The influence of reducing agents on the reduced graphene oxide specific surface area determined on the basis of nitrogen adsorption isotherm

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The most common way to determine the specific surface of materials is to utilise direct methods, such as the flow method and the adsorptive method with the implementation of the adsorption isotherm equations. In our work we used the Brunauer, Emmet and Teller (BET) equation for the nitrogen adsorption isotherm description. Our goal was to examine the influence of reducing agents on the specific surface area of reduced graphene oxide. Graphene oxide was reduced by thiourea dioxide, thiourea, ammonium thiosulfate and sodium hydrosulfite.

Key words: graphene oxide (GO), reduced graphene oxide (rGO), specific surface area, adsorption, BET methods

Wpływ substancji redukujących na wielkość powierzchni właściwej zredukowanego tlenku grafenu określoną na podstawie izotermy adsorpcji azotu

Do określania powierzchni właściwej materiałów najczęściej stosowane są metody bezpośrednie, takie jak metoda przepływowa oraz adsorpcyjna, w której wykorzystywane są równania izotermy adsorpcji. W naszej pracy do określenia powierzchni właściwej zredukowanego tlenku grafenu do opisu wyznaczonej izotermy adsorpcji azotu zastosowano równanie Brunauera, Emmeta i Tellera (BET). Celem niniejszej pracy było zbadanie wpływu substancji redukujących na wielkość powierzchni właściwej zredukowanego tlenku grafenu. Do badań użyto tlenku grafenu redukowanego dwutlenkiem tiomocznika, tiomocznikiem, tiosiarczanem amonu, oraz podsiarczynem sodu.

Słowa kluczowe: tlenek grafenu (GO), zredukowany tlenek grafenu (rGO), powierzchnia właściwa, adsorpcja, metoda BET

1. Introduction

The specific surface area is the measure of an external surface area of a solid, recalculated per its mass unit and usually expressed in m^2 g^{-1}. This parameter reflects physicochemical properties of materials that determine their applications, e.g. as catalysts in chemical reactions or photovoltaic cells.

Depending on the utilized physicochemical phenomena and measuring apparatus, the methods of the specific surface area determination can be divided into direct and indirect. Indirect methods are based on the knowledge of the grain-size distribution and material density. The specific surface area, defined as the external surface area per mass unit, is determined numerically through a distinction of various types of graining and summing the areas of individual grains. The main weakness of the indirect methods lies in their low accuracy, which depends on the number of the grain types distinguished and the grain shape.

Direct methods enable much more accurate measurements of specific surface area. These methods take into account the external surface area of the material examined, together with open pores, but excluding closed pores, which have no connection with the exterior. The following methods belong to this group:

- flow methods – the specific surface area measurement is based on the properties of a laminar Poiseuille-type flow through a laminar layer. In this method, a Blaine apparatus is most often used for measuring the specific surface area;

- porosimetric methods – consisting in the determination of the pore size in the material studied. The measurement is here based on the phenomena related to the behavior of wetting liquids in capillaries;

- adsorptive methods – apply the equation of monolayer adsorption (Langmuir) isotherm and the Brunauer, Emmet and Teller (BET) equation of multilayer adsorption isotherm.

On the basis of the literature review [8 - 17, 26 - 28], it can be stated that BET method gives the best possibility to obtain the most accurate values of the specific surface area that correspond to the real surface area. However, the BET measurements are time-consuming and require

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sophisticated measuring apparatus. The BET method is a typical laboratory method, thus it is very accurate. As it happens we are in the posession of such equipment in the laboratory so this very technique for specific surface area examination was the most natural choice.

In our work we adopted the adsorptive method based on multilayer adsorption theory, elaborated by Brunauer, Emmett and Teller (BET). The fundamental assumption of this theory is the applicability of Langmuir equation to each adsorbed layer. It is assumed that the adsorbent becomes uniformly covered with a multilayer of molecules and the first adsorbed layer acts as a substrate for the successive layers, forming adsorptive complexes [1-7]. The number of adsorbed molecules depends on vapour pressure (p_0). The following equation of an adsorption isotherm was used in the measurements:

$$\frac{p}{V(p_0 - p)} = \frac{1}{V_m C} + \left(\frac{C-1}{V_m C}\right) \times \frac{p}{P_0}, \qquad (1)$$

where: C is a constant, V - the total volume of the adsorbed gas, V_m – the volume of gas in the case of a complete coverage of the whole adsorbent surface with a monolayer and p/p_0 denotes the ratio of the measured pressure to the saturated vapour pressure of the adsorbate at the measurement temperature.

