V.A. Diamant, L.M. Rozhdestvenska, K.O. Kudelko

MODIFIED SILICA GEL AND CATION-EXCHANGER BASED ON ACTIVATED CARBON FOR FULLERENES SEPARATION

V.I. Vernadsky Institute of General and Inorganic Chemistry of National Academy of Sciences of Ukraine
32/34 Academician Palladin Ave., Kyiv, 03141, Ukraine, E-mail: carbon.h.4@gmail.com

Fullerenes are interesting objects of research in view of their promising use as a nano-sized additive to coatings, films, adsorbents, as well as active components in medicine, pharmacy, cosmetology. This paper considers the possibility of modifying commercial adsorbents - silica gel and cation-exchanger based on activated carbon with available and inexpensive linear carbon radicals. Behentrimonium chloride ($C_{22}H_{45}(CH_3)_3N^+Cl^-$) and cetyl alcohol ($C_{16}H_{33}OH$) were chosen as the latter. The obtained adsorbents were compared with a commercial sample of silica gel modified with a linear hydrocarbon radical $-C_{18}H_{37}$. The adsorbents were described by the methods of IR spectroscopy, thermogravimetry, the main characteristics of the porous structure were determined by the method of low-temperature adsorption-desorption of nitrogen. Modification of adsorbents based on silica gel leads to a decrease in the specific surface area to 202.4 and 236.5 m^2/g and the total pore volume to 0.32 and 0.39 cm^3/g, which is almost 2 half source material. Increasing the fraction of micropores contributes to better separation rates of large molecules. Treatment of cation-exchanger based on activated carbon by cation modifier leads to a significant decrease in the specific surface area, as well as to an increase in the size of pores with the predominant formation of mesopores.

It is shown that the modification of silica gel is carried out both through silanol and siloxane groups, in contrast to the commercial sample of silica gel. The approximate number of modifier groups on the surface of the original SiO_2 matrix was estimated, which is one modifier group ~ per 11 SiO_2 molecules.

To study the behavior of adsorption of C_{60}, C_{70} fullerenes and their mixtures on adsorbents, column experiments were carried out with changes in the geometrical parameters of the column and the initial concentrations of the solutions. The results showed that the modified silica gels are potential adsorbents for the separation of a mixture of fullerenes with a ratio of 65/25. Silica gel modified with cetyl alcohol $C_{16}H_{33}OH$ showed the best separation efficiency. By the help of an adsorbent, it is possible to separate C_{60} - 90.52 % from a less concentrated solution and 87.26 % from a more concentrated solution. To increase the purity of the product, it is necessary to pass the solution through the sorbent 2–3 times.

The competitive capability of the proposed modified silica gels, together with economic efficiency, ease of modification, and the possibility of fullerene separation characterize the proposed adsorbents as potential materials for practical application. Due to the significantly lower cost and simpler manufacturing methods, the proposed adsorbents can be used for separation at a large scale.

Keywords: fullerenes, C_{60}, C_{70}, separation, silica gel, activated carbon, behentrimonium chloride, cetyl alcohol

INTRODUCTION

Fullerene is an allotropic form of carbon, a molecule that is a closed sphere of sixty carbon atoms in the form of an empty spherical frame. C_{60} is the most stable and used for research [1, 2], is obtained by various methods, for example, thermal decomposition of graphite, laser or microwave irradiation, plasma method, reduction of CO_2 with metallic lithium.

