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SYNTHESIS AND PHYSICO-CHEMICAL PROPERTIES OF HIGH-QUALITY EXPANDED GRAPHITE

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The purpose of the work is to establish the possibility of obtaining expanded graphite of high purity (carbon content more than 99.5 % wt.) from flotation-enriched graphite (carbon content 94–97 % wt.) by combining into one process intercalation of graphite with a solution of potassium dichromate in concentrated sulfuric acid with subsequent hydrolysis, and chemical purification using solutions of ammonium bifluoride in sulfuric or hydrochloric acid and Trilon B in an alkaline buffer as purification reagents, and to confirm this possibility by quantum chemical calculations. It has been experimentally shown that combining oxidized graphite synthesis and its chemical purification into one process allows obtaining expanded graphite of high purity, with a carbon content of 99.75–99.85 % wt. The methods of X-ray diffraction and thermogravimetry show that the interaction of oxidized graphite (the residual compound of intercalation of graphite with sulfuric acid) with cleaning reagents does not reduce the ability to expand. The magnitude of the mass loss of oxidized graphite according to various variants of chemical post-cleaning and the temperature range of such loss remain practically unchanged.

Quantum chemical calculations of the adsorption energy (ΔE_{ads}) of one molecule of Trilon B on the surface of a graphene-like plane (GLP), the complexation reaction of metal sulfates, the energy effect of the interaction of Trilon B with sulfates of alkaline earth metals in an aqueous solution, and with the participation of the surface of the graphene plane were carried out using the GAMESS (US) program by the density functional theory (DFT) method with the B3LYP functional and the 6-31G(d,p) basis set, taking into account the Grimme D3 dispersion correction within the PCM polarizable continuum. The results of the analysis of quantum chemical calculations indicate that the Trilon B molecule is better physically sorbed on the oxidized GLP (–412 kJ/mol) than on its native form (–188 kJ/mol). The values of the energy effect of the complexation of magnesium and calcium cations with Trilon B have a negative value both in an aqueous solution and in the presence of the oxidized form of GLP. This indicates the thermodynamic probability of this process, which is consistent with the experimental results. Regardless of the nature of the cation, its interaction with Trilon B is thermodynamically more likely in an aqueous solution than in the adsorbed state on the surface of oxidized GLP.

Keywords*: expanded graphite, graphite intercalation compounds, thermogravimetry, X-ray diffraction, density functional theory method, cluster approximation*

INTRODUCTION

One of the important directions of organizing the stable operation of enterprises of the fuel and energy complex is providing equipment with reliable seals of friction nodes in pump units, rods of various types of fittings, flange connections, etc., since according to known statistics, the most likely stops of such equipment occur precisely because of a violation of its tightness [1, 2]. The modern, most reliable and widely used material for creating high-temperature (up to 600 °C in air) and chemically resistant (petroleum products, diluted acids and alkalis) seals is the so-called expanded graphite (EG), which is obtained from natural graphite. After thermochemical treatment, graphite in the EG state, unlike natural matter, has the properties of pressing and rolling, and in the dense state acquires elastic-plastic characteristics.

Natural graphite is found in the Earth's crust in the form of deposits, where it is a companion of other minerals such as quartz, feldspars, mica, pyrites, calcium carbonate minerals, complex silicates and aluminosilicates, *etc*. The content of graphite in deposits can range from a few fractions of a percent to 10–20 % wt. Deposits with a graphite content of 5 % wt. and more are considered suitable for industrial production. Graphite is extracted from natural ore by the flotation method described, for example, in works [3, 4]. The production gives flotoconcentrate, for the most part, with a carbon content in the range of 94–97 % wt., the latter consists of ash impurities.

The approximate chemical composition of ash impurities of the Zavalliv graphite deposit is close to the following (Table 1) [4].

For comparison in the Table 2 shows the chemical composition of coal [5].

Table 1. Chemical composition of impurities of the Zavalliv graphite deposit, % wt. [2]

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	S
50—65	11–20	6–20	1–4	1–5	0.5–3.0

Table 2. Chemical composition of coal, % wt.

Compound	C	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	others
Content, % wt.	81.07	8.05	4.39	4.21	0.922	0.327	0.36	0.248	0.423

From the data in the Tables 1, 2 it follows that the main contribution to mineral impurities of graphite-containing ores is made by aluminosilicates 60–70 % wt. and oxides of iron, calcium and magnesium.

Graphite sublimates at temperatures higher than 3000 °C. Based on this, in industry, the only possibility of obtaining rolled or pressed solid material from natural graphite is the so-called expanded graphite technology, which is described in sufficient detail in the work [6].

Carbon materials with a graphite-like (layered) structure, such as natural graphite with varying degrees of structural perfection, can form graphite intercalation compounds (GICs).

Residual compounds of graphite intercalation with sulfuric acid are raw materials for obtaining EG (as the safest and having the maximum effect of unidirectional expansion) [7, 8]. Electrochemical intercalation or anodic oxidation is the most ecologically clean, resource- and energy-saving method of obtaining GIC. This process takes place in controlled modes [9, 10], which makes it possible to achieve the specified characteristics of EG, namely to regulate the structural and chemical state of its surface [6, 8].

Natural graphite with a carbon content of 99.0–99.5 % wt. is required for the production of EG, which provides sealing materials for the equipment of enterprises of general industrial purpose: the fuel and energy complex, the petrochemical industry, utilities, *etc*. [7]. In supply, nuclear power plants use materials from EG, the so-called “atomic purity”, in which the carbon content must be at least 99.85 % wt.