Basing on the above equation, we established various models of a measuring apparatus for the determination of the specific surface area [8 - 10], depending on the expected area value. The improvement of the measurement accuracy, requires high vacuum (10^{-5} Tr) and low temperature (at least as low as 100 K in case of nitrogen). Before the experiment, the samples are degassed and then the amount of adsorbed gas on the examined material surface is measured. Thus, we are able to determine the adsorption isotherms and also the volume of the gas adsorbed on a monolayer. The adsorbed gas volume can be easily recalculated into the number of adsorbed molecules.

If the surface occupied by one molecule is equal to α per the total surface area of the material examined, then:

$$S = \frac{V_m \times N_A}{V_{mol}}, \qquad (2)$$

$$\alpha = 1.09 \left(\frac{M}{N_A \rho}\right)^{2/3}, \qquad (3)$$

where N_A is Avogadro number (6.02×10^{23}), V_m – the molar volume of gas under the experimental conditions, V_{mol} – molar volume of adsorbate, M – the molecular weight and ρ denotes the density of the adsorbate.

The BET measurements can be performed using various gases: nitrogen, argon, helium, xenon, carbon dioxide [11 - 17]. In this work we used nitrogen. This gas is usually used in the BET surface analysis due to its availability in a high degree of purity and its strong interactions with most of the solids. Since the interaction between gas and solid phases is usually weak, the surface needs cooling by liquid nitrogen in order to obtain the detectable amounts of the adsorbate. Next, definite amounts of nitrogen are progressively released into the sample-containing chamber. The production of partial vacuum conditions allow lower relative pressure than atmospheric pressure. The value of α for nitrogen, given by Emmett and Brunauer, is 16.2×10^{-16} cm^2. For loose materials, BET method is regarded as the most adequate method for the determination of specific surface area as a physicochemical boundary between a solid and the surrounding gas or the liquid phase on a molecular level. This method is applied in the laboratories dealing with catalysis, surface structure of solids, powder metallurgy and ceramic powder technology for special applications, e.g. nuclear reactor cores. Thanks to the knowledge of the development of specific surface area it is possible to determine the usability of a given material for its further treatment and its prospective applications.

2. Experimental

The goal of the experiment was to examine the influence of synthesis conditions and reducing agents on specific surface area of reduced graphene oxide. In this paper we describe the measurements of the specific surface area of the starting material (graphite), graphene oxide and reduced graphene oxide.

2.1. Methodology

Specific surface area measurements were performed using a Quadrasorb Evo analyzer (Quantachrome Instruments). This apparatus consists of a FLOVAC Degasser degassing station and an analytic station, both of them shown in Fig. 1. The analyzer is equipped with a computer software which helped to control the experiment and

Fig. 1. An apparatus for the measurement of specific surface area (a) and a sample degassing station (b).
Rys. 1. Urządzenie do pomiaru powierzchni właściwej (a) oraz stacja do odgazowywania próbek (b).

record the data during the adsorption and desorption processes. This is a fully automatic system that allows to measure specific surface area in the range from 0.01 $m^2 g^{-1}$ to 6000 $m^2 g^{-1}$. [18].

Before the measurements the samples were degassed in vacuum for 5 hours. Graphene oxide was degassed at 323 K, because higher temperature could have caused its reduction inside the degassing station. Graphite and reduced graphene oxide were degassed at 523 K. For each sample analyzed, 13 measuring points were collected within the relative pressure range 0.05 - 0.30 p/p_0. Adsorption measurements were carried out using nitrogen at temperature 77 K.

Morphology analysis was performed with an AURIGA Cross Beam Workstation (Carl Zeiss) scanning electron microscope (SEM) [19].

2.2. Materials and synthesis

The investigations on the influence of the reduction conditions on specific surface area were carried out with the use of graphene oxide (GO) and reduced graphene oxide (rGO). Asbury 1 graphite was used as a starting material [20].

In the first stage, Asbury 1 graphite was oxidized to graphene oxide (GO) applying Marcano method [21 - 25] with the use of a mixture of nitric acid, ortophosphoric acid and potassium permanganate. The oxidation process was conducted in the temperature range 318 - 328 K within 5 hours. After the oxidation termination the product was purified in order to remove acids and other post-reaction impurities. The purified material was subjected to a chemical reduction by both organic and inorganic reducing agents. Graphene oxide used for the reduction was denoted as GO_A1 (after "Asbury 1").