C_{60} is a promising material for the modification of inorganic, polymer, and carbon materials and the creation of composites based on them [3]. C_{60}-based nanomaterials are used for energy needs (supercapacitors, electrocatalysts), in the production of semiconductors, in sensitive sensor devices, coatings with antibacterial properties, for medical needs fullerene is interesting as an antioxidant, in the production of functional cosmetics [4–9]. Inorganic composites containing C_{60} improve the mechanical strength of critical inorganic materials for engineering and aerospace. Fullerene-containing nanocomposites based on polymers are used as anti-corrosion coatings for medical purposes [10]. The use of C_{60} fullerenes functionalized with carboxyl groups for the manufacture of anodes of lithium-ion batteries is proposed in [11]. The possibility of using fullerene-containing materials to modify the surface of membranes, to generate reactive oxygen species for the degradation of traces of organic compounds, disinfection, suppression of the formation of biofilms and reduction of biofouling of polymer membranes was investigated [12]. When included in the polymer

matrix, fullerene retains its unique properties, while the properties of the polymer change [9–12].

Extraction of fullerenes, their separation and purification is carried out by preparative liquid chromatography [13, 14]. In this case, compounds of tetravalent elements (oxides [15] and phosphates [16]) can be used as a stationary phase (sorbent). This is due to their significant exchange capacity and increased selectivity, chemical resistance and mechanical strength, as well as ease of modification. Thanks to this, these compounds are also used for traditional sorption processes [17–20] as well as for electromembrane ones [21]. The use of these compounds as a matrix for incorporating active components (graphene [22, 23] and graphene-like carbon nanomaterials [24], hexacyanoferrates (II) of transition metals [25], lithium-titanium [26] and lithium-titanium-manganese spinel [26, 27]) provides possibility to increase selectivity and expand the working pH range of solutions from which toxic and valuable components are extracted, and in some cases - to increase the rate of sorption [24, 25]. For the same purpose, oxide and hydrogen phosphate sorbents are used to modify ion exchange resins [28–31]. Functionalization of the surface of oxides and hydrogen phosphates contributes to the increase in selectivity [17, 18, 32]. Another direction of research is hydrophobization of the surface of oxide materials to give them capability to adsorb organic substances from polar and non-polar solvents [33–35]. For the most part, the technique of surface functionalization is used for silica gel. In the case of sorbents designed to remove fullerenes from solutions, this technique is the only possible one.

To concentrate C_{60}, silica gel is added to activated carbon (ratio 2 to 1 by mass), the mobile phase is toluene, CCl_4, pyridine. As a result of the separation, the purity of C_{60} is only 95 % [36]. A similar technique in the chromatographic purification method is the use of a mixture of activated carbon/silica gel = 1:1, the mobile phase is a mixture of orthodichlorobenzene/toluene, using nitrogen under pressure [37]. The disadvantage of the method is the involvement of large volumes of sorbent and low productivity. The use of a polymer sorbent modified with aromatic functional groups for chromatographic separation of C_{60} (mobile phase - organic solvents) also has several disadvantages, including the low purity of the eluate obtained and low productivity, as well as the high cost of the

sorbent [38]. It should be noted that the use of other carbon materials in their primary, unmodified form does not lead to obtaining a product of sufficient purity [39]. There is a well-known separation method [40], according to which, at the first stage, a hot toluene solution containing 70 % C_{70} is removed from the Soxhlet apparatus and the second phase, which consists of 95 % C_{60}, is dissolved. Further, the solution is purified chromatographically on activated carbon. At the same time, according to [41–43], the solubility of C_{60} and C_{70} in hot toluene is the same. Accordingly [44, 45], a toluene solution with fullerites obtained by fractional crystallization from orthoxylene to a purity of 96 % on C_{60} was chromatographed through nitrogen-containing activated carbon. The purity of the obtained product was 99.6 %. The disadvantage of this separation is the high cost of the sorbent and the insufficient degree of its regeneration. In [45], to separate fullerene oxide, the mixture is heated to a temperature of 180–200 °C for 2–4 hours, however, long-term heating of fullerites above a temperature of 100–110 °C leads to a partial loss of the final product [41]. Another known approach is the separation of fullerenes by the formation of toluene-insoluble guest-host complexes with calixarenes [45]. The disadvantages of the method include the insufficient purity of the product (98 %), multistage, high cost of calixarene and the need for chromatographic purification.

