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Improving the technology and equipment for industrial production of nanoplates by liquid-phase shear exfoliation of layered crystals

Ali M. Mashhadani, Ruaa A. Al-Jarah, Vladimir F. Pershin✉

Tambov State Technical University,
106 Sovetskaya St., 392000 Tambov, Russian Federation

✉ pershin.home@mail.ru

Abstract: For the production of nanoplates from layered crystals by liquid-phase shear exfoliation, patent-protected technologies and equipment have been developed. The main difference between the proposed technologies and equipment from the known ones is that the exfoliation process is possible only by shearing in continuous operation. Particular interest in liquid-phase exfoliation can be explained by the following advantages of this technology in relation to others: chemical reagents are used in minimal amounts (3–4 $mL{\cdot}L^{-1}$) as surfactants to prevent agglomeration of nanoplates that are formed during exfoliation; as a rule, one of the components of the created structural or functional material serves as a liquid dispersion medium; material and energy costs are much less than when using other technologies; this technology is easily scalable. The kinetics of the exfoliation process has been studied and it has been established that the concentration of nanoplate-layered crystals mainly depends on the total path of particles traveled by them in the exfoliation zone, i.e. in the zone of contact of the movable blades with the inner surface of the stator. A mathematical model has been developed for the distribution of nanoplates in a liquid, and the critical concentration of agglomeration of these plates in a liquid has been determined. A cascade technology for the production of nanoplates and a method for calculating the main regime and geometric parameters of rotary devices with moving blades are proposed.

Keywords: layered materials; graphite; low-layer graphene; multilayer graphene; molybdenum disulfide; boron nitride; shear exfoliation.

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Совершенствование технологии и оборудования для промышленного производства нанопластин жидкофазной сдвиговой эксфолиацией слоистых кристаллов

А. М. Аль-Машхадани, Р. А. Аль-Джарах, В. Ф. Першин✉

Тамбовский государственный технический университет,
ул. Советская, 106, Тамбов 392000, Российская Федерация

✉ pershin.home@mail.ru

Аннотация: Для производства нанопластин из слоистых кристаллов жидкофазной сдвиговой эксфолиацией разработаны патенто-защищенные технологии и оборудование. Основное отличие предлагаемых технологий и оборудования от известных заключается в том, что процесс эксфолиации реализуется только за счет сдвига в непрерывном режиме работы. Особый интерес к жидкофазной эксфолиации можно объяснить следующими преимуществами данной технологии по отношению к другим: химические реактивы используются в минимальных количествах (3…4 мл/л) в качестве поверхностно-активных веществ, для предотвращения агломерации нанопластин, которые образуются в процессе эксфолиации; жидкой дисперсионной средой, как правило, служит один из компонентов создаваемого конструкционного или функционального материала; материальные и энергетические затраты значительно меньше, чем при использовании других технологий; данная технология легко масштабируется. Исследована кинетика процесса эксфолиации и установлено, что концентрация нанопластин слоистых кристаллов в основном зависит от суммарного пути частиц, пройденного ими в зоне эксфолиации, т.е. в зоне контакта подвижных лопастей с внутренней поверхностью статора. Разработана математическая модель распределения нанопластин в жидкости и определена критическая концентрация агломерации этих пластин в жидкости. Предложена каскадная технология производства нанопластин и методика расчета основных режимных и геометрических параметров роторных аппаратов с подвижными лопастями.

Ключевые слова: слоистые материалы; графит; малослойный графен; многослойный графен; дисульфид молибдена; нитрид бора; сдвиговая эксфолиация.

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1. Introduction

Layered crystals (LCs) form strong in-plane chemical bonds, but they exhibit weak inter-plane bonding, allowing them to exfoliate into nanoplates that can be micrometers in length and width and are in the nanorange, i.e., less than 100 nm thick. The state standard [1] gives the following definition: "Nanoplate: A nanoobject, the linear dimensions of which in one dimension are in the nanorange (less than 100 nm), and the dimensions in two other dimensions are much larger." The nanoplate is a 2D nano-object. When layered materials are exfoliated and make a transition from 3D macro-objects to 2D nano-objects, there is a very large increase in the specific surface area (more than 1000 m^2 g^{-1}), which leads to the manifestation of unique properties.

There are many types of layered materials [2], which can be grouped into different families. The simplest are atomically thin, hexagonal sheets of graphene and hexagonal boron nitride (BN). Transition metal dichalcogenides (TMD) such as MoS_2 and WSe_2 and transition metal halides (TMH) such as PbI_2 and $MgBr_2$ have an almost identical structure and consist of planes of metal atoms sandwiched between planes of halide/chalcogen atoms. Other interesting families are such as indium selenide InSe and gallium sulfide GaS, bismuth telluride Bi_2Te_3 and antimony triselenide Sb_2Se_3, metal trichalcogenides and trihalides. Although there are many different LCs, they all have a planar, anisotropic bond and hence the potential to exfoliate into nanoplates.

One of the significant advantages of LCs is their diversity. Even before exfoliation, many LC families show a very wide range of properties. However, LC exfoliation is beneficial as it significantly improves the properties of the material. For example, as a result of stratification, the ion-exchange capacity of vermiculite increases many times during water purification [3].

To date, a number of methods for exfoliation of LCs into nanoplates are known, among which the main types of delamination are mechanical, chemical and thermal.

Each of these methods includes several options. For example, mechanical exfoliation can be divided into: micromechanical exfoliation (using adhesive tape); exfoliation in a high-gradient suspension flow, in which the solid phase is LC [4]; exfoliation resulting from the complex impact of shearing forces and forces arising due to cavitation [5]; exfoliation with purely shear effects [6].

In 2008, very important results were reported on obtaining a defect-free graphene monolayer by mechanical exfoliation of graphite in a number of solvents [7]. Particular interest in liquid-phase exfoliation (LPE) can be explained by the following advantages of this technology in relation to others: chemical reagents are used in minimal quantities (3–4 $mL \cdot L^{-1}$) as surfactants to prevent nanoplate agglomeration, which are formed in the process of exfoliation; as a rule, one of the components of the created structural or functional material serves as a liquid dispersion medium; material and energy costs are much less than when using other technologies; this technology is easily scalable. Currently, LPE technology is implemented either by ultrasonic processing of the suspension, or due to shear effects in rotary devices.

In [7], graphene was prepared in the following way. A dispersion of sieved crystalline graphite powder was prepared in N-methylpyrrollidone (NMP) and sonicated in a bath. After sonication, a gray liquid, consisting of a homogeneous phase and a large number of macroscopic aggregates, was prepared. As with the nanotube dispersions, these aggregates were removed by centrifugation (CF) and a homogeneous dark dispersion resulted. Such dispersions were prepared at various concentrations of graphite. Although moderate levels of settling and agglomeration occurred within three weeks of centrifugation, high quality dispersions remained for at least five months after preparation.

To date, LPE is used to obtain nanoplates of many layered crystals: transition metal dichalcogenides (MoS_2); transition metal trichalcogenides ($TaSe_3$); oxides (MnO_2), etc. One of the main disadvantages of LPE methods is the low concentration of nanoplates in suspension, usually no more than 1 $mg \cdot mL^{-1}$ [8, 9]. There are no dependences that allow, at least approximately, calculating the maximum concentration of nanoplates in a suspension that can be achieved in industrial installations.

The most studied is ultrasonication of a suspension containing layered crystals in a bath or with a tip. During ultrasonication, two main forces – compressive and shearing – act on a particle. Compressive forces can arise from hydrodynamic perturbations in the form of microshock waves during a sharp collapse of bubbles. Shear effects cause cumulative jets and fluid microflows. The main disadvantage of ultrasonication is very high consumption of electrical energy. This disadvantage has not been practically investigated, since the price of grapheme covers any costs.