The following reducing agents were chosen for the reduction of graphene oxide:

- **SAMPLE 1**
  Suspension with GO_A1 (2 mg ml^{-1}) + thiourea + metallic catalyst.

- **SAMPLE 2**
  Suspension with GO_A1 (2 mg ml^{-1}) + NaOH + sodium hydrosulfite.

- **SAMPLE 3**
  Suspension with GO_A1 (2 mg ml^{-1}) + ammonium thiosulfate.

- **SAMPLE 4**
  Suspension with GO_A1 (2 mg ml^{-1}) + thiourea dioxide.

Sample 1 was obtained by mixing 250 ml of GO with thiourea and a metal catalyst substrate. Ammonia was added to the resulting suspension to obtain pH = 11.80. The process was carried out in a glass reactor for 6 hours at 95°C. At the end of the process, the suspended material was repeatedly washed with deionized water and then dried to obtain a powder. Sample 2 was prepared by mixing 250 ml of GO with sodium hydrosulfite in the presence of NaOH. The process was carried out in a glass reactor for 6 hours at 95°C . At the end of the process, the suspended material was repeatedly washed with deionized water and then dried to obtain a powder. Sample 3 was prepared by mixing the GO suspension with ammonium thiosulfate. The process was carried out on a magnetic stirrer for 10 hours in a temperature range 95 - 100°C . Sample 4 was obtained by mixing the GO suspension with thiourea dioxide. The process was carried out in a glass reactor for 4 hours at 85° C. At the end of the process, the suspended material was repeatedly washed with deionized water and then dried to obtain the powder.

3. Results and discussion

The results of the specific surface area measurements for the reference samples, i.e. graphite and graphene oxides, and for the reduced graphene oxide samples are given in Tab. 1. Since the material examined was not homogeneous, 4 measurements were performed for each sample. An average value from these 4 measurements was taken

Tab. 1. Values of specific surface area according to reducing agents applied.
**Tab. 1.** Wartości powierzchni właściwej w zależności od zastosowanego reduktora.

Sample	Reducing agent	Specific surface area [$m^2 g^{-1}$]
Asbury 1 graphite	-	1
Graphene oxide	-	8
1	Thiourea	58
2	Sodium hydrosulfite	285
3	Ammonium thiosulfate	35
4	Thiourea dioxide	478
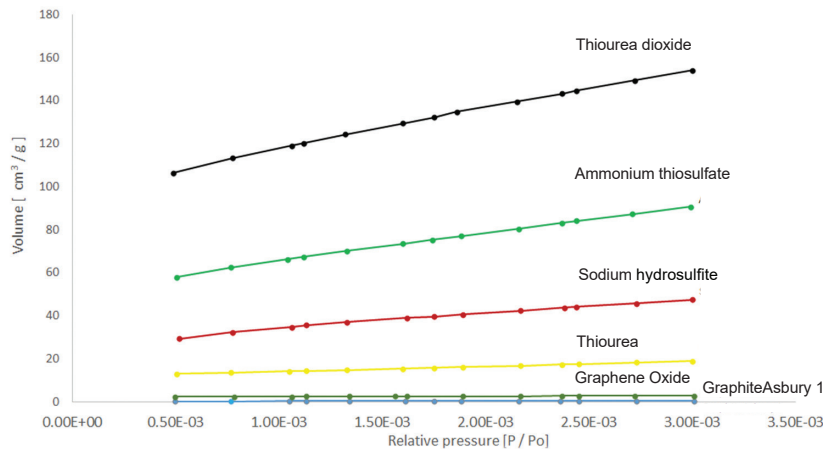
Fig. 2. Dependence of the adsorbed nitrogen volume per mass unit for various adsorbents on the pressure normalized with respect of the adsorbate saturated vapour pressure at the measurement temperature.