The most effective methods of separation and purification of fullerenes are liquid chromatography and high-performance liquid chromatography on modified sorbents [46–49]. For surface modification of sorption materials, the most promising grafted groups are pyrenylpropyl and pentabromobenzyl [42], chain alkyl C18 and up to C30 [46], as well as benzene carbon compounds [47]. In [48], a number of sorbents modified by *n*-alkyl radicals C4, C8, and C18 were compared and the dependence of separation on the structure of the grafted radical was determined, namely, with the growth of the radical chain, the degree of separation of fullerenes increases. It is shown that increasing the degree of separation of fullerenes can also be achieved by lowering the temperature. But it should be noted that sorbents based on silicon dioxide modified by the Si-C bond are very expensive due to the difficulty of obtaining trialkylchlorosilane modifiers.

Therefore, taking into account the problems that can be solved with the help of high-purity fullerenes, studying the processes of their separation from mixtures with the help of sorbents is a relevant research. To achieve this goal, it is advisable to modify the surface of existing sorbents, while the modifier should be characterized by a long hydrocarbon chain radical. The purpose of this work is the development of sorbents based on cheap and available starting matrices - commercial activated carbon and silica gel with inexpensive and available chain carbon radicals - behentrimonium chloride ($C_{22}H_{45}N(CH_3)_3^+Cl^-$) or cetyl alcohol $C_{16}H_{33}OH$), which can be easily grafted to sorbent matrix and perform the role of a functional group in the separation of fullerenes in the column. Under conditions of application of hydrophobic solvents, this approach to modification is quite reliable.

EXPERIMENTAL

The synthesis was carried out according to the method of obtaining carbon cation exchanger, the prototype of which was the patent [49]. According to [49], the surface of BAU brand activated carbon (Ukraine) was oxidized with nitric acid in the presence of an inhibitor of oxidation completeness (urea). The coal was washed with an excess of sodium hydroxide solution and washed with water until the pH of the eluate was 7. As claimed by the patent the sorbent represents a sorption capacity for cations of up to 2 mmol/g. Porous structure of carbon cation exchanger was described as pore volume ~ 0.35 cm³/g, specific surface area 717 m²/g, pore size 5 nm). The obtained Na-form of the adsorbent was used for modification with chain radicals. To do this, the sorbent was heated with an excess of an aqueous solution of $C_{22}H_{45}N(CH_3)_3^+Cl^-$. The obtained product was washed with hot water on a filter from $C_{22}H_{45}N(CH_3)_3^+Cl^-$ and NaCl residues and dried at 100 °C. The sorbent was labeled as D 101.

Silica gel brand 60 (Ukraine, pore volume ~ 0.75 cm³/g, specific surface area 500 m²/g) was suspended in a solution of cetyl alcohol ($C_{16}H_{33}OH$) in 50 ml of tetrahydrofuran. Subsequently, tetrahydrofuran was distilled off in a rotary evaporator, and the solid residue was heated for 4–5 hours at 200 °C. The final product, labeled as D 102, was a yellow-red powder.

A sample of modified silica gel with grafted alkyl groups $C_{18}H_{37}$ SOL00718 "Solaris Chem" (Canada) (marking D 103) was used to compare the obtained sorbents.

To characterize the obtained adsorbents, an IR-Fourier spectrometer Spectrum BX-II (PerkinElmer, USA) was used in the wavelength range of 200–4000 cm⁻¹. The structural characteristics of the surface of adsorbents were determined from nitrogen adsorption-desorption isotherms using an automatic gas adsorption surface and porosity analyzer Quantachrome AS1Win (Quantachrome Instruments, USA). The specific surface area was estimated by BET isotherms, the total volume of micro- and mesopores was determined by the BJH method (Gregg, Sing 1982).

Differential thermal analysis was performed in the range of 20–600 °C with a scanning speed of 5 °C/min ("Derivatograph Q - 1500 D", Paulik-Paulik-Erday, Hungary).