For medium- and heavy-enriched graphite ores, it is considered [3, 4] to be the most justified use of sintering with caustic soda at temperatures of 300–500 °C followed by treatment under normal conditions with a 5 % solution of sulfuric acid. If a deeper cleaning is necessary (up to an ash content of 0.2 % wt. and less), the third stage of cleaning is implemented with a 3–5 % solution of hydrofluoric acid or a solution of ammonium bifluoride in sulfuric or hydrochloric acids. Such processes are quite expensive and environmentally dangerous, which, of course, significantly increases the cost of seals and reduces the profitability of the entire technological chain. Therefore, the search for methods of obtaining high-purity EG continues, for example [11–14], and the tasks of optimizing the processes of purification of flotation-enriched natural graphite and its oxidation (intercalation and hydrolysis) are combined into a single process for obtaining high-purity EG, considered in this work, are relevant.

Residues from the action of sulfuric acid on graphite during intercalation, obvious metal oxides are converted into sulfuric acid salts, $MgSO_4$, $CaSO_4$. It is also important that Trilon B, which is still widely investigated as a reagent for the additional purification of EG, interacting with sulfates many metals. These salts can be either in adsorbed on the surface of graphene planes, or in an aqueous intercalate solution in the gap between in partoxidized graphene planes. The mechanism of complexation and extraction of polluting metal cations (Mg^{2+}, Ca^{2+}) by Trilon B remains unknown. Two cases of Trilon B interaction with these cations are possible: from an aqueous solution between the graphene planes of the intercalated graphite compound and in an adsorbed state on the surface of the graphene-like planes. Therefore, in order to clarify these features, the adsorption of Trilon B with native and oxidized graphene surfaces was investigated using quantum chemistry methods, and the geometric and energetic characteristics of the interaction of Trilon B with the corresponding metal cations (which are impurities in graphite) in an aqueous solution and in the adsorbed state were found on a graphene-like plane.

EXPERIMENTAL PART

Materials and reagents. The work used flotation-enriched graphite from Xiang Yang, China (carbon content ~ 94 % wt.); sulfuric acid DSTU GOST 2184:2018; ammonium bifluoride GOST 4518-75; potassium dichromate GOST 4220-75; hydrogen ammonia solution; disodium salt of ethylenediaminetetraacetic acid (EDTA) GOST 10652-73; deionized water.

Research methods. Oxidation and purification of flotation-enriched graphite by chemical method was carried out in two variants.

Natural flotation-enriched graphite was first treated with a solution containing sulfuric acid and an oxidizing agent, which is potassium dichromate. Then it was treated with a fluorinating reagent for 2–4 hours at a temperature of 75–85 °C, where a solution of ammonium bifluoride was added as a fluorinating reagent. Washed with deionized water to neutral pH, squeezed on a filter, added ammonia solution to pH 9–11. And then a Trilon B solution was added, heated to a temperature of 50–100 °C for 0.5–2 hours, washed with deionized water until a negative reaction to ammonium ions occurred, the solid phase was separated from the solution, dried and heat-treated by rapid heating at temperatures of 800–1200 °C.

In the second option, after chemical oxidation of graphite with a solution of potassium dichromate in sulfuric acid, hydrolysis and washing to neutral pH, squeezing on a filter, a solution of ammonia and Trilon B was added to the mixture, stirred at a temperature of 50–100 °C for 0.5–2 hours, washed to a negative reaction to ammonium ions, squeezed on a filter. Then a solution of ammonium bifluoride was added, stirred for 6–12 hours at a temperature of 50–70 °C, washed with deionized water to a neutral pH, the solid phase was separated from the solution, dried and heat-treated by rapid heating at a temperature of 800–1200 °C.

X-ray photoluminescence spectra were recorded on ElvaxPlus (Elvatech, Ukraine).

Derivatograms (thermographic curves of TG, DTG, DTA) were recorded on a Q-1500D derivatograph with digital data recording 20–1000 °C, with a heating rate of 10 °C/min. X-ray phase analysis was carried out on a DRON-3M diffractometer, Cu*K*α radiation (range in the range of angles 5–90 °, step 0.05 °, accumulation 3 sec/point).

EXPERIMENTAL RESULTS AND THEIR DISCUSSION

The basis for obtaining graphite intercalation compounds with Brønsted acids, which thermally expand (swell) upon heating, is the following principal scheme of coupled oxidation and intercalation reactions:

$$\boldsymbol{C_n + HA \xrightarrow{O_x,(I)} C_n^{+}A^{-} \cdot xHA \xrightarrow{R,(II)}} RGIC \quad (1)$$

where: C_n is a fragment of the graphene layer of the graphite matrix; NA – acid; O_x – chemical oxidizer, electric current; *R* is a chemical reagent (for example: H_2O, NH_4OH, *etc*.); RGIC – residual graphite intercalation compounds.

At the first stage, there is a process of oxidation of graphite with the formation of GICs. At the second stage of the process, the GICs is treated with the formation of the final product – residual compounds of graphite intercalation.