Rys. 2. Zależność objętości zaadsorbowanego azotu na jednostkę masy od ciśnienia znormalizowanego względem prężności pary nascyonej adsorbatu w temperaturze pomiaru.
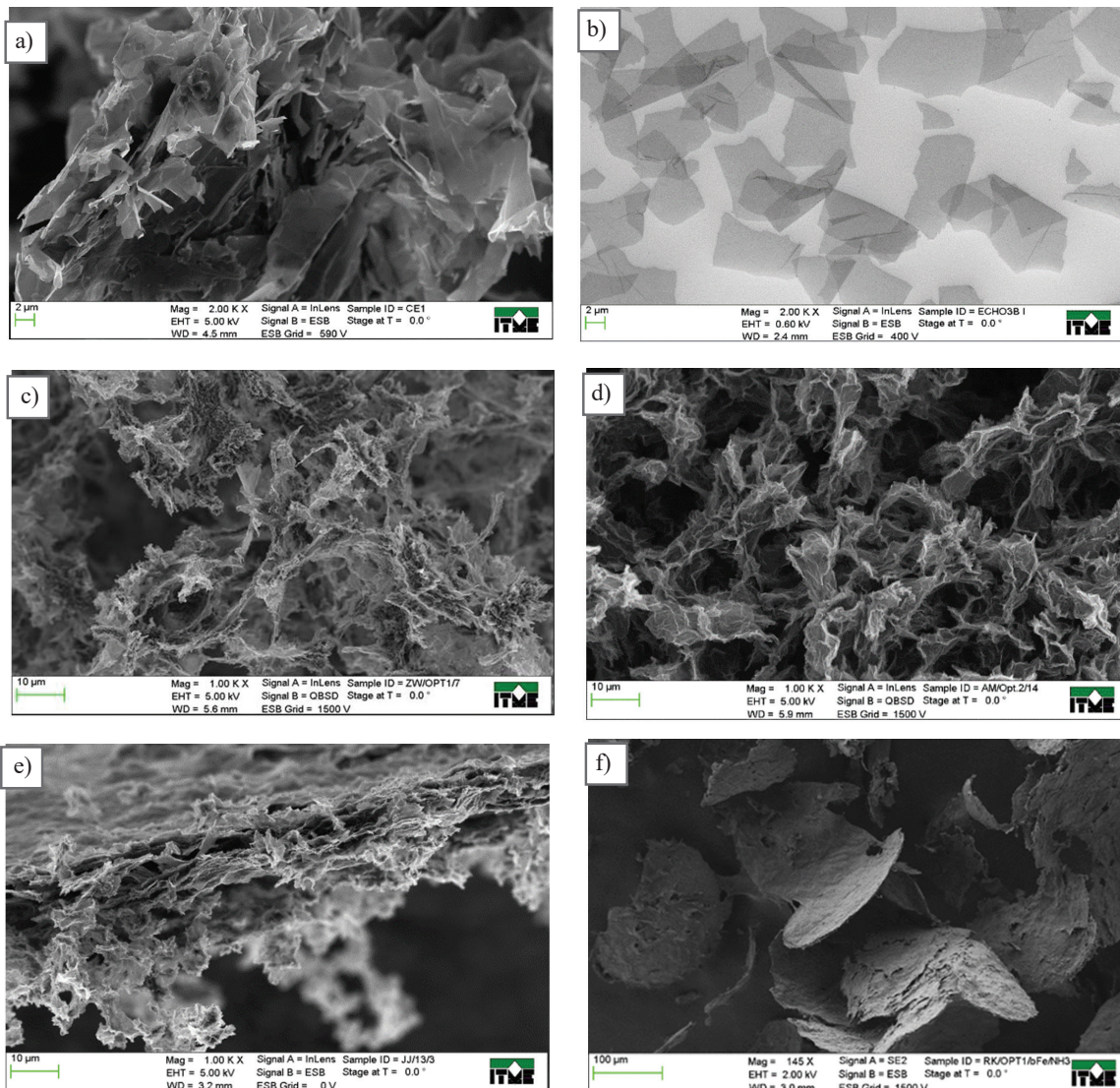
Fig. 3. Images of materials surface obtained by scanning electron microscopic (SEM): a) Asbury 1 graphite; b) graphene oxide; c) rGO obtained by GO reduction with thiourea; d) rGO obtained by GO reduction with sodium hyposulfite; e) rGO obtained by GO reduction with ammonium thiosulfate; f) rGO obtained by GO reduction with thiourea dioxide.

Rys. 3. Zdjęcia powierzchni otrzymane za pomocą mikroskopu skaningowego SEM: a) grafitu Asbury 1; b) tlenku grafenu; c) rGO otrzymany w wyniku redukcji tlenku grafenu tiomocznikiem; d) rGO otrzymany w wyniku redukcji tlenku grafenu podsiarczynem sodu; e) rGO otrzymany w wyniku redukcji tlenku grafenu tiosiarczanem amonu; f) rGO otrzymany w wyniku redukcji tlenku grafenu dwutlenkiem tiomocznika.

as the actual result. For each sample, the specific surface area values were determined in 13 measuring points of the BET isotherm in the range of relative pressure from 0.05 to 0.30 p/p_0. The experimental error is $\pm$ 3.97 m^2 g^{-1}.