The second method of liquid-phase exfoliation is thin high-gradient suspension flows. These flows are created in different ways. In [9], graphene was prepared using a tube 10 mm in diameter and 160 mm long, rotating at a speed of 7000 rpm. A mixture of crystalline graphite and NMP was preliminarily prepared. Under the action of gravitational and centrifugal forces, a thin film of suspension was formed on the surface of the tube. Shear of graphite in the film arose due to the interaction between centrifugal and gravitational forces. In the Taylor-Couette apparatus, shear effects on graphite particles are created in a thin high-gradient suspension flow between a stationary cylindrical stator and a rapidly rotating rotor.

In [5], a Silversonmodel L5M mixer (highshearmixer) was used to prepare graphene-containing suspensions. Inside the perforated cylindrical stator there is a rotor with blades. The gap between the inner surface of the stator and the rotor blades is less than 0.1 mm. The main condition for the mutual dependence of the stator diameter and the rotor speed is the value of the shear rate in the zone between the stator and the rotor exceeding 10^4 s^{-1}. The authors of the paper believe that the exfoliation of graphite particles into graphene plates occurs due to shear, shear (at the moment the particle passes through the hole in the stator) and cavitation.

This study aims to handle several problems: to determine the influence of the operating and geometric parameters of rotary devices on the kinetics of the LPE process when it is implemented in a continuous mode; to determine the limiting values of the concentration of nanoplates in suspension depending on their size and the number of layers, using a mathematical model of their distribution in suspension; to develop a methodology for calculating the operating and geometric parameters of the rotary apparatus during the transition from laboratory to industrial installations; to substantiate the choice of a method for controlling the size of nanoplates in industrial production.

2. Materials and methods

2.1. Materials

Nanoplates were prepared by the LPE method from the following materials: GSM-2 crystalline graphite powder (Zavalevsky Graphite Ltd., Kirovograd region, Ukraine); molybdenum disulfide powder (Aladdin Reagent, Shanghai); boron nitride powder (Hongwu Materials Technology Co., Ltd. Guangzhou, China). The following were used as the dispersed phase: water; industrial oil I20A (Lukoil-Nizhegorodnefteorgsintez Ltd., Russia).

2.2. Methods and equipment

Exfoliation was carried out in rotary mixers with movable blades of periodic [10, 11] and continuous operation [12].

Shear effects on graphite particles are organized in a method for preparing graphene-containing suspensions and a device for its implementation [10]. The block diagram of a mixer is shown in Fig. 1.

The method for preparing a graphene-containing suspension includes: (i) preparing a mixture of crystalline graphite with a liquid; (ii) supplying the resulting suspension in the field of centrifugal forces occurring between the cylindrical stator and the rotating rotor with radial blades; (iii) exfoliation of graphite particles in the zone between the stationary inner surface of the stator 1 and the moving surface of the radial blade *4* of the rotor *2*. The method differs from those described in the introduction in that normal and tangential forces that are constant in magnitude and independent of their size are created in the particles.

The device for the implementation of the described method contains a stator 1 in the form of a cylindrical shell with holes, a rotor *2* with blades *4*, a rotation drive *3*. In contrast to those previously used in the design in Fig. 1, the rotor has grooves in which movable blades *4* are installed in the form of plates

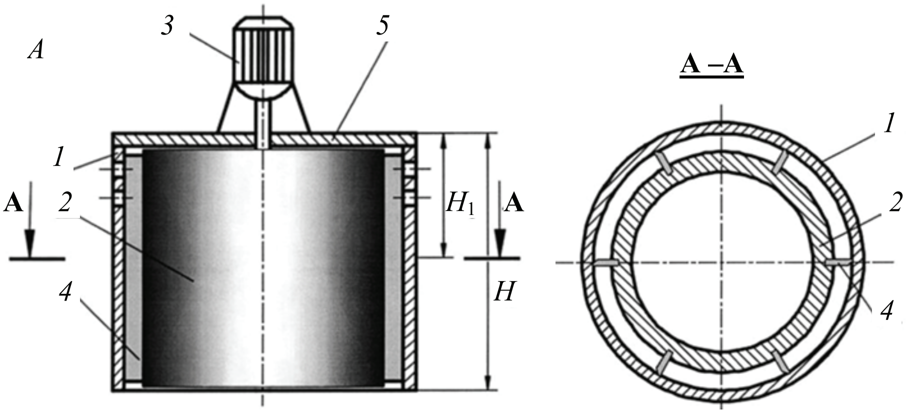


Fig. 1. A block diagram of a rotary device of periodic mode with movable blades:
1 – stator; *2* – rotor; *3* – rotor rotation drive; *4* – movable blade; *5* – lid

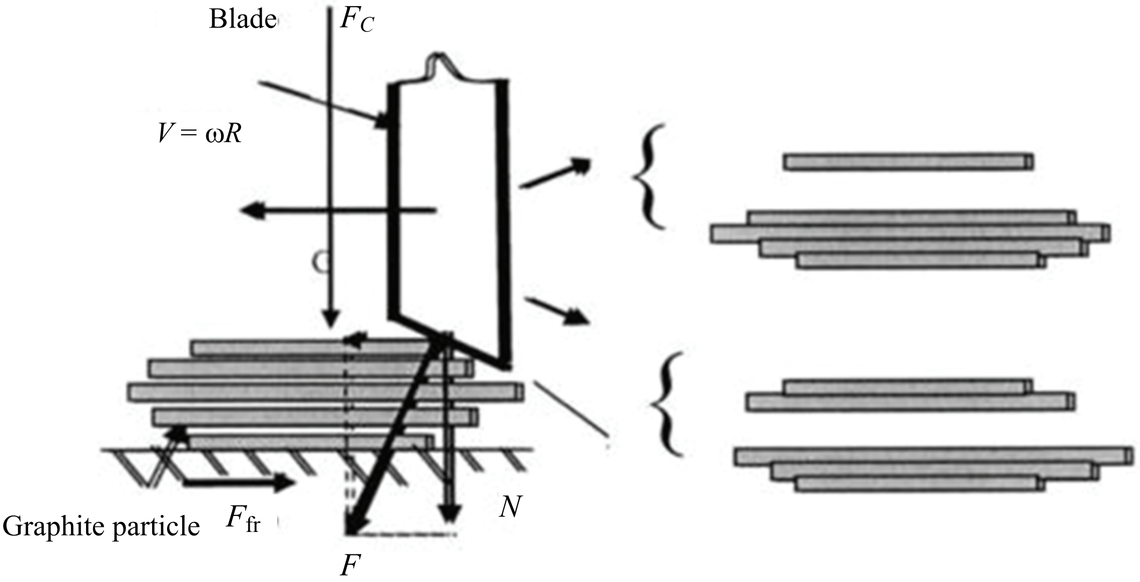


Fig. 2. Shear exfoliation of graphite particles

with clamps for their vertical movement, and on the end side adjacent to the inner surface of the stator, the blades have chamfers at an angle of up to 45°. The cylindrical shell of the stator has a lid *5* and is divided into two zones in height. Holes are located only in the upper zone. The height of the lower zone is from 2 to 5 times the height of the upper zone. The holes on the outer side of the stator surface are countersunk with a depth of 0.7–0.9 of the thickness of the stator cylindrical shell, with an angle of 60 to 120 degrees.