In this work, for the production of thermally expanded graphite by a chemical method, H_2SO_4 and the oxidizing agent $K_2Cr_2O_7$ are used as an intercalant, which can be represented by the following reaction:

$$C_n + 25H_2SO_4 + K_2Cr_2O_7 \rightarrow$$

$$\rightarrow 6C_{24}^{+}\,HSO_4^{-}\cdot 2.5H_2SO_4 + Cr_2(SO_4)_3 + K_2SO_4 +$$

$$+7H_2O + C_{n-144}. \quad (2)$$

Studies on chemical intercalation processes and their features depending on the type (species) of NA, O_x(I), R(II) according to scheme (1) are devoted to in works, for example [9, 15], and many others.

Usually, if an intercalant is included between the graphene planes, the period of identity (I_c) of the crystal structure in the direction of the ***c*** axis increases:

$$I_c = d_i + (N - 1)\cdot d_o, \qquad (3)$$

where d_i is the thickness of the intercalant layer; d_0 = 0.335 nm – interplanar distance in graphite; N is the stage number.

For the compound of intercalation of graphite with sulfuric acid of the first stage, the interplanar distance increases from 0.335 nm to ~ 1.2 nm [16, 17]. Apparently, the graphene planes shift during the intercalation process, which can improve the access of the cleaning compound to the mineral impurities included in the graphite lattice. At the same time, it is important to preserve the ability to expand, that is, not to lose the content of the intercalant.

So, the idea of the work is to carry out the intercalation of the flotation concentrate as the first step of obtaining GICs and improving the possibilities of chemical post-treatment.

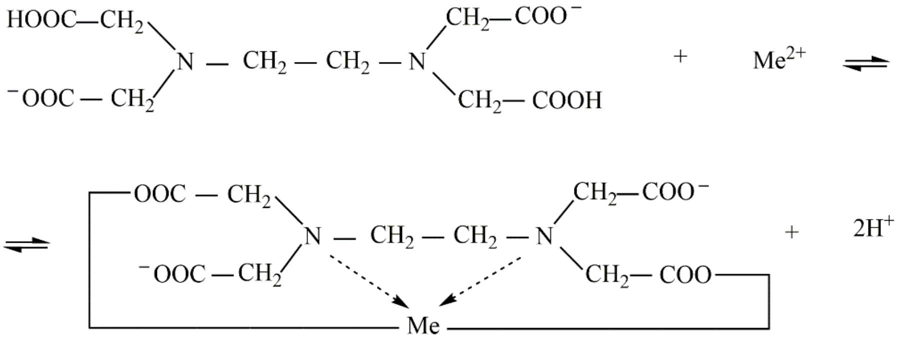
Ammonium bifluoride and Trilon B in a buffer solution were used as cleaning compounds.

The first process can be represented by the following reactions:

$$NH_4(HF_2) + H_2SO_4 \rightarrow (NH_4)_2SO_4 + 2HF. \qquad (4)$$

$$2Me_n^{+}Me_m^{2+}Al_xSi_yO_z + HF_{(excess)} + H_2SO_{4(excess)} \rightarrow$$
$$\rightarrow nMe_2SO_4 + 2mMeSO_4 + 2xAlF_3 + 2ySiF_4 +$$
$$+ 2zH_2O \qquad (5)$$

Most metals are capable to replace hydrogen atoms of the carboxyl groups of EDTA, simultaneously binding coordinately to the nitrogen of the amino group, which is the subject of a large number of works, in particular [18–21]. At the same time, very stable complex compounds with several five-membered rings are formed. The interaction of Trilon B with metal cations is accompanied by the formation of internally complex compounds. The structure of a complex with a divalent metal can be represented by the scheme:



(6)

Therefore, the work used the method of chemical intercalation of natural graphite, after which the intercalated graphite was further purified by adding ammonium bifluoride and the disodium salt of ethylenediaminetetraacetic acid (Trilon B) in two versions, which differed in the order of adding cleaning reagents.

Table 3 shows the optimal parameters of the chemical intercalation, cleaning process and the final carbon content in thermally expanded graphite after processing oxidized graphite with the sequence Trilon B + ammonium bifluoride.

It should be noted that both proposed options for further purification give a positive result, that is, the carbon content in the obtained EG is not less than 99.75 % by mass. Analyzing the data of X-ray fluorescence analysis of the samples of natural and oxidized graphite (Table 4), we can state that the combination of the processes of intercalation, hydrolysis, and further purification of natural graphite with the help of ammonium bifluoride and Trilon B gives oxidized graphite of high purity. At the same time, the best result is observed in sequential cleaning with ammonium bifluoride and Trilon B.

Chemical oxidation requires an oxidizing agent, which is represented by potassium dichromate, the remains of which we observe (Table 4).

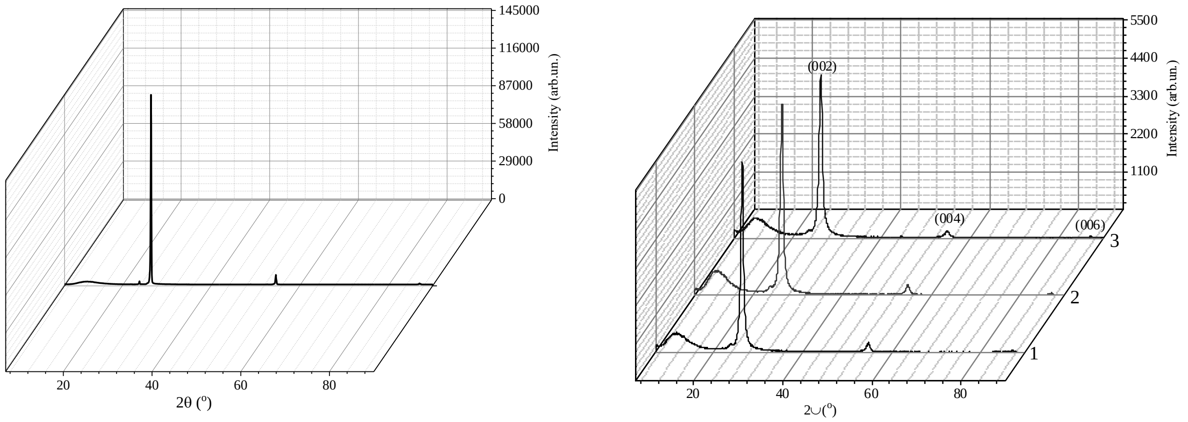
Fig. 1 shows X-ray diffractograms of samples of natural graphite (*a*) and oxidized and chemically purified one (*b*).