The quantitative content of fullerenes in the toluene solution was analyzed by spectro-photometer using a Shimadzu-1240 UV-Vis according to the method [51]. The essence of this technique is as follows. The direct mixture calibration method cannot be used for this purpose, since the C_{60} and C_{70} spectra mostly overlap. Therefore, the spectrophotometric determination involves the construction of calibration graphs of separate C_{60} and C_{70} solutions, from which the molar extinction coefficients (ε) were determined. Pure fullerenes C_{60} and C_{70} (purity 99.9 % "Solaris Chem", Canada) were used for this purpose. Quantitative analysis of multicomponent systems is based on the additivity of optical density:

$$A = \Sigma_1 \varepsilon_i C_i b , \qquad (1)$$

where C_i is the concentration of the *i*-component, ε_i is the molar extinction coefficient of the mixture of components, b is the thickness of the absorbing layer, cm.

The amount of C_{60} and C_{70} in a solution of a mixture of fullerenes is determined by solving two linear equations:

$$A_1 = \varepsilon_1(C_{60}) \cdot (C_{60}) + \varepsilon_1(C_{70}) \cdot (C_{70}) , \qquad (2)$$

$$A_2 = \varepsilon_2(C_{60}) \cdot (C_{60}) + \varepsilon_2(C_{70}) \cdot (C_{70}) \qquad . \qquad (3)$$

Here, ε_1 and ε_2 are the extinction coefficients obtained from the calibration absorption curves of standard C_{60} and C_{70} solutions. The absorption value of A_1 and A_2 is determined experimentally for a solution of a mixture of fullerenes. Indices 1 and 2 refer to the values of two different wavelengths. UV-Vis spectra of the solutions were recorded in the range of 250–750 nm. According to [52], the wavelengths with the least interference were chosen for determination: 1–336 nm and II- 471 nm. Solutions with a known content of C_{60} and C_{70} fullerenes were used to construct the calibration curves. Standard solutions of C_{60} and C_{70} (1000 µg/ml) were obtained by dissolving fullerenes of 99.99 % purity in toluene. C_{60} or C_{70} solutions (5–80 µg/ml) were prepared by

diluting standard solutions. A standard solution of a mixture of C_{60} and C_{70} (15 µg/ml C_{60} and 5 µg/ml C_{70}) was prepared by appropriately mixing and diluting the standard solutions of C_{60} and C_{70}.

According to methodology [51], the peaks of 336, 382.6, and 471 nm were chosen as the main working wavelengths of fullerenes in toluene with the least interference. Although C_{70} shows strong absorption at the first two of these wavelengths, it also exhibits medium absorption at the last wavelength. On the other hand, C_{60} showed relatively strong absorption at 336.0 nm, medium absorption at 382.6 nm, and weak absorption at 471.0 nm. The concentration ranges in which C_{60} and C_{70} obey Beer–Lambert law is 0–80 mg/ml.

Table 1. Extinction coefficients ($mL \cdot cm^{-1} \mu g^{-1}$) of the toluene solutions of C_{60} and C_{70} for the specified wavelengths λ -336 and 471 nm and the concentration in the mixture determined from solving equations (*1*) and (*2*)

Fullerene	ε		Fullerenes concentration in mixture C_{60} and C_{70}, µg/ml
	$\lambda = 336$ nm	$\lambda = 471$ nm	
C_{60}	0.068201	0.0007494	14.935
C_{70}	0.034588	0.017984	5.231

Based on the above methodology, the content (*K*) of one of the fullerenes in relation to their total number was determined:

$$K = \frac{mC_{60}}{mC_{60} + mC_{70}} \cdot 100\% ,\qquad (4)$$

where mC_{60}, mC_{70} are the masses of the corresponding fullerenes.