Fig. 2 shows the dependence of adsorbed nitrogen volume (cm^3 g^{-1}) on the relative pressure (p/p_0). The measurements were conducted in the range of relative pressure from 0.05 to 0.30. This is a standard specific surface area measuring range.

On the basis of the specific surface area measurements by the BET method we can observe an important dependence of these values on the kind of a reducing agent applied and the reduction process conditions. Fig. 2 shows that the value of the specific surface area becomes greater with the increasing amount of adsorbed nitrogen. According to a correlation, the BET adsorption isotherms are usually linear for relative pressure within the range of 0.05 - 0.30 p/p_0. For the relative pressure lower than 0.05 the experimental points usually tend to deviate towards underrated values (greater V values) because the BET theory does not take into consideration the fact of energetic heterogeneity of the adsorbent surface. On the other hand, for the relative pressure higher than 0.35 the adsorption is often smaller than that predicted by Eq. (1), therefore the experimental points exhibit positive deviations.

The effect of the reducing agent application is also evident in scanning electron microscopic (SEM) images. Figs. 3a - f show the morphology changes from graphite, through graphene oxide, up to reduced graphene oxide.

4. Conclusions

The aim of the presented research was to examine the influence of reducing agents on the specific surface area of the reduction product, i.e. reduced graphene oxide. The inhomogeneity and morphology of the material obtained affect the value of the specific surface area, which can be visible in scanning electron microscopic (SEM) images. On the basis of SEM observations we can state that utilizing various reducing agents in the process of graphene oxide reduction enables us to obtain products of a diverse morphology. Graphene oxide is present in the form of flakes (see Fig. 3b), while after reduction these flakes become agglutinated, have uneven edges and are more porous.

The differences in the values of the specific surface area may also result from the presence of functional groups and elements which remained on the surface of the reduced graphene oxide. Those groups can hinder gas (i.e. nitrogen) adsorption on the surface of the examined material. Annealing and degassing the samples before the measurements does not allow these groups to be fully removed, and it referes especially to the groups covalently bound to the graphene flakes. Small amounts of sulfur embedded into the obtained reduction product result directly from the application of the reducing agent and, to a lesser degree, from the catalyst. The existence of the unremoved functional groups may cause the agglutination of graphene oxide flakes, and thus lead to the formation of agglomerates. Oxygen functional groups contained in the graphene material after the reduction process completion occurred in a moderate degree, which confirms the efficiency of the process conducted with the use of the aforementioned reagents. The best specific surface area was obtained for graphene oxide reduced by thiourea dioxide. The purity of the materials studied can be determined by FTIR analysis, which will be a subject of further research.

Acknowledgements

References

[1] Brunauer S., Emmett P. H., Teller E.: Adsorption of Gases in Multimolecular Layers, *J. Am. Chem. Soc.*, 1938, 60, 309

[2] Kordek J., Gawenda T., Kępys W.: Powierzchnia właściwa proszków, porównanie wyników policzonych i zmierzonych metodami przepływowymi i adsorpcyjnymi, *Górnictwo i Geoinżynieria*, 2006, 30, 3/1

[3] Dai J.-F., Wang G.-J., Ma L., Wu C.-K.: Surface properties of graphene: relationship to graphene-polymer composites, *Rev. Adv. Mater. Sci.,* 2015, 40, 60 – 71

[4] Sing K.: The use of nitrogen adsorption for the characterisation of porous materials, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2001, 187 – 188, 3 – 9

[5] Gadipelli S., Guo Z. X.: Graphene-based materials: Synthesis and gas sorption, storage and separation, *Progress in Materials Science,* 2015, 69, 1 – 60

[6] Marban G.: BET adsorption reaction model based on the pseudo steady-state hypothesis for describing the kinetics of adsorption in liquid phase, *Journal of Colloid and Interface Science,* 2016, 467, 170 – 179

[7] Gomez-Serrano V., Gonzalez-Garcıa C. M., Gonzalez-Martın M. L.: Nitrogen adsorption isotherms on carbonaceous materials. Comparison of BET and Langmuir surface areas, *Powder Technology,* 2001, 116, 103 – 108