Table 3. Optimal parameters of chemical intercalation and purification of natural graphite by treatment with Trilon B + ammonium bifluoride

Process parameters	**Optimal values**
Mass ratio of sulfuric acid to potassium dichromate	27.7:1.7 to 45.5:2.5
The mass of the oxidizing solution per 100 g of graphite, g	300–480
Volume of EDTA solution per 100 g of graphite, cm^3	250–400
The content of EDTA in the solution, % wt.	8–10
Ammonia content in the solution, % wt.	7–9
Heating temperature of the solid phase mixture with EDTA, ºC	50–100
Heating time of the solid phase mixture with EDTA, h.	0.5–2.0
Volume of ammonium bifluoride solution per 100 g of graphite, cm^3	450–550
Concentration of ammonium bifluoride, % wt.	2–4
Mixing time, h	6–12
Heating temperature of the solid phase mixture with ammonium bifluoride, ºC	50–0
Thermal shock temperature, ºC	800–1200
Carbon content, % wt.	**99.75–99.85**

Table 4. X-ray fluorescence analysis of samples of natural and chemically oxidized graphite

Elements	**Graphite float concentrate, % wt.**	**Oxidized graphite with additional purification:**		
		ammonium bifluoride, % wt.	**ammonium bifluoride, Trilon B, wt. %**	**Trilon B, ammonium bifluoride, % wt.**
Al	34.54	2.10	0.96	1.38
Si	36.93	0.19	±0	0.35
P	0	0	4.06	0
S	0.15	77.37	78.51	82.17
K	0.70	1.38	1.16	1.32
Ca	2.57	0.47	0.16	0.26
Cr	0	17.57	14.47	13.48
Fe	24.86	0.89	0.65	1.01
Co	0.107	0.00	0	0
Ni	0.03	0.00	0.00	0.00
Cu	0.04	0.00	0.00	0.00
Zn	0.05	0.01	0.02	0.01



a *b*

Fig. 1. X-ray diffraction spectra: *a* – original natural graphite; *b* – oxidized and purified samples: *1* – with ammonium bifluoride; *2* – ammonium bifluoride, Trilon B; *3* – Trilon B, ammonium bifluoride

Fig. 1 a shows an X-ray pattern of natural graphite: line (002), at an angle of approximately 27, high intensity (~150,000 conventional units), small half-width, much weaker reflections of the second (004) and third orders (006). Intercalation and hydrolysis lead to a decrease in the intensities of the reflections (002) by almost thirty times and a clearly visible broadening of the lines (~25' for oxidized and chemically cleaned compared to the original graphite ~7'). However, we note that spectra 1, 2, 3 in Fig. 1 *b* are almost indistinguishable, which indicates that the alkaline buffer after treatment with Trilon B, as well as the solution of bifluoride in hydrochloric acid, does not cause significant deintercalation of oxidized graphite.