For separation, a column filled with 28 g of adsorbent was used, the ratio of the column diameter (*d*) to the height of the sorbent layer (*h*) was 1:35 (the height of the sorbent layer was 36 cm, the diameter of the column was 1–1.2 cm). The column was saturated with a solution of a mixture of fullerenes with a ratio of $C_{60}/C_{70} = 65/35$: a sample volume of 4 ml with an initial concentration of 0.1 g/l. After some time, fullerenes were eluted with toluene, and the solutions were analyzed.

The separation was also investigated when the column parameters were changed. For this aim, the geometric dimensions of the column were varied: the diameter and height of the column at a sorbent mass of 28 g, the ratio diameter: height = 1:100 (the height of the sorbent layer is 70 cm, the diameter of the column is 0.7 cm). Sample volume 1 ml, concentration 2 g/l.

Fullerenes mixture of the YMFNANO® brand (Ukraine) obtained according to patented synthesis methods were used for the separation research [37, 38]. The quantification of quality was performed with standard solutions of C_{60} and C_{70} by liquid chromatograph technique with detection at 330 and 319 nm and was obtained content as: 65 % C_{60} and 25 % C_{70}.

RESULTS AND DISCUSSIONS

Fig. 1 shows UV-Vis spectra of toluene solutions that were used to separate C_{60} and C_{70} fullerenes, as well as their mixtures. The analysis of these spectra showed the presence of bands at 336 nm (Fig. 1 *a*) and 382 and 471 nm (Fig. 1 *b*), which are characteristic of fullerene C_{60} and its allotrope C_{70}, respectively.

The data given were used to found the extinction values of the calibration curves and determine the quantitative composition of the components in the mixture.

The presence of grafted groups of modifiers in sorbents was found based on infrared spectroscopy data (Fig. 2). Direct determination of surface modification and through which bond is quite a difficult task, because the IR spectrum signal is extinguished against the background of

