the carboxyl bond (C–O), band at 1540 cm⁻¹ can be attributed to the vibration of the C=C bond, band at 2360 is due to carbon dioxide from the air, and bands at 2850 cm⁻¹, 2934 cm⁻¹ and 2966 cm⁻¹ refers to C-H vibrations in the methyl group [26]. From EDX, Raman spectroscopy and FTIR data, it can be concluded that the structure of FLG obtained by self-propagating high-temperature synthesis is close to the structure of reduced graphene oxide.

The average particle size determined by laser diffraction was 1 μm (Fig. 2A). The most significant volume contribution was made by particles 20 – 28 μm (Fig. 2B).

3.2. Adsorption of organic dyes

To investigate the adsorption mechanism of cationic organic dyes, FLG was annealed in vacuum at 1100 °C. As a result of annealing, the specific surface area of FLG decreased from 661 m²/g to 377 m²/g, the pore volume (*V_{pore}*) from 0.397 to 0.263, and the micropore volume (*V_{micropore}*) from 0.263 to 0.126 (Tabel 1). Also, as a result of annealing, the zeta potential (ζ) from –30 mV became almost equal to zero and the content of “O” heteroatoms decreased from 10 at.% to 8 at.% and “N” from 5 at.% to 0 at.%. A decrease in the concentration of heteroatoms leads to a decrease in the content of functional groups, which in turn becomes practically impossible to detect by FTIR spectrometry (Fig. 3). A series of experiments were carried out on the adsorption of Rh6G and MB with FLG particles and FLG annealed in vacuum at 1100 °C. From Fig. 4 it can be seen that the adsorption capacity of FLG annealed in vacuum is almost two times lower than that of the original FLG for both dyes.

If we consider the process of adsorption of cationic organic dyes on the FLG surface from the point of view of electrostatic forces that is positively charged particles are attracted to a negatively charged surface, then the reduction of ζ to almost zero (from –30 to –1 mV) after annealing in a vacuum should almost eliminate the possibility of cationic dyes adsorption on FLG annealed in vacuum. If we consider the process of adsorption of cationic organic dyes on the FLG surface from the point of view of hydrophobic interactions – dye molecules interact with areas of the FLG surface with the formation of H-π or π-π bonds, thereby reducing the surface energy, then the adsorption capacity should depend from the specific surface of the adsorbent. In general, such a dependence is observed in this case. Annealing FLG in vacuum leads to a decrease in specific surface area by 42.9 %, while the adsorption capacity decreases by 38.7 % and 44.9 % for Rh6G