In this device, exfoliation is caused by shear as shown in Fig. 2 [11]. When the rotor rotates, graphite particles, under the action of centrifugal forces, are pressed against the inner surface of the stator. The circumferential speeds of their movement decrease and these particles are overtaken by a moving blade. Figure 2 shows two options of exfoliation of a particle that initially contained 5 graphene layers. In both cases, two particles are formed as a result of exfoliation. In the first version, one of the particles has 1 layer, and the second particle has four layers, in the second version it has 2 and 3 layers. In the zone where there are holes in the stator, the particles are affected by the same forces as in the mixer [5], i.e. by shear force.

The rotary devices discussed above operate in a periodic mode. The device is placed in a container with the initial suspension, in which the particles of the layered material are placed and the rotor rotation drive is switched on. Under the action of centrifugal forces, the suspension is ejected through the holes in the stator. A discharged state is created in the zone between the stator and the rotor, and the suspension is drawn through the lower end of the apparatus into the space between the stator and the rotor. In this case, the rotary apparatus works like a pump. Particles fall

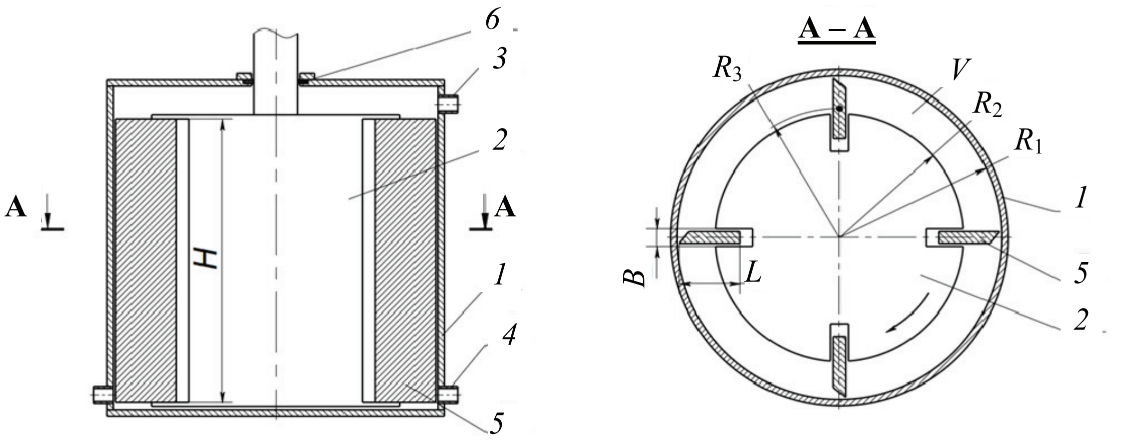


Fig. 3. A diagram of a rotary device of continuous operation:
1 – stator; *2* – rotor; *3* – branch pipe for supplying the initial suspension; *4* – branch pipe for draining the treated suspension; *5* – movable blade; *6* – rotor shaft seal

into the contact zone of the rotor blades with the inner surface of the stator randomly. Some particles are processed multiple times, while others do not enter the processing zone at all. Apparently, this is the reason for the low intensity of the process and the small fraction of graphite particles transformed into graphene plates.

Figure 3 shows a diagram of a rotary device with movable blades of continuous operation [12].

The fundamental difference between this apparatus and the one shown in Fig. 1 is that in the upper part of the stator there is one branch pipe *3* for supplying the initial suspension, and in the lower part of the stator there is one or two branch pipes *4* for draining the treated suspension.

Figure 4 shows a diagram of an experimental setup on which the kinetics of the process of exfoliation of layered crystals in a continuous mode was studied.When operating in a continuous mode, the suspension was fed into the rotary apparatus *2* from the tank *1* by the pump P_1 with a fixed capacity from 1 to 10 liters per minute. Having been treated, the suspension was fed into the container *3*. After the entire suspension from the container *1* through the rotary apparatus *2* flowed into the container *3*, the rotor rotation drive was turned off. The treated suspension was pumped by pump P_2 into container *1*, and the suspension processing cycle was repeated. Periodically, after a certain number of processing cycles, samples of the suspension are taken from the tank *3* for analysis. At the outlet pipes *4* (Fig. 3), valves were installed for precise control of the volumetric flow rate of the suspension through the rotary device. This suspension treatment scheme has the following main advantages over the batch treatment scheme: 100 % of the suspension in each treatment cycle passes through the rotary apparatus; the residence time of the suspension in the processing zone is strictly controlled by the pump P_1 and the valves on the outlet pipes *4*.

The diagram shown in Fig. 4 makes it possible to simulate the process of cascade exfoliation of layered crystals under laboratory conditions, i.e. when treatment is carried out in several series-connected rotary devices with movable blades.

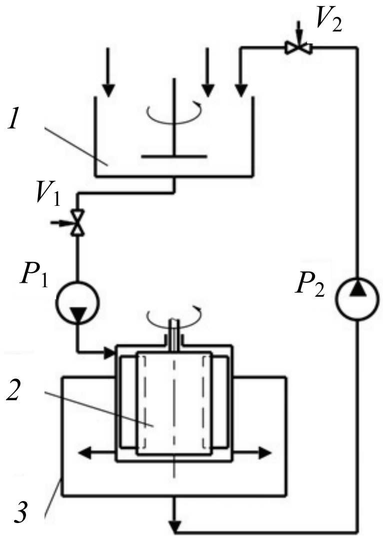


Fig. 4. A diagram of a laboratory setup with a rotary apparatus operating in a continuous mode:
1 – the capacity of the initial suspension; *2* – rotary device; *3* – capacity of the treated suspension; P_1, P_2 – pumps; V_1, V_2 – valves

3. Results and discussion

3.1. Study of shear exfoliation kinetics

In addition to graphite, boron nitride, molybdenum disulfide, and vermiculite were used as layered crystals. Figure 5 shows the results of a comparison of the kinetic dependences of the process of liquid-phase exfoliation of graphite in periodic and continuous modes.

The graphs show that the intensity of the exfoliation process when using an apparatus with moving blades operating in continuous mode is much higher and the final concentration is 30 % higher than when using a rotary device with fixed blades operating in a periodic mode.

Figure 6 shows the characteristic kinetic dependence of the graphite exfoliation process.

Three zones can be distinguished on the graph: I: constant intensity of the process (the concentration is directly proportional to the number of treatment cycles); II: decreasing intensity of the process; III: zero intensity. With an increase in the concentration of nanoplates in suspension, i.e. with an increase in the number of nanoplates per unit volume of the suspension, the intensity of the reverse process, i.e., particle agglomeration, increases, combining two particles into one. Apparently, in zone III, the intensities of the direct and reverse processes become equal, and a dynamic equilibrium sets in between the number of formed and combined particles.