[8] Pajdak A., Skoczylas N.: Porównanie powierzchni właściwej i rozmiarów porów węgla metodami sorpcyjnymi w różnych temperaturach, *Prace Instytutu*

Mechaniki Górotworu PAN, 2014, 16, 3 – 4, 85 – 92

[9] Gauden P., Furmaniak S., Terzyk A.: Węgiel aktywny w ochronie środowiska i przemyśle, Pozorność a realność pola powierzchni materiałów węglowych otrzymywanych z modelu BET, Wyd. Politechniki Częstochowskiej, 2008, 95 – 103

[10] Choma J., Jaroniec M., Ustinov E.: Adsorpcyjna charakterystyka węgli aktywnych o bardzo dobrze rozwiniętej porowatości, *Ochrona Środowiska*, 2004, 4, 3 – 7

[11] Ramakrishna Matte H. S. S., Subrahmanyam K. S., Rao C. N. R.: Synthetic aspects and selected properties of graphene, *Nanomaterials and Nanotechnology*, 2011, 1, 3 – 13

[12] Srinivas G., Zhu Y., Piner R., Skipper N., Ellerby M., Ruoff R.: Synthesis of graphene-like nanosheets and their hydrogen adsorption capacity, *CARBON*, 2010, 48, 630 – 635

[13] R. Canty, E. Gonzalez, C. MacDonald, S. Osswald, H. Zea, C.Luhrs: Reduction expansion synthesis as strategy to control nitrogen doping level and surface area in graphene, *Materials*, 2015, 8, 7048 – 7058

[14] Si W., Wu X., Zhou J., Guo F., Zhuo S., Cui H., Xing W.: Reduced graphene oxide aerogel with high–rate supercapacitive performance in aqueous electrolytes, *Nanoscale Research Letters,* 2013, 8:247

[15] Birch E., Ruda – Eberenz T., Chai M., Andrews R., Hatfield R.: Properties that influence the specific surface areas of carbon nanotubes and nanofibers, *Ann. Occup. Hyg.*, 2013, 57, 9, 1148 – 1166

[16] Guo F., Creighton M., Chen Y., Hurt R., Kulaots I.: Porous structures in stacked, crumpled and pillared graphene-based 3D materials, *CARBON,* 2014, 66, 476 – 484

[17] Kaniyoor A., Baby T. T., Ramaprabhu S.: Graphene synthesis via hydrogen induced low temperature exfoliation of graphitic oxide, *Supplementary Material (ESI) for Journal of Materials Chemistry*, 2010

[18] http://www.quantachrome.com/index.html

[19] http://www.zeiss.com/

[20] http://www.asburystore.com/

[21] Marcano D. C., Kosynkin D. V., Berlin J. M., Sinitskii A., Sun Z., Slesarev A., Alemany L. B., Lu W., Tour J. M.: Improved Synthesis of Graphene Oxide, *ACS Nano*, 2010, 4 (8), 4806 – 4814

[22] Gómez I., Mejía E., Cabanzo R.: Synthesis of graphene oxide and chemically reduced graphene nanosheets, *Revista Colombiana de Materiales,* 2014, 5, 177 – 184

[23] Peng S., Fan X., Li S., Zhang J.: Green synthesis and characterization of graphite oxide by orthogonal experiment, *J. Chil. Chem. Soc.*, 2013, 58, 4

[24] Wojtoniszak M., Mijowska E.: Controlled oxidation of graphite to graphene oxide with novel oxidants in a bulk scale, *J. Nanopart Res.,* 2012, 14(11): 1248

[25] Sheshmanil S., Fashapoyeh M. A.: Suitable Chemical Methods for Preparation of Graphene Oxide, Graphene and Surface Functionalized Graphene Nanosheets, *Acta Chim. Slov.* 2013, 813, 60, 813 – 825

[26] Szymańska-Czaja M.: Porównanie metod pomiaru powierzchni właściwej materiałów drobno uziarnionych ze względu na zastosowanie tej wielkości w niektórych procesach technologicznych, *Gospodarka Surowcami Mineralnymi*, CPPGSMiE PAN, 1997, 13, 197 – 204

[27] Radomski P., Jarosiński A.: Wyznaczanie powierzchni właściwej materiałów ziarnistych w aspekcie stosowania jej wielkości w wybranych procesach technologicznych, *Chemia Czasopismo Techniczne*, 2010, 107, 267 – 276

[28] Allen T.: Particle Size Measurement London, Chapman and Hall LTD, 1971