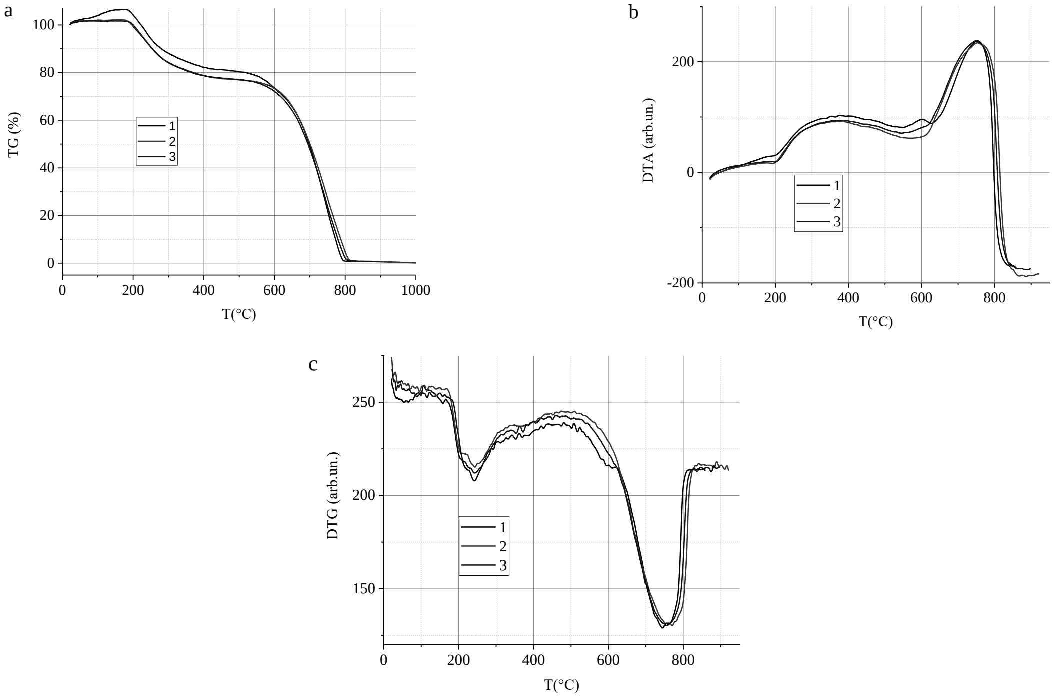


Fig. 2. Thermogravimetric analysis: *a* – TG; *b* – DTA; *c* – DTG, samples of natural graphite oxidized and purified: *1* – oxidation, additional purification with bifluoride; *2* – oxidation, post-cleaning with bifluoride, Trilon B; *3* – oxidation, additional cleaning with Trilon B, bifluoride

Fig. 2 shows the results of thermogravimetric analysis of samples of chemically oxidized graphite purified by bifluoride, Trilon B in different sequences.

It can be seen from these data that all samples of oxidized graphite, regardless of processing, have almost identical derivative diagrams. Thus, for all samples at temperatures from 200 to 600 °C (Fig. 2 *a*, *b*), the first stage of weight loss (loss of intercalant and water) is observed with a maximum of ~400 °C, and the second stage from 600 to 800 °C, where the process of combustion of graphite proper takes place. The determined ash content differs little for the studied samples.

QUANTUM CHEMICAL ANALYSIS

Research methods and objects A graphene-like plane (GLP) with the general formula $C_{54}H_{18}$ (Fig. 3 *a*) was chosen as a model of graphene, and a structure similar to the previous one with two hydroxyl groups on its surface, with the composition $C_{54}H_{18}(OH)_2$ (Fig. 3 *b*).

Trilon B is the disodium salt of ethyldiaminetetraacetic acid, which was sufficiently modeled in the literature [22–24].

Quantum chemical calculations were carried out using the GAMESS (US) program [25] using the density functional theory (DFT) method with the B3LYP functional [26, 27] and the 6-31G(d,p) basis set, taking into account the Grimme D3 dispersion correction [28, 29] within the polarization continuum of PCM [30, 31].

Calculations of the adsorption energy (ΔE_{ads}) of one Trilon B molecule on the surface of a graphene-like plane were carried out according to formula (7):

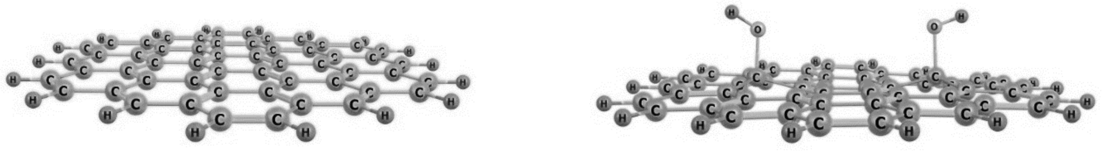
$$\Delta E_{ads.} = E_{tot}\,(ads.\ compl) - ((E_{tot}(surf) + E_{tot}\,(mol)), \quad (7)$$

where: E_{tot} (ads. compl) is the total energy of the adsorption complex, E_{tot} (surf) and E_{tot} (mol) are the total energies of the GLP cluster and Trilon B, respectively.

Complexation reaction of metal sulfates:

$$\text{MeSO}_4 + \text{H}_2\text{Na}_2\text{EDTA} \rightarrow \text{MeNa}_2\text{EDTA} + \text{H}_2\text{SO}_4, \quad (8)$$

where Me are atoms of alkaline earth metals Mg, Ca, H_2Na_2EDTA is Trilon B, $MeNa_2EDTA$ is a metal complex with Trilon B.



a *b*

Fig. 3. Models of the native (*a*) and oxidized form (*b*) of the graphene-like plane

The values of the energy effect of the interaction of Trilon B with sulfates of alkaline earth metals in an aqueous solution were calculated according to formula (9):

$$\Delta E_{reac} = E_{tot}\,(\text{MeNa}_2\text{EDTA}) + E_{tot}\,(\text{H}_2\text{SO}_4) - E_{tot}\,(\text{MeSO}_4) - E_{tot}\,(\text{H}_2\text{Na}_2\text{EDTA}), \quad (9)$$

where E_{tot} ($MeNa_2EDTA$) is the total energy of Trilon B complex with the cation of the corresponding alkaline earth metal, E_{tot} (H_2SO_4) is the total energy of sulfuric acid, E_{tot} ($MeSO_4$) is the total energy of sulfate of the corresponding alkaline earth metal, E_{tot} (H_2Na_2EDTA) is the total energy of Trilon B.