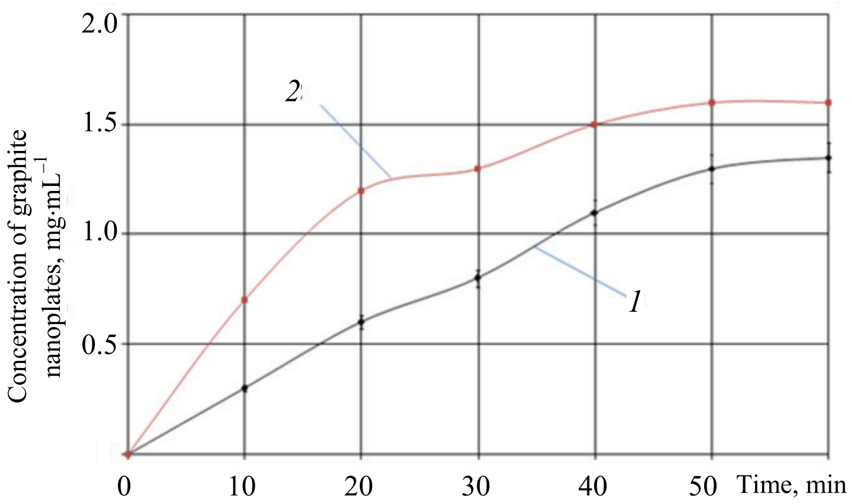


Fig. 5. Kinetics of the graphite exfoliation:
1 – apparatus with fixed blades [5]; *2* – apparatus with movable blades [12]

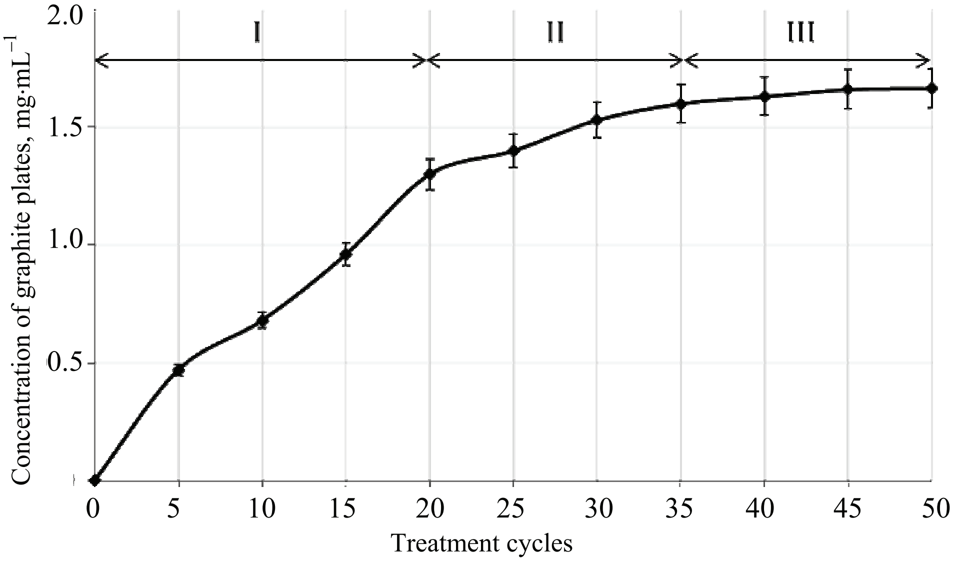


Fig. 6. Effect of a number of treatment cycles on the concentration of graphene plates in suspension

Similar kinetic curves were obtained during liquid-phase shear exfoliation of boron nitride, molybdenum disulfide (Fig. 7). The results of the study of the kinetics of the exfoliation process showed that all layered materials are characterized by the presence of these three zones. The differences are in the numerical values of the concentration of nanoplates in suspension and the number of cycles for each zone. It was found that the intensity of the exfoliation process in zone I is directly proportional to: the inner diameter of the stator; rotor speed; the residence time of the particle in the exfoliation zone; concentration of LC particles in the initial suspension.

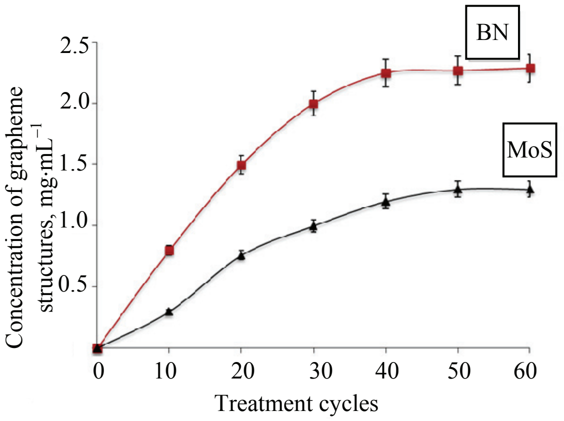


Fig. 7. Kinetic curves of the exfoliation process: boron nitride; molybdenum disulfide

These results suggest that the concentration of LC nanoplates mainly depends on the total path of particles traveled by them in the exfoliation zone, i.e., in the zone of contact of the movable blades with the inner surface of the stator.

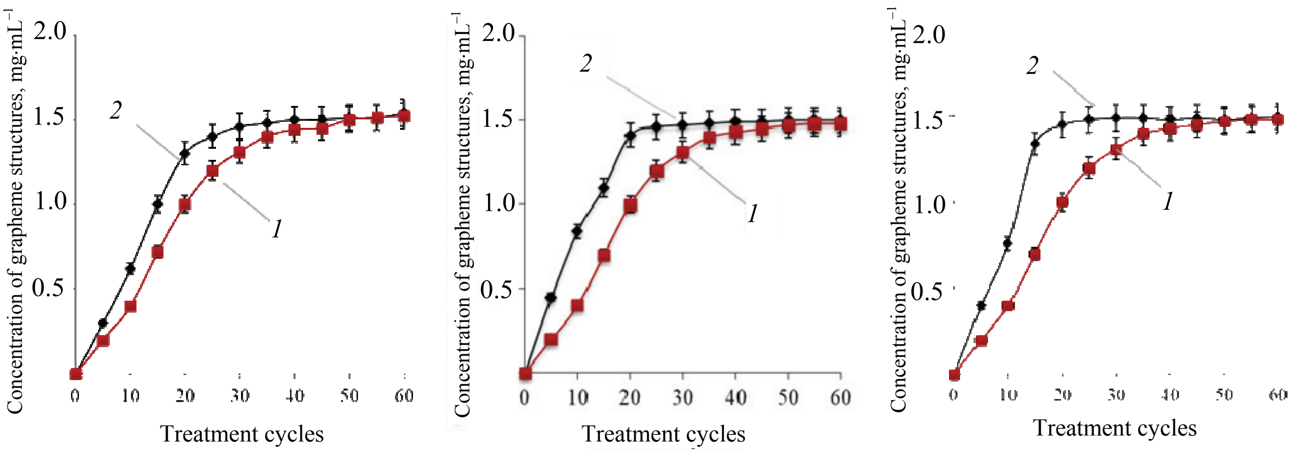
Calculations have shown that the same concentrations of graphene plates in suspension are achieved when the total path traveled by the particles in the exfoliation zone is the same. We consider this with specific examples.

Figure 8 shows the kinetic curves for different values of the operating parameters of the exfoliation process.

Figure 8*a* shows that the rotor speeds differ by 1.5 times. Since the volumetric performance of the pump supplying the suspension to the rotary apparatus has not changed, the residence time of particles in the exfoliation zone is the same for curves *1* and *2*. By increasing the rotor speed, the path of particles in the exfoliation zone has increased by 1.5 times. In the area of constant intensity of the process (zone I in Fig. 6), after 15 treatment cycles, the concentration of graphene plates is 0.7 (curve *1*) and 1 mg·mL^{-1} (curve *2*).

Figure 8*b* shows that the curves with an increase in the concentration of graphite in the initial suspension by 1.5 times. This means that the number of particles increased by about 1.5 times, therefore, the total path length of particles in the exfoliation zone increased by 1.5 times, since the total path length is equal to the product of the path length of one particle by the number of particles. The graphs show that the concentration on curve *2*, after 20 treatment cycles, is approximately 1.5 times higher than on curve *1*.