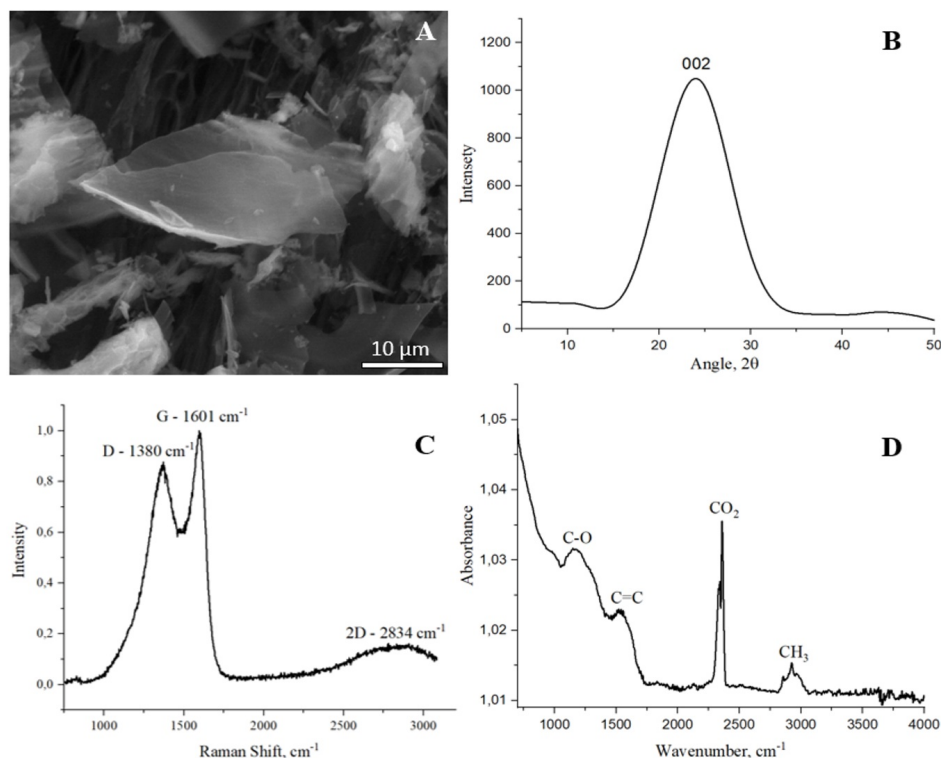


FIG. 1. (A) SEM image of the FLG, (B) X-Ray diffraction of the FLG, (C) Raman spectrum of the FLG, (D) FTIR spectrum of the FLG

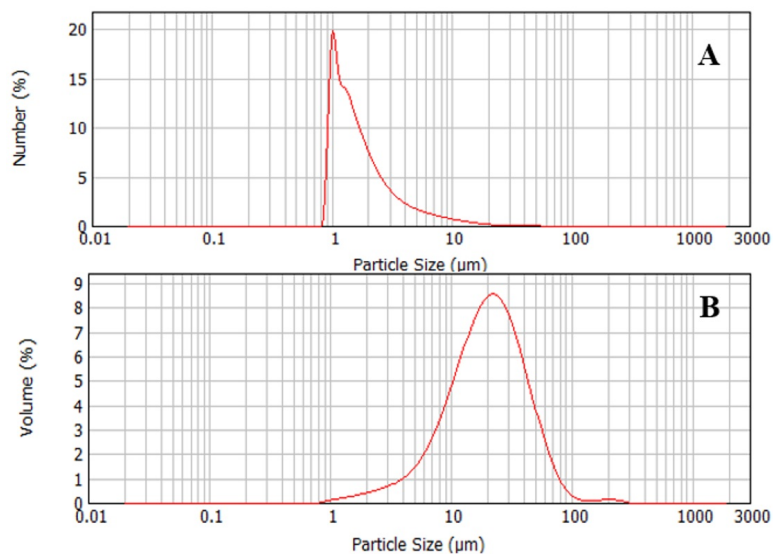


FIG. 2. Distribution of FLG particles by (A) number and (B) volume after milling

and MB, respectively. Of course, in a real process, all of the above interactions between the adsorbent and the adsorbate may occur, but the specific surface area has the greatest influence on the adsorption capacity.

3.2.1. Effect of pH. The pH of the aqueous solution is one of the most important factors in adsorption studies. The adsorption of Rh6G and MB at different pH values of the solution are shown in Fig. 5. As can be seen from Fig. 5, the acidity of the solution has little effect on the adsorption of both dyes. Increasing pH from 2 to 11 leads to a slight increase in sorption capacity by 8 and 11 % for Rh6G and MB, respectively. An approximately similar result was observed in [8], where non-functionalized graphene was used for MB adsorption. When using graphene oxide, the acidity of the medium strongly affects the adsorption of cationic organic dyes, as was shown in [27]. This difference is due to the presence of a huge number of oxygen-containing functional groups – carboxyl and hydroxyl – on the surface of graphene oxide. This makes adsorption possible due to electrostatic interaction, and as the pH of the solution increases, additional ionization of