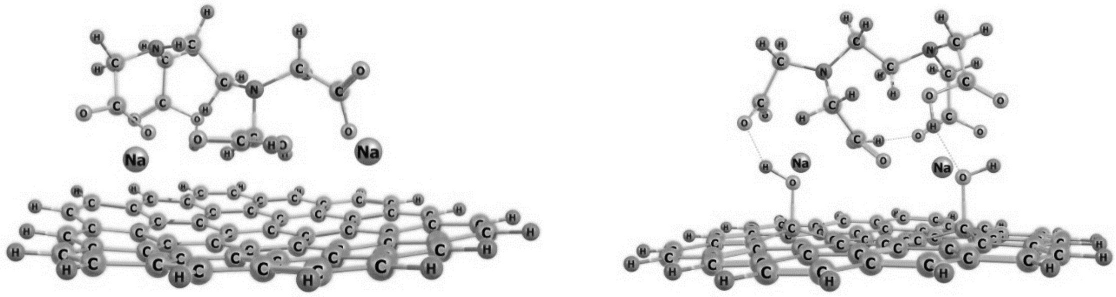
The energetic effect of the interaction of Trilon B with sulfates of alkaline earth metals with the participation of the GP surface was calculated as the difference in the total energies of the complexes of the reaction product and starting substances according to the formula (10):

$$\Delta E_{reac} = E_{tot}\,(RP) - E_{tot}\,((IR), \quad (10)$$

where: E_{tot} (RP) is the total energy of the complex of reaction products, E_{tot} (IR) is the total energy of the complex of starting substances.

RESULTS OF CALCULATIONS AND THEIR DISCUSSION

Adsorption characteristics of Trilon B on oxidized and native graphene-like planes. To begin with, it was necessary to find the interaction energy of Trilon B with the native and oxidized forms of the graphene-like plane. For this, intermolecular adsorption complexes were localized (Fig. 4).



a *b*

Fig. 4. Interaction of Trilon B with native and oxidized graphene surface

The energy of Trilon B adsorption on pure and oxidized GP was calculated according to formula (7). Comparing the values of the adsorption energy for these complexes, it was found that the adsorption energy of Trilon B on GP with two hydroxyl groups is 224 kJ/mol greater (–412 kJ/mol), compared to adsorption on pure GP (–188 kJ/mol). This can be explained by the fact that the hydroxyl groups of the oxidized GP form hydrogen bonds with the carboxyl groups of the Trilon B molecule (Fig. 4 *b*), while the adsorption on the clean surface of the GP of the Trilon B molecule occurs only due to dispersion forces (Fig. 4 *a*). Therefore, we considered the reaction of Trilon B complexation of Mg, Ca cations with the participation of an intercalated graphite compound as an adsorption complex of Trilon B with oxidized GP.

Complex formation of magnesium and calcium cations with Trilon B in an aqueous environment. The next step was to study the reaction of complex formation with the participation of Trilon B with magnesium and calcium sulfates according to equation (8). In particular, in the case of magnesium, the equilibrium geometry of the starting compounds: Trilon B and magnesium sulfate was localized for this (Fig. 5 *a, b*). The reaction products were also optimized, namely the chelate complex of Trilon B with a magnesium cation (Fig. 5 *c*) and sulfuric acid (Fig. 5 *d*). Since Trilon B is a hexadentate ligand, it forms six coordination bonds with the magnesium cation, two of which involve amine nitrogen atoms and four involve oxygen atoms of the carboxyl groups of Trilon B.

The energy effect of this reaction, calculated according to formula (8), has a negative value and is –635.6 kJ/mol (see Table 5), which indicates the thermodynamic probability of this reaction.

The interaction of Trilon B with calcium sulfate is also considered. This reaction occurs according to equation (9). The localized equilibrium geometries of the participants of this reaction (Fig. 6) are similar to those discussed above.

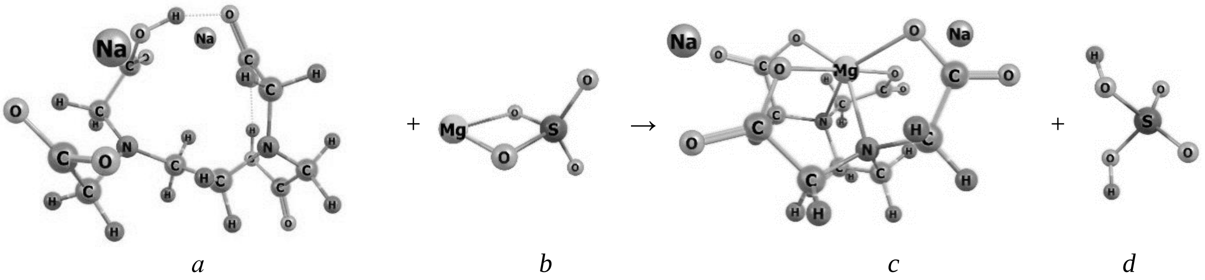


Fig. 5. Equilibrium geometry of the components of the reaction of Trilon B (*a*) with magnesium sulfate (*b*) to form a chelate complex of Trilon B with magnesium cation (*c*) and sulfuric acid (*d*)