Figure 8*c* shows the curves with a decrease in the volumetric performance of the pump supplying



(*a*) (*b*) (*c*)

Fig. 8. Kinetic curves for different values of exfoliation regime parameters:
a – rotor speed: *1* – 1047 s^{-1}, *2* – 1570 s^{-1}; *b* – concentration of graphite in the initial suspension: *1* – 10 %, *2* – 15 %;
c – volumetric performance of the pump supplying the suspension to the apparatus: *1* – 5 L·min^{-1}, *2* – 2.5 L·min^{-1}

the suspension to the rotary apparatus. Since all other process parameters have not changed, with a decrease in pump performance, the residence time of particles in the exfoliation zone increases, thereby increasing the total path length of the particles. An increase in the total path length leads to an increase in the concentration of graphene plates in one exfoliation cycle.

It should be noted that it is possible to increase the rotor speed or graphite concentration in the initial suspension up to certain limits. For example, the analysis of experimental results shows that with an increase in graphite concentration from 2.5 to 15 %, the intensity of the process increases in direct proportion. However, when the concentration increases from 15 to 20 %, the intensity of the process increases less than the concentration increases.

A similar dependence is observed with an increase in the rotor speed. With a decrease in the volumetric productivity of the pump supplying the suspension to the rotary apparatus, the intensity of the process for one processing cycle and the cycle time increase. Thus, a change in the performance of the pump supplying the suspension to the rotary apparatus does not affect the increase in the concentration of graphene plates over time. However, it is possible to find the optimal values of the rotor speed and the concentration of graphite in the initial suspension in terms of the intensity of the process.

By reducing the volumetric efficiency of the pump, it is possible to reduce the number of rotary devices in the implementation of the cascade exfoliation of graphite described above. Naturally, this will reduce the productivity of the production line, so the decision on this issue is made taking into account real production capabilities.

Further improvement of the technology of cascade exfoliation of graphite is implemented in a method characterized in that during the exfoliation, intensive mixing of the suspension in the rotary apparatus is periodically carried out. Separation is carried out on a filter whose mesh size is smaller than large particles. The device for implementing the method differs from those described above in that the length of the rotor is divided into *N* sections and the blades in each subsequent section along the circumference are offset relative to the blades in the previous section by an angle:

$$\varphi = \varphi_0 + 360 / Nn ,$$

where *n* is the number of blades in the cross section, and along the length of the rotor between the blades of adjacent sections there is a gap of 5 to 10 mm in size.

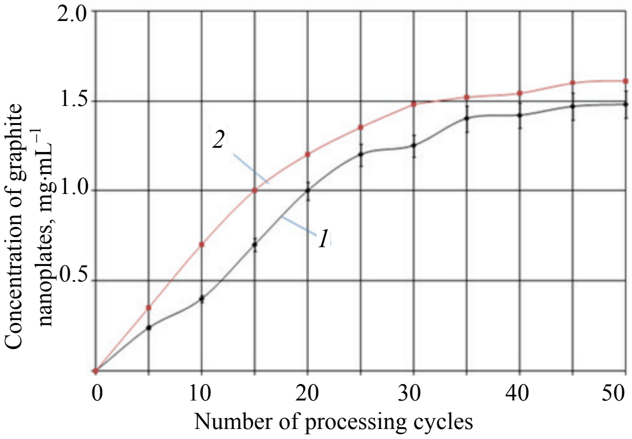


Fig. 9. Effect of a number of processing cycles on the concentration of graphene plates: *1* – prototype [12]; *2* – proposed method

Figure 9 compares the kinetic dependences of the method described above with the prototype [12] when exfoliating graphite in water.

The graphs show that the intensity of the exfoliation process of the proposed method is higher than that of the prototype and the final concentration is 10 % higher. This circumstance can be explained by the fact that during the same treatment time, due to intensive mixing of the suspension, a greater number of graphite particles fall into the exfoliation zone.

Figure 10 compares the kinetic dependences of the method described above with the prototype [12] during exfoliation of graphite in industrial oil I20A. The graphs in Figs. 7–9 and Fig. 10 show that there are limiting values for the concentrations of graphene plates.

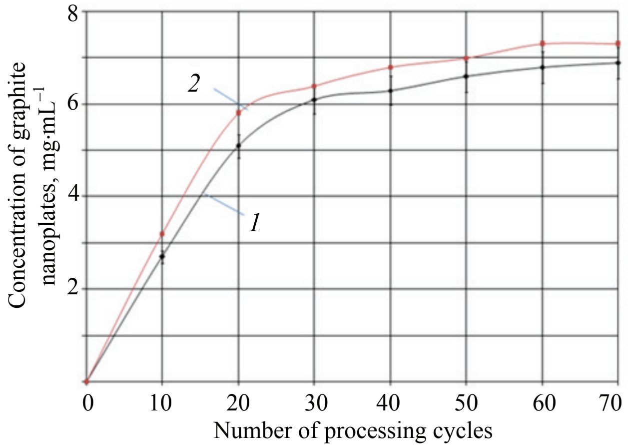


Fig. 10. The changes in the concentration of graphene plates in industrial oil: *1* – prototype; *2* – proposed method

To assess the prospects for the production of graphene-containing suspensions on an industrial scale, it is necessary to determine the limiting values of the concentration of nanoplates when implementing the technology of liquid-phase shear exfoliation of layered crystals.

3.2. Determination of the critical concentration of agglomeration of nanoplates obtained by layered crystals liquid-phase shear exfoliation

Agglomeration, coagulation, flocculation is the process of contact and adhesion, by which individual molecules or particles are held together due to weak physical interactions, ultimately leading to phase separation with the formation of precipitate particles larger than colloidal [13]. Unlike aggregation, agglomeration is a reversible process. The critical concentration of agglomeration is understood as the minimum concentration of particles in suspension at which agglomeration begins and precipitates.

When modeling the distribution of nanoplates in suspension, it was assumed that the dispersion medium is distributed around the nanoplate in the form of a sphere with a diameter equal to the length of the nanoplate [14]. This assumption is based on the fact that the orientation of the nanoplate in space is random, that is, the nanoplate can rotate relative to its own center of gravity. The critical state occurs when the adjacent areas (spheres) in which the nanoplates are located are in contact and two nanoplates can be combined, followed by their agglomeration. Thus, the problem of determining the critical (maximum) concentration of nanoplates in a suspension is reduced to determining the possible packing density of a polydisperse material whose particles have the shape of a sphere. It should be noted that the analogy of various objects with the packing of spheres is widely used in various branches of science, for example, in crystal chemistry.

When modeling the distribution of nanoplates in a liquid, we make the following assumptions:

– nanoplates have an elliptical shape with known dimensions (length and width);

– the distribution of nanoplates over the number of layers is known;

– agglomeration of nanoplates begins as a result of their contact;

– there is no spatial movement of particles, but they rotate relative to their own centers of gravity.

When considering three-dimensional spherical packings, two ways of superimposing layers on each other are usually considered: dense (ball on ball) or densest (balls of the upper layer fall into holes between the balls of the lower layer) [15]. By superimposing layers in such ways, the following options for the arrangement of balls in three-dimensional space are obtained:

– simple cubic masonry: tetragonal layers are superimposed in a dense manner;

– simple hexagonal masonry: hexagonal layers are superimposed in a dense manner;

– the densest spherical packing of different layers: hexagonal layers are superimposed in the densest way, while the distance between the balls in the layer and between the layers is the same;

– body-centered cubic masonry: tetragonal layers are superimposed according to the “ball-to-hole” principle, while the distance between the balls in the layer is slightly greater than the distance between the layers (in other words, the balls in the layer move apart).