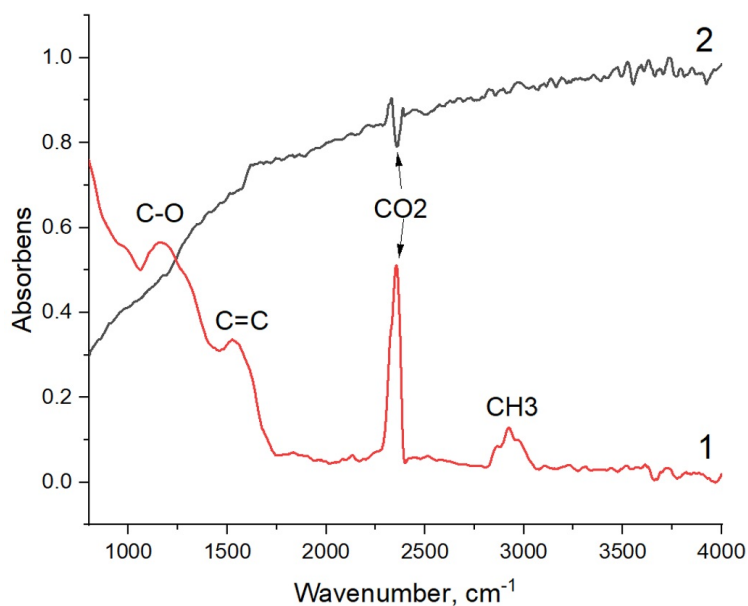


FIG. 3. FTIR spectrum of FLG (1) and FLG annealed in vacuum 1100 °C (2)

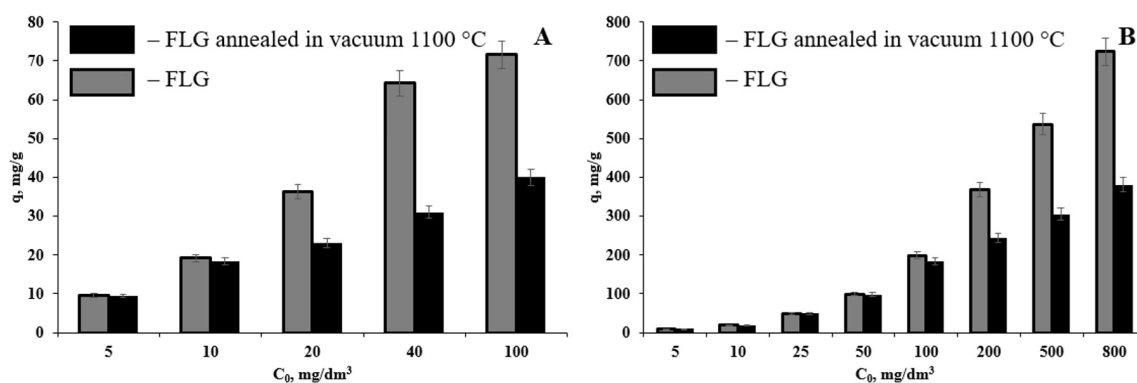


FIG. 4. Dependence of FLG and FLG annealed in vacuum 1100 °C adsorption capacity on the initial dye concentration: (A) Rh6G, (B) MB

these groups occurs, which further stimulates adsorption by this mechanism. In the case of FLG, the obtained dependence confirms the conclusion made earlier that the adsorption of the studied dyes on the FLG surface is due predominantly to the hydrophobic interaction of the adsorbate with the adsorbent due to the low content of functional groups.

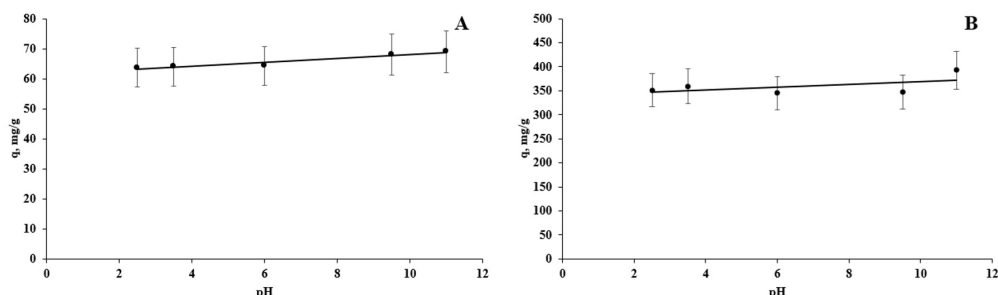


FIG. 5. pH effect on adsorption capacity of FLG (A) Rh6G, (B) MB

3.2.2. Adsorption isotherms. The solution temperature is another important factor in adsorption studies. In Fig. 6. adsorption isotherms of Rh6G and MB at 20 and 60 °C are presented. It can be seen that the adsorption capacity increases as the temperature increases. The maximum adsorption capacity increases from 71,6 to 76,1 mg/g for Rh6G and from 723 to 969 for MB with the increase in temperature from 293 to 333 K. These results demonstrate that Rh6G and MB