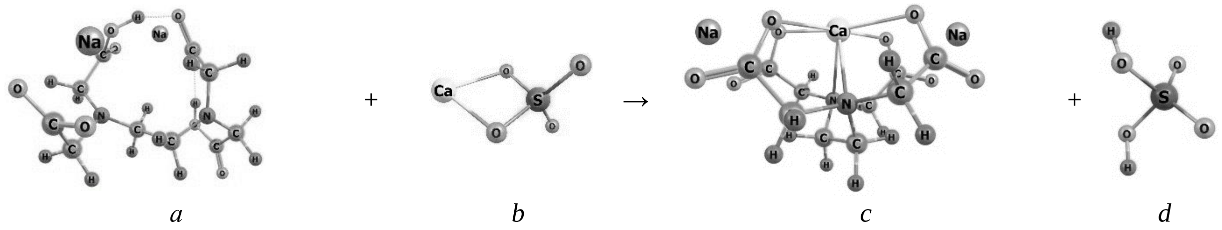
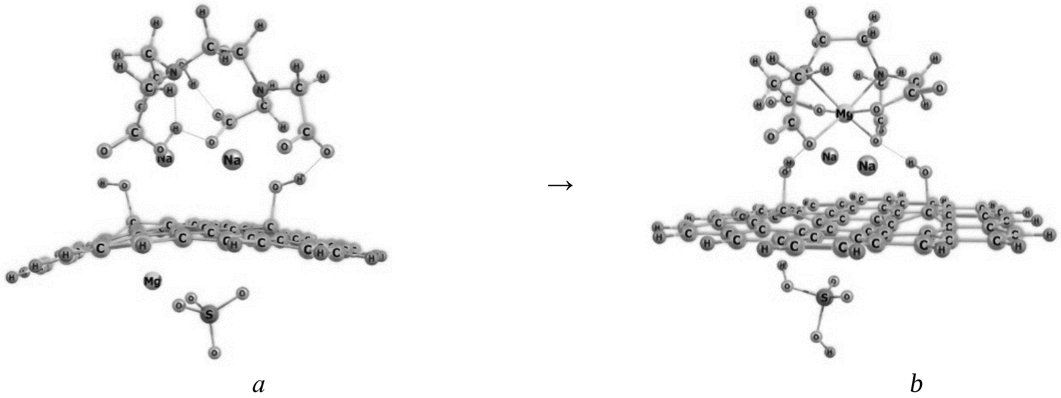


Fig. 6. Equilibrium geometry of the reaction components of the interaction of Trilon B (*a*) with calcium sulfate (*b*) with the formation of a chelate complex of Trilon B with a calcium cation (*c*) and sulfuric acid (*d*)

For this reaction, the energy effect calculated by formula (9) is also a negative value and equals to –574.8 kJ/mol (Table 5).

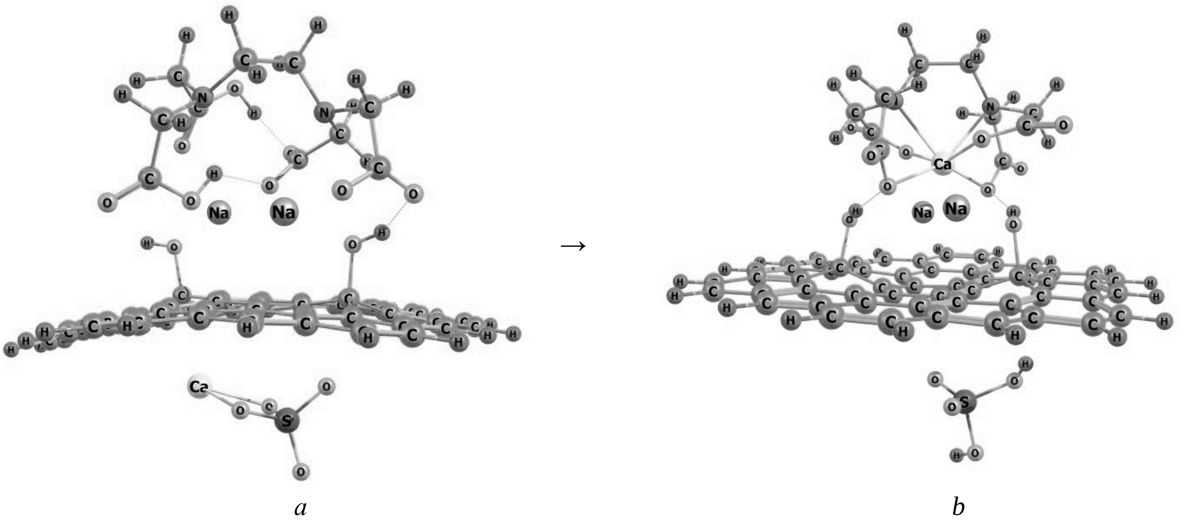
Interaction of magnesium and calcium sulfates with Trilon B on the surface of an oxidized graphene-like plane. The next task was to find out the influence of oxidized GP on the reaction of complex formation during the interaction of adsorbed sulfates of alkaline earth metals with Trilon B adsorbed on the surface of GP. For this purpose, appropriate magnesium and calcium sulfates were added to the adsorbed complex of Trilon B with oxidized GP (Fig. 4 *b*). As a result of the optimization of the geometry, intermolecular complexes of the starting substances of reactions (8) were obtained for the interaction of magnesium sulfate (Fig. 7 *a*) and calcium sulfate (Fig. 8 *a*) with Trilon B on the surface of the oxidized graphene-like plane.

Complexes of the reaction products are a molecule of sulfuric acid and chelate complexes of Trilon B with magnesium (Fig. 8 *a*) and calcium (Fig. 8 *b*) cations, which are physically sorbed on the oxidized GP.



a *b*

Fig. 7. Equilibrium geometry of complexes of starting substances (*a*) and reaction product (*b*) interaction of magnesium sulfate with Trilon B on the surface of an oxidized graphene-like plane



a *b*

Fig. 8. Equilibrium geometry of complexes of starting substances (*a*) and reaction product (*b*) interaction of calcium sulfate with Trilon B on the surface of an oxidized graphene-like plane

The energy effects of these reactions, calculated according to formula (10), have values in the case of magnesium cation complexation –378.3 kJ/mol and –200.9 kJ/mol in the case of calcium cation complexation, respectively (Table 5).