With a cubic packing, each ball touches six neighboring balls, and with a hexagonal one – 12. The packing density, that is, the fraction of the volume occupied by the balls, is: for a cubic one – 0.52 (52 %); hexagonal – 0.74 (74 %). Thus, even under the assumptions made, the packing density of the balls, and hence the limiting concentration of nanoplates in suspensions, can vary by a factor of 1.4. Since the critical concentration is considered, we will further assume that the packing density is 0.74.

The sphere volume at the nanoplate length L is equal to:

$$V_{1\mathrm{S}} = \frac{\pi L^3}{6} = 0.52 L^3 . \tag{1}$$

Volume occupied by spheres in one cubic meter of suspension:

$$V_{\mathrm{S}} = 0.74 \text{ m}^3. \tag{2}$$

The number of spheres, therefore, and nanoplates in 1 m^3 of suspension is:

$$N = \frac{V_{\mathrm{S}}}{V_{1\mathrm{S}}} = \frac{0.74}{0.52 L^3} = \frac{1.4}{L^3} . \tag{3}$$

If the length of an elliptical nanoplate is L and the width is 0.5. If the length of an elliptical nanoplate is L and the width is 0.5 L, then the area of the plate is, then the area of the plate is equal to

$$S_{1\mathrm{NP}} = 0.125 \pi L^2 = 0.39 L^2 . \tag{4}$$

The weight of one nanoplate containing n graphene layers is:

$$M_{1\mathrm{NP}} = n \gamma S_{1\mathrm{NP}} = 0.39 n \gamma L^2 , \tag{5}$$

where γ is weight of 1 m^2 of a single-layer exfoliating material, g.

The total weight of nanoplates in one meter of a cubic suspension is equal to the product of the mass of one nanoplate by the number of nanoplates:

$$M_{\text{NP}} = M_{1\text{NP}} N . \qquad (6)$$

Knowing the mass of nanoplates in 1 m^3 of suspension and the density of this suspension ρ_{S}, it is easy to determine the critical concentration of agglomeration C_{CCA}:

$$C_{\text{CAA}} = \frac{M_{\text{NP}}}{\rho_{\text{S}}} . \qquad (7)$$

For a polydisperse material, the packing density of spheres, the total weight of M_{NP}, and the critical concentration of C_{CCA} can be much higher. For example, in [16], the authors state that for a mixture of four fractions with different ball sizes, the maximum density is 0.95. Thus, for polydispersed nanoplates, the critical concentration of agglomeration can be 1.3 times higher than for monodispersed ones.

The highest concentrations of graphene (up to 1.2 mg·mL^{-1}) were obtained using mild sonication for a long time (343 h) in the solvent *p*-methylpyrrolidone [8]. The results of the analysis of transmission electron microscopy showed that the dispersions almost exclusively contain plates with the number of graphene layers N equal to 3 and the length $L = 1$ μm. After substituting the values of N and L in (5) and recalculating to the mass concentration, we obtain the value of 0.93 mg·mL^{-1}. This calculated value is less than the experimental value obtained in [8] by 22.5 %. A rather large difference between the calculated and experimental values can be explained by the higher packing density of polydispersed nanoplates. With a packing density of polydisperse balls equal to 0.95, the calculated critical concentration of agglomeration is 1.21 mg·mL^{-1}, i.e. completely coincides with the experimental value.

In [17], a suspension with concentrations of graphene plates of 0.3–0.4 mg·mL^{-1} was obtained by ultrasonic exfoliation. The nanoplates had a length of 2.5 μm and consisted, on average, of 3 graphene layers. The calculated concentration using formula (6) is 0.375.

When using isopropyl alcohol as a dispersion medium with the addition of an ammonium carbonate salt [18] after sonication for 60 min, a suspension with a concentration of 1 mg·mL^{-1} of single-layer graphene plates with a length of 0.1–0.3 μm was obtained. The critical concentration calculated using (7) for a plate length of 0.3 μm is 1 mg·mL^{-1}.

The experimental verification of the adequacy of the developed mathematical model to the real process was checked as follows. Using a 40 % aqueous concentrate of graphene plates, suspensions were prepared with a concentration of 2 to 10 mg·mL^{-1}. Next, the samples of suspensions were centrifuged at fixed centrifugal accelerations in the zone of centrifuge and sediment separation. After centrifugation, the concentration in the centrifuge was determined. The centrifuge was filtered and samples of concentrates were obtained containing nanoplates with certain distributions along the length. Suspension samples with concentrations from 1 to 5 % were prepared from concentrates. Suspension stability was measured: visually, by the rate of sediment formation; by a decrease in time of the optical density coefficient; in terms of the zeta potential. The results of comparing the concentration of nanoplates in stable suspensions with the calculated values of the critical concentration of aggregation according to the proposed mathematical model showed that these values agree satisfactorily, which confirms the adequacy of the model to the real process.

Figure 11 shows the dependence of the critical concentration of agglomeration on the length of nanoplates constructed using the proposed method. It can be seen from the graph that the C_{CCA} sharply increases when the length of the nanoplates is less than 1 μm. To determine the C_{CCA} for nanoplates with n layers, it is necessary to multiply the corresponding values from the graph (Fig. 11) by *n*.

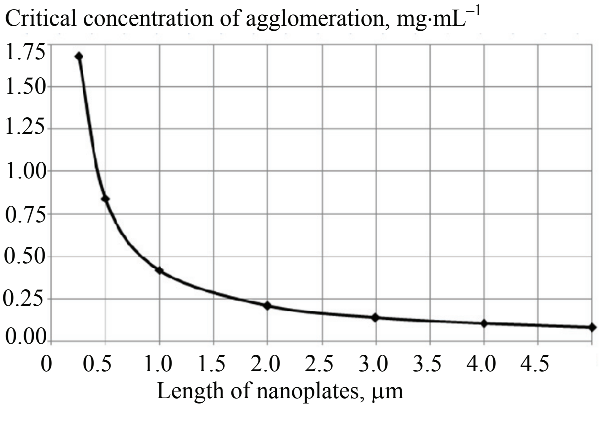


Fig. 11. Effect of the length of graphene nanoplates a the critical concentration of agglomeration

An analysis of the results on determining the performance characteristics of structural materials modified with graphene plates made it possible to formulate the following working hypothesis: the efficiency of modification of structural materials to a greater extent depends not on the mass, but on the numerical concentration of these plates.

The practical interest of this hypothesis lies in the fact that with a decrease in the length of nanoplates by a factor K, their area decreases by a factor of K^2 times.

In addition, as shown by numerous experimental studies by different authors, with a decrease in the length of nanoplates, as a rule, the number of layers that make up the plate decreases. For example, with a plate length of 1 μm, the average number of graphene layers is approximately 3, and with a length of 0.5 μm, the number of layers is 2. Thus, reducing the length of platinum from 1 to 0.5 μm, with a constant number of particles per unit volume suspension, mass concentration decreases 5.6 times. With a decrease in the length of the plates from 1 μm to 0.25 μm, the mass concentration decreases by a factor of 38. Reducing the mass concentration can significantly reduce the cost of modifying structural and functional materials with nanoplates.

3.3. Calculation of the main geometric and operating parameters of the rotary apparatus in continuous operation

The calculation of a rotary apparatus operating in a continuous mode has a number of fundamental differences from the calculation of apparatus operating in a batch mode.