adsorption onto FLG is endothermic. The more significant effect of increasing adsorption capacity for MB with increasing temperature can be associated with the size and shape of the dye molecules. In Rh6G, the xanthene part is rotated relative to the benzoyl part by almost 90° [28], and the Rh6G molecule is bigger than the MB molecule. Thus, the Rh6G molecule can create enormous steric hindrances when filling adsorption sites.

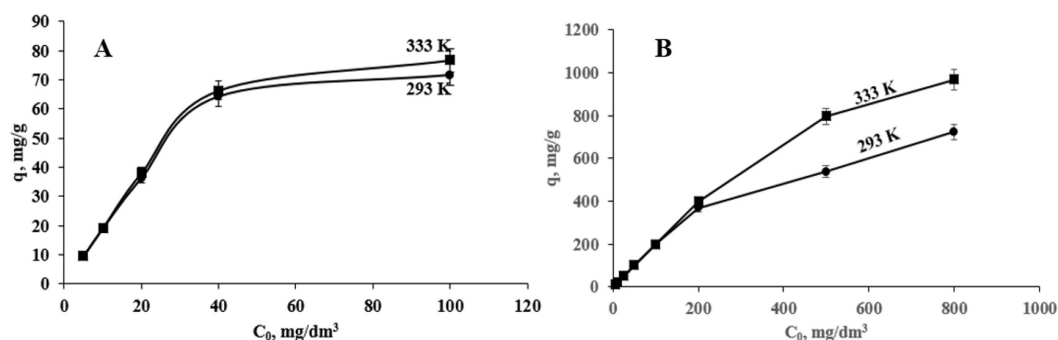


FIG. 6. Adsorption isotherms of (A) Rh6G and (B) MB at 293 and 333 K on FLG

In Tabel 1, the obtained results were compared with other works on this topic. It can be concluded that the resulting FLG obtained by self-propagating high-temperature synthesis has potential for use in water purification from cationic organic dyes. Moreover, the simplicity of synthesis may allow it to find its industrial application as an adsorbent.

TABLE 1. Comparison with other adsorbents

Material	Adsorptive	Conditions	$q_{\max}$ (exp)	Reference
FLG	Rh6G	293 K, pH6	71.6	This work
	MB		723.8	
FLG	Rh6G	293 K, pH 6	9.4	Our previous work [19]
AC	MB	293 K pH 2.8	625	[3]
CNT	MB	333 K, pH 7	60	[6]
Graphene	MB	333 K, pH 7	205	[8]
AC-PEI-SAA	Rh6G	298 K, pH 4.45	122.5	[30]
AC	MB	333 K	324.4	[31]
GO	MB	298 K, pH 7	570.4	[22]
AC	MB	298 K, pH 7	19.5	[32]
GO	Rh6G	–	23.3	[33]
RGO-Fe ₃ O ₄	Rh6G	298 K, pH 7	30	[34]

Langmuir, Freundlich, and Temkin models were used to describe adsorption isotherms. The Langmuir model assumes that adsorption is monomolecular and occurs on a homogeneous surface; adsorbed molecules do not interact with each other [35, 36]. The Langmuir isotherm is a straight line described by equation (2):

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} \times k_L \times C_e}, \quad (2)$$

where C_e is the equilibrium concentration of the solution after sorption (mg/dm^3), $q_{\max}$ is the maximum adsorption capacity (mg/g), k_L is the Langmuir constant, characterizing the interaction of the adsorbate and the adsorbent (dm^3/mg).

The Freundlich equation is empirical (3) and describes adsorption on a heterogeneous surface [36, 37].

$$\lg(q_e) = \lg(k_F) + \frac{1}{n} \times \lg(C_e) \quad (3)$$

where k_F is the Freundlich constant (dm^3/mg), characterizing the adsorption capacity, $1/n$ is an empirical parameter characterizing the intensity of adsorption.