Table 5. Energetic effects of the interaction of magnesium and calcium cations with Trilon B in an aqueous solution and in an adsorbed state on the surface of an oxidized graphene-like plane (in kJ/mol)

	Mg^{2+}	**Ca^{2+}**
Water solution	–635.6	–574.8
In the adsorbed state	–378.3	–200.9

As can be seen from Table 5, the value of the energy effect of the interaction of magnesium and calcium cations with Trilon B has a negative value both in the aqueous solution and in the adsorbed state on the oxidized GP. This testifies to the thermodynamic probability of this process in all considered cases. Regardless of the nature of the cation, its interaction with Trilon B is thermodynamically more likely in an aqueous solution than in the adsorbed state on the surface of oxidized GP.

From the data in the Table 5 also shows that both in the aqueous solution and in the adsorbed state, the energy effect of the interaction of magnesium sulfate with Trilon B is greater compared to similar processes involving calcium sulfate. This indicates that magnesium complexation is thermodynamically more likely, which can be explained by the fact that calcium sulfate is less soluble in water than magnesium sulfate.

CONCLUSIONS

It has been experimentally shown that combining into one process the synthesis of oxidized graphite, that is, the intercalation of flotation-enriched graphite with a solution of potassium dichromate in concentrated sulfuric acid followed by hydrolysis, and chemical purification using solutions of ammonium bifluoride in sulfuric or hydrochloric acid and disodium salt of ethylenediaminetetraacetic acid in an alkaline buffer allows to obtain thermally expanded graphite of high purity, with a carbon content of 99.75–99.85 % wt. The chemical interaction of oxidized graphite (residual compound of graphite intercalation with sulfuric acid) with cleaning reagents (solutions of ammonium bifluoride in sulfuric or hydrochloric acid and disodium salt of ethylenediaminetetraacetic acid in an alkaline buffer) does not reduce the ability to expand. The magnitude of the mass loss of oxidized graphite according to various variants of chemical post-cleaning and the temperature range of such loss remain practically unchanged. Using sequences of applications for cleaning bifluoride and Trilon B increases the degree of cleaning, and the best result is given by this sequence: ammonium bifluoride, Trilon B.

The results of the analysis of quantum chemical calculations indicate that the Trilon B molecule is better physically sorbed on the oxidized graphene-like plane (–412 kJ/mol) than on its native form (–188 kJ/mol).

The magnitudes of the energy effect of complexation of magnesium and calcium cations with Trilon B have a negative value both in an aqueous solution and in the presence of an oxidized form of a graphene-like plane. This indicates the thermodynamic probability of this process, which is consistent with the experimental results.

Regardless of the nature of the cation, its interaction with Trilon B is thermodynamically more likely in an aqueous solution than in the adsorbed state on the surface of an oxidized graphene-like plane.

Синтез та фізико-хімічні властивості високочистого терморозширеного графіту

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Мета роботи – встановити можливість одержання терморозширеного графіту високої чистоти (вміст вуглецю більше 99.5 % мас.) із флотаційно збагаченого графіту (вміст вуглецю 94–97 % мас.), об'єднавши в один процес інтеркалювання графіту розчином біхромату калію в концентрованій сульфатній кислоті з подальшим гідролізом, і хімічну очистку з використанням як очищаючих реагентів розчинів біфториду амонію в сульфатній або хлорводневій кислоті та Трилону Б в лужному буфері, та підтвердити таку можливість квантово хімічними розрахунками. Експериментально показано, що об'єднання в один процес синтезу *окисненого графіту та його хімічну очистку дозволяє одержати терморозширений графіт високої чистоти, з вмістом вуглецю 99.75–99.85 % мас. Методами рентгенофазового аналізу та термогравіметрії показано, що взаємодія окисненого графіту (залишкової сполуки інтеркалювання графіту сульфатною кислотою) з очищаючими реагентами не зменшує здатність до розширення. Величина втрати маси окисненого графіту за різними варіантами хімічної доочистки й температурний інтервал такої втрати залишаються практично незмінними.*

Квантовохімічні розрахунки енергії адсорбції (ΔE_{ads}) однієї молекули Трилону Б на поверхні графеноподібної площини (ГП), реакцію комплексоутворення сульфатів металів, енергетичний ефект взаємодії Трилону Б з сульфатами лужноземельних металів у водному розчині, та за участі поверхні графенової площини проведені за допомогою програми GAMESS (US) методом теорії функціонала густини (DFT) з функціоналом B3LYP і базисним набором 6-31G(d,p) з врахуванням дисперсійної поправки Грімме - D3 в межах поляризаційного континууму PCM. Результати аналізу квантовохімічних розрахунків свідчать, що молекула Трилону Б краще фізично сорбується на окисненій ГП (–412 кДж/моль), ніж на її нативній формі (–188 кДж/моль). Величини енергетичного ефекту комплексоутворення катіонів магнію і кальцію з Трилоном Б мають негативне значення як у водному розчині, так і в присутності окисненої форми ГП. Це свідчить про термодинамічну ймовірність цього процесу, що узгоджується з результатами експерименту. Незалежно від природи катіону взаємодія його з Трилоном Б термодинамічно ймовірніша у водному розчині, ніж в адсорбованому стані на поверхні окисненої ГП.

***Ключові слова**: спучений графіт, інтеркаляційні сполуки графіту, термогравіметрія, рентгенівська дифракція, метод функціоналу густини, кластерне наближення*

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