During the operation of devices operating in a periodic mode, the volume of the suspension passing through the zone between the stator and the rotor depends on many parameters (diameters of the stator and rotor, rotor speed, diameter and number of holes in the stator, etc.). Moreover, the numerical value of the path length traveled by an individual particle in the specified zone is random, since it is impossible to determine through which hole the particle will leave this zone. In continuous operation, the displacement is controlled by a pump that delivers the slurries to the area between the stator and the rotor. In addition, each particle goes from the upper hole (Fig. 3), into which the suspension is fed along a helical line, to the lower hole, through which the suspension exits the apparatus at the laboratory installation and make a large-scale transition to the industrial apparatus.

Let us determine the productivity of an industrial apparatus with fixed geometric and operating parameters, if the concentration of graphene plates is known for one processing cycle at the $C_{1\mathrm{L}}$ laboratory facility. Let the parameters of the industrial apparatus be equal: R_S the stator radius, m; R_R is the rotor radius, m; H_R is the rotor height, m; ω is the angular speed of rotation of the rotor, s^{-1}; Q_S is the volumetric performance of the pump supplying the suspension to the apparatus, $\mathrm{m}^3 \cdot \mathrm{s}^{-1}$; V_S is the volume of the processed suspension, m^3. Since as the concentration of graphene plates in the suspension increases in direct proportion to the number of treatment cycles the beginning of the process, let us determine the main parameters of one treatment cycle.

The length of the path traveled by the particle in the exfoliation zone in one treatment cycle:

$$L_1 = 2\pi R_\mathrm{S}\, \omega \tau_\mathrm{E}\,, \tag{8}$$

τ_E is residence time of the particle in the exfoliation zone, s.

Time τ_E is equal:

$$\tau_E = \frac{V_\mathrm{RS}}{Q_\mathrm{S}} = \pi\left(R_\mathrm{S}^2 - R_\mathrm{R}^2\right)\frac{H_\mathrm{R}}{Q_\mathrm{S}} \tag{9}$$

where V_RS is volume between stator and rotor, m^3.

After substituting (2) into (1), we obtain:

$$L_1 = 2\pi^2 R_\mathrm{S}\omega\left(R_\mathrm{S}^2 - R_\mathrm{R}^2\right)\frac{H_\mathrm{R}}{Q_\mathrm{S}}\,. \tag{10}$$

The concentration of graphene plates in suspension after one treatment cycle is:

$$C_1 = C_{1\mathrm{L}}\frac{L_1}{L_{1\mathrm{L}}}\,, \tag{11}$$

where C_1 is concentration after one treatment cycle, and the subscript L refers to the laboratory facility.

The time of one treatment cycle τ_1 is equal to:

$$\tau_1 = \frac{V_\mathrm{S}}{Q_\mathrm{S}}\,. \tag{12}$$

The number of treatment cycles N in time τ is equal to:

$$N = \tau/\tau_1\,. \tag{13}$$

The concentration of graphene plates in the suspension $C(\tau)$ by the time τ is equal to:

$$C(\tau) = C_1\left(\tau/\tau_{1\mathrm{L}}\right)N\,. \tag{14}$$

After substituting (10) – (13) into (14) we get:

$$C(\tau) = C_{1\mathrm{L}} \left[\frac{R_{\mathrm{S}}\omega\left(R_{\mathrm{S}}^2 - R_{\mathrm{R}}^2\right)\dfrac{H_{\mathrm{R}}}{Q_{\mathrm{S}}}}{R_{\mathrm{SL}}\omega L\left(R_{\mathrm{SL}}^2 - R_{\mathrm{RL}}^2\right)\dfrac{H_{\mathrm{RL}}}{Q_{\mathrm{SL}}}} \right] \frac{\tau Q_{\mathrm{S}} C_0}{V_{\mathrm{S}} C_{0\mathrm{L}}}, \quad (15)$$

where $C_{1\mathrm{L}}$ is concentration of graphene plates in suspension after one treatment cycle in a laboratory facility, $C_{0\mathrm{L}}$ и C_0 are graphite concentrations in the initial suspension of laboratory and industrial facilities, respectively.

Dependence (15) includes all the main parameters of the plant being designed. The productivity of the installation, in terms of dry graphene plates, is equal to:

$$Q_{\mathrm{G}} = \frac{VC(\tau)}{\tau}. \quad (16)$$

Thus, in this case, it is quite simple to determine the time during which one processing cycle of a suspension of a certain volume is carried out and the average length of the particle path in the zone between the stator and the rotor.

3.4. Preparation of suspensions containing nanoplates for modification of structural and functional materials

For the practical use of suspensions, it is necessary to classify graphene plates according to lateral sizes and the number of layers. To modify structural and functional materials with nanoplates obtained by liquid-phase shear exfoliation of layered crystals, suspensions containing: different concentrations of nanoplates are required; different sizes of nanoplates; different number of layers.

When using small volumes of suspension, centrifugation is used to achieve these goals. For example, in [5], samples of the suspension obtained in a batch rotary apparatus were centrifuged for 100 minutes at rotor speeds: 1000; 2000; 2500; 3000; 5000 rpm Centrifugation was carried out on a HettichMikro 22R centrifuge in test tubes with a volume of 10 ml and a height of 55 mm. Taking into account the geometric dimensions of this centrifuge, the centrifugal accelerations were: 1132; 4506; 7061; 10155; 28214 $\mathrm{m{\cdot}s^{-2}}$. Relative centrifugal accelerations, i.e. expressed in units of g (gravitational acceleration equal to 9.8 $\mathrm{m{\cdot}s^{-2}}$) are respectively: 115.5; 460; 720.5; 1036; 2879 g.

It was shown in [8] that after centrifugation at 500 rpm (29 g), the average length of nanoplates is 1000 nm.

It should be noted that the size of nanoplates depends not only on the values of centrifugal accelerations, but also on the centrifugation schedule.

It was noted in [19, 20] that most of the material in the dispersion after sonication consists of thick graphite-like flakes, which can be removed by various strategies based on differential ultracentrifugation in a homogeneous medium or in a density gradient medium (DGM). A liquid phase graphite exfoliant typically produces flakes with a transverse dimension of one micrometer or less, so it is too small for many applications such as mechanical reinforcement of composites.