Temkin's model assumes that the heat of adsorption of all molecules in a layer decreases linearly as the layer is filled, while adsorption occurs with a uniform distribution of maximum binding energy. However, it does not describe data well at very high and very low concentrations [38], equation (4) expresses this model in linear form.

$$q_e = B_t \times \lg(K_t) + B_t \times \lg(C_e), \quad (4)$$

where K_t is the Temkin constant (dm^3/mg), characterizing the adsorption capacity, B_t is a constant, characterizing the heat of adsorption (J/mol).

The constants calculated using these models are given in Tabel 2. The highest value of R^2 is observed in isotherms calculated using the Langmuir model, however, the calculated values of the adsorption capacity of the monolayer ($q_{\max}$) are less than the experimental ones by 9 and 14 % at 293 and 333 K, respectively, for Rh6G and by 44 and 6 % at 293 and 333 K, respectively, for MB. Langmuir adsorption is monomolecular and the adsorption capacity of a monolayer ($q_{\max}$) is a limiting value that must be greater than or equal to the experimental value of the adsorption capacity. This fact indicates that the Langmuir model cannot adequately describe the process of adsorption of organic dyes on FLG. The calculated Freundlich isotherms have the lowest R^2 values among used models, while an increase in temperature leads to an increase in K_F , which is consistent with experiment. Isotherms calculated using the Temkin model have a fairly high value of R^2 , the nature of the change in the constant B_t , which takes into account the effect of temperature, is consistent with the experiment – an increase in temperature has little effect on the Rh6G adsorption process and significantly affects to MB adsorption process.

TABLE 2. Calculated constants based on adsorption models

Model	Parameters	Rh6G		MB	
		293 K	333 K	293 K	333 K
Langmuir model	$q_{\max}$ (mg/g)	67.57	65.36	500	909.09
	k_L (dm^3/gm)	0.94	1.28	1.25	1.38
	R^2	0.99	0.99	0.98	0.99
Freundlich model	k_F (dm^3/gm)	23.81	26.13	181.89	341.43
	$1/n$	0.34	0.33	0.22	0.1859
	R^2	0.89	0.84	0.95	0.91
Temkin model	B_t (J/mol)	11.2	11.5	74.05	10.7
	K_t (dm^3/gm)	15.75	22.35	14.79	20.78
	R^2	0.95	0.92	0.96	0.95

3.2.3. Adsorption kinetics. An increase in temperature accelerates the adsorption process, and an inflection in the graph occurs at 20 minutes for Rh6G (Fig. 7A). The adsorption process also slows down due to a significant decrease in adsorption centers and steric difficulties created by bulky molecules. Adsorption of MB at 293 K also slows down significantly after 1.5 hours, and a further slight change in adsorption capacity indicates complete saturation of the adsorbent (Fig. 7B). At 333 K, MB adsorption curve also has an inflection at 90 min. An increase in temperature increases the mobility of MB molecules, which allows them to more actively occupy adsorption sites, and because MB molecules create less steric hindrance, we observe an increase in adsorption capacity.

Adsorption kinetics can be described by pseudo-first (5) and pseudo-second (6) order kinetic models [39]. The limiting factor in the pseudo-first-order model is physical adsorption, and in the pseudo-second-order model, the limiting stage is chemical adsorption [40].

$$\lg(q_e - q_t) = \lg(q_e) - \frac{k_1 \times t}{2.303}, \quad (5)$$

$$\frac{t}{q_e} = \frac{1}{k_2 \times q_e^2} + \frac{t}{q_e}, \quad (6)$$

where q_t and q_e (mg/g) are dye concentrations in the sorbent at the time (t) and equilibrium, respectively, k_1 is the adsorption rate constant in the pseudo-first-order model, k_2 is the adsorption rate constant in the pseudo-second-order model, t is adsorption time (min).

The pseudo-first-order model does not allow the calculation of the adsorption capacity with sufficient accuracy (Table 3). The deviation of the experimental value of the adsorption capacity from the calculated is 25 and 64 % at 293 and

333 K for Rh6G and 64 and 53 % at 293 and 333 K, respectively, for MB. The deviation of the experimental value of the adsorption capacity calculated by the pseudo-second-order equation is 12 and 21 % at 293 and 333 K for Rh6G and 1 and 3 % at 293 and 333 K, respectively, for MB. Thus, the pseudo-second-order kinetic model better describes the process of adsorption of Rh6G and MB on the FLG surface.

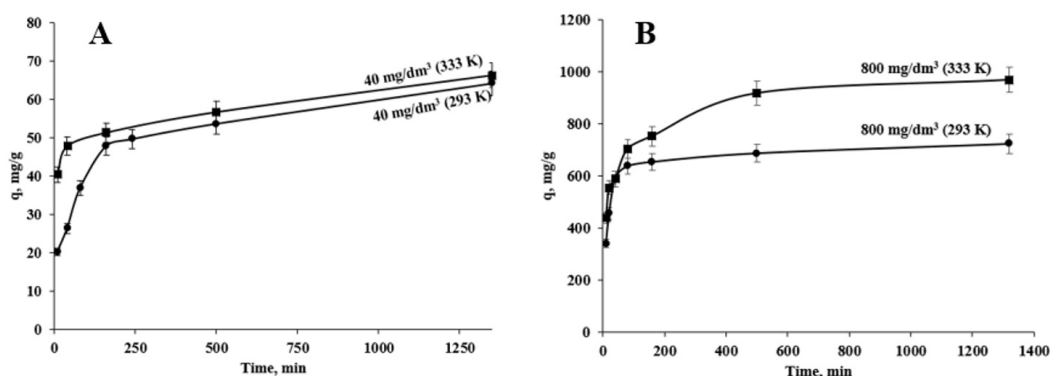


FIG. 7. The dependence of FLG adsorption capacity on time (A) rhodamine 6G, (B) MB

TABLE 3. Parameters of organic dyes adsorption on the FLG surface, calculated using pseudo-first and pseudo-second order kinetic models

Model	Parameters	Rh6G		MB	
		293 K	333 K	293 K	333 K
Pseudo-first-order kinetic model	q_{exp} (mg/g)	64.29	66.32	723.83	969.5
	q_{cal} (mg/g)	47.81	24.02	202.82	456.14
	k_1 (1/min)	$1.26 \cdot 10^{-3}$	$6.08 \cdot 10^{-4}$	$7.38 \cdot 10^{-4}$	$8.25 \cdot 10^{-4}$
	R^2	0.97	0.98	0.69	0.98
Pseudo-second-order kinetic model	q_{exp} (mg/g)	64.29	66.32	723.83	969.5
	q_{cal} (mg/g)	56.18	52.36	714.29	1000
	k_2 (g/mg/min)	$5.42 \cdot 10^{-4}$	$5.69 \cdot 10^{-3}$	$9.95 \cdot 10^{-5}$	$3.55 \cdot 10^{-5}$
	R^2	0.99	0.99	0.99	0.99

4. Conclusions

FLG obtained by self-propagating high-temperature synthesis can be used as an effective sorbent for cationic dyes – rhodamine 6G and methylene blue. Based on EDX, Raman spectroscopy and FTIR data, it can be concluded that the structure of FLG obtained by self-propagating high-temperature synthesis is close to the structure of reduced graphene oxide.

The adsorption of the studied cationic organic dyes on the FLG surface is due to hydrophobic interaction with the formation of π – π and H– π bonds between the adsorbent and the adsorbate. The smaller the size of the dye molecule, the greater the adsorption capacity for this dye.

The adsorption process of cationic dyes is endothermic and it is better described by the Temkin model. This model assumes a polymolecular type of adsorption. The possibility of dimers formation for dyes used in this work also satisfies this position in the Temkin model.

The pseudo-second-order kinetic equation satisfactorily interprets the kinetics of the process, which is quite common in graphene materials. The FLG adsorption capacity value of rhodamine 6G and methylene blue is higher or comparable to the already studied analogs. FLG obtained by self-propagating high-temperature synthesis can be an industrial organic dye adsorbent, considering the simplicity and easily scalable synthesis method.

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