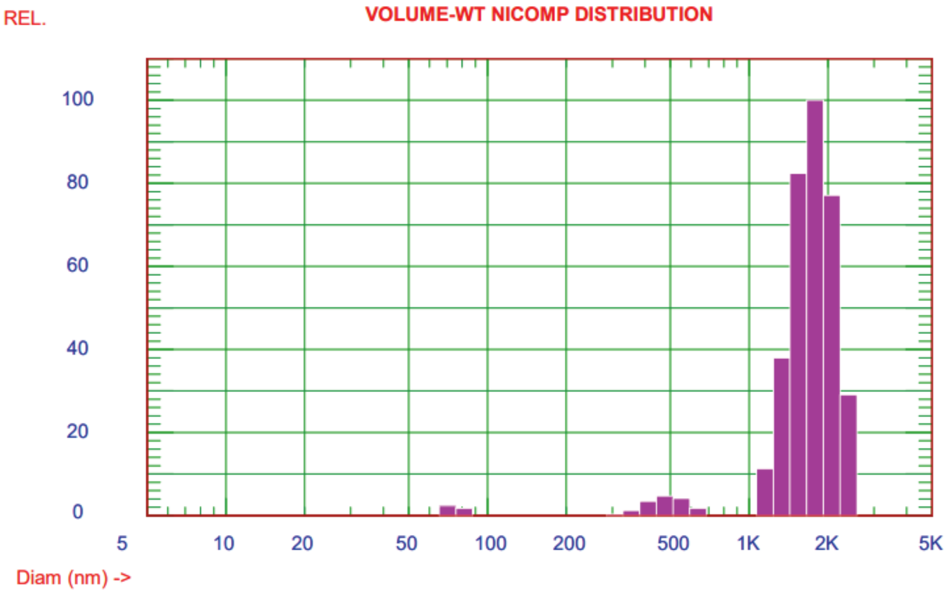


Fig. 12. Particle size distribution in initial suspension

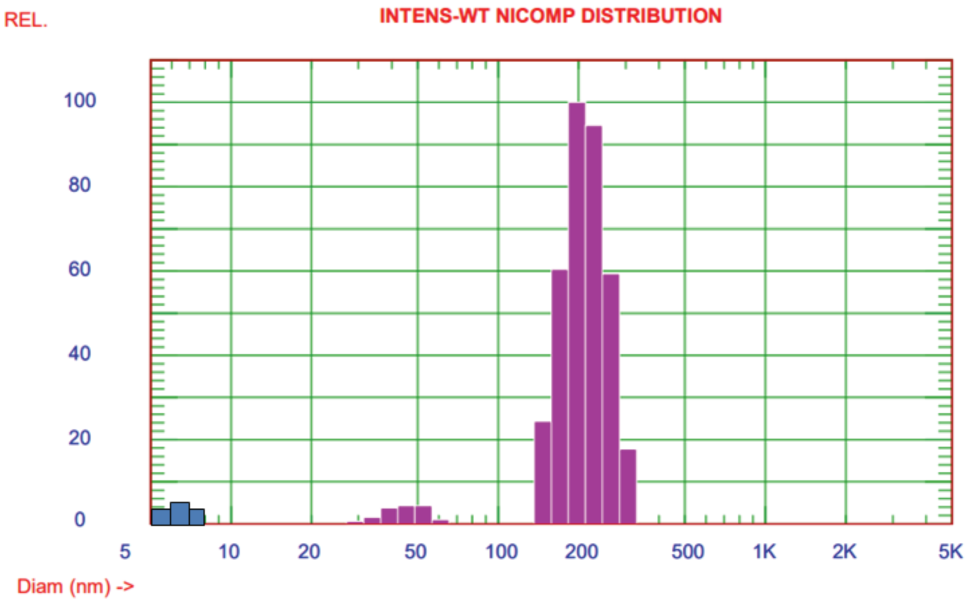


Fig. 13. Particle size distribution after centrifugation at 5000 rpm

To solve this problem, a method was developed for separating graphene plates into fractions. The initial dispersion of graphene in n-methyl-pyrrolidone was centrifuged at a high centrifugation speed (5000 rpm), separating small flakes in the supernatant from large flakes in the sediment. Re-dispersion of the sediment followed by successive cycles of centrifugation, separation and re-dispersion led to the separation of the flakes by size.

This procedure resulted in a range of dispersions with an average flake length from 1 μm for the maximum centrifugation speed to 3.5 μm for a sample whose final centrifugation speed was 500 rpm. The size of the plates was determined by analysis of TEM images as well as Raman spectra. It was found that with a decrease in the centrifugation speed, the number of graphene layers in the plates increased.The authors of this paper carried out centrifugation of suspensions containing graphene plates obtained by liquid-phase graphite shear exfoliation. The size of the nanoplates was determined on a NICOMP 380 ZLS nanosizer (NICOMP, USA) (Fig. 12 and Fig. 13).

Figure 12 shows three peaks: 75 nm; 489 nm; 1793 nm. It can be assumed that these peaks correspond to the thickness, width, and length of the nanoplates. Similar peaks, but with values of 6, 48 and 192 nm, are observed after centrifugation at 5000 rpm (Fig. 13).

Figure 14 shows a comparison of the dependences of the length of nanoplates on the relative centrifugal acceleration during centrifugation, obtained as a result of: processing images taken with an optical microscope [5]; TEM image analysis [5]; nanosizer analysis.

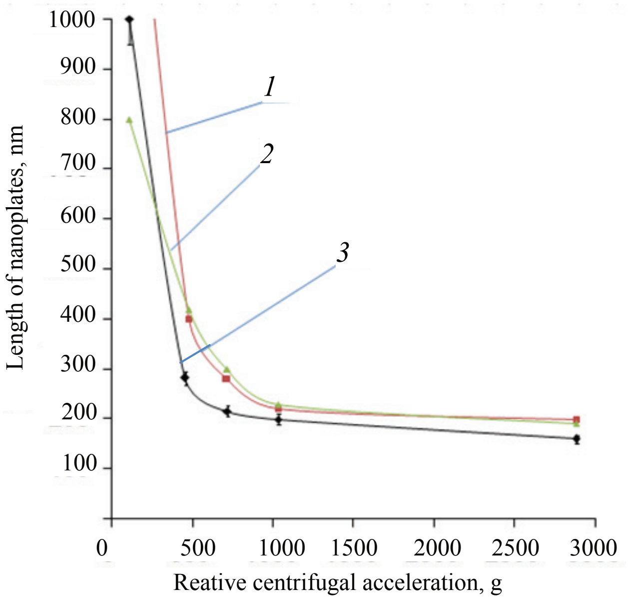


Fig. 14. Effect of the relative centrifugal acceleration on the length of nanoplates:
1 – according to the results of [5]; *2* – on the nanosizer; *3* – optical microscope

As can be seen from the graphs, when determining the length of nanoplates after centrifugation with relative centrifugal accelerations of more than 450 g, the results agree satisfactorily.

Thus, in the industrial production of nanoplates, their dimensions can be controlled using a nanosizer.

4. Conclusion

The results of the studies on the development of rotor apparatus designs and the study of the parameters of the process of liquid-phase shear exfoliation confirm the prospects of using this technology for the industrial production of nanoplates from layered crystals. The transfer of shearing effects on the particle from the moving blade made it possible not only to increase the intensity of the exfoliation process, but also the degree of transformation of particles of layered crystals into nanoplates. The concentration of graphene particles in the suspension reaches 1.5 mg·mL^{-1}, and due to periodic stirring it increases to 1.7 mg·mL^{-1}. There is no evidence in the scientific literature of reaching such high concentrations. It should be especially noted that the developed technology is absolutely environmentally safe and waste-free. Of great importance is the option of obtaining a concentrate (40 wt. %), from which a suspension with a given concentration is easily prepared for further use, for example, when modifying concrete. Material and energy costs for shear exfoliation are much less than when using other technologies, and this technology is easily scalable.

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6. Conflict of interests

The authors declare no conflict of interest.

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Информация об авторах / Information about the authors

Али Мохаммед Рашид Аль-Машхадани, аспирант, кафедра «Техника и технологии производства нанопродуктов», ФГБОУ ВО «Тамбовский государственный технический университет» (ТГТУ), Тамбов, Российская Федерация

Руаа Амер Аль-Джарах, аспирант, кафедра «Техника и технологии производства нанопродуктов», ТГТУ, Тамбов, Российская Федерация

Владимир Федорович Першин, доктор технических наук, профессор, кафедра «Техника и технологии производства нанопродуктов», ТГТУ, Тамбов, Российская Федерация; ID 7006967856,
e-mail: pershin.home@mail.ru

Al-Mashhadani Ali Mohammed Rashid, Postgraduate, Department of Technique and Technology of Nanoproducts Production, TSTU, Tambov, Russian Federation

Ruaa Amer Al-Jarah, Postgraduate, Department of Technique and Technology of Nanoproducts Production, TSTU, Tambov, Russian Federation

Vladimir F. Pershin, Dr. Sc. (Engineering), Professor, Department of Technique and Technology of Nanoproducts Production, TSTU, Tambov, Russian Federation; ID 7006967856,
e-mail: pershin.home@mail.ru

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