signals associated with the sorbent and the modifier itself. Adsorbents thoroughly washed with toluene were used. The part of the modifier that was not removed by washing was considered as grafted according to the corresponding chemical bonds. Therefore, IR spectroscopy was used to identify the modifier based on the characteristic vibrations of the hydrocarbon modifier, and TG analysis was used to determine its content in the sorbent and the number of grafted groups. Spectra of unmodified SiO_2 are also given for comparison.
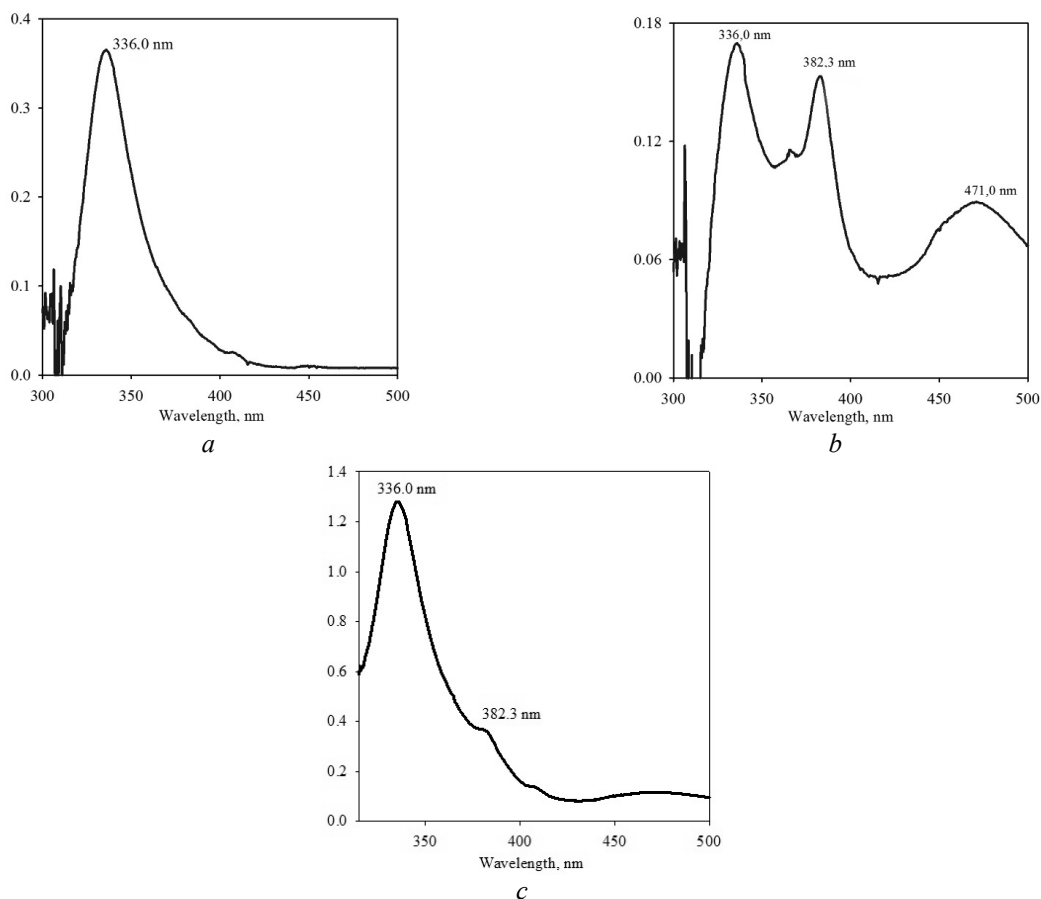
Fig. 1. UV-Vis spectra of fullerenes C_{60} (*a*), C_{70} (*b*), and their mixtures C_{60} (15 μg/mL) and C_{70} (5 μg/mL C_{70}) (*c*)
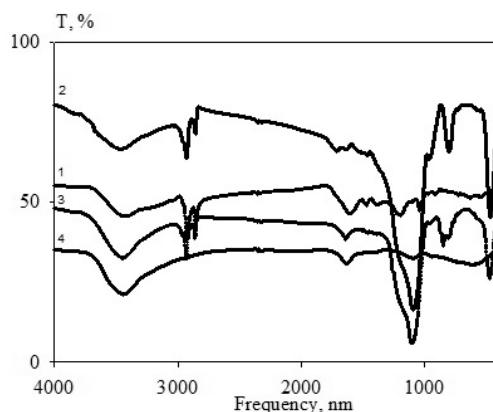
Fig. 2. Infrared spectra of modified sorbent: D 101(*1*), D 102(*2*), D 103(*3*), Silica gel brand 60 (*4*)

The main bands for identifying the hydrocarbon modifier on coal are asymmetric –

CH_2-, symmetric $-CH_3$ and $-CH_2-$ stretching vibrations at 2920 and 2849 cm^{-1} [55] and deformation C=O (1596 and 1466) [56] C-H (722, 636) [57] The situation is similar for SiO$_2$ modified with C16 (D 102): Asymmetric $-CH_2-$, symmetric $-CH_3$ and $-CH_2-$ stretching vibrations at 2923 and 2855 cm^{-1} [55, 58] and C=O stretching vibrations 1723 cm^{-1} [55]. For SiO$_2$ modified with C18 (D 103). Asymmetric $-CH_2-$, symmetric $-CH_3$, and $-CH_2-$ stretching vibrations at 2927 and 2857 cm^{-1} and deformation C=O 1471 cm^{-1} [55] can be found characteristic of Si-C 800 and 853 cm^{-1} [56]. Both for SiO$_2$ modified with C16 (D 102) and for C18 (D 103) there is a noticeable decrease in the vibrations of the –OH group at frequencies of 3460 cm^{-1}.

The interaction of silica gel with alcohols is well known [63]. Silanol groups lying on the outer surface, as well as siloxane groups, are mainly involved in the modification of silica gel. So, siloxane groups react with alcohols:

$$\equiv SiOSi \equiv + ROH \rightarrow \equiv SiOH + \equiv SiO-R. \qquad (5)$$

The interaction mechanism of behentrimonium chloride with carbon sorbent is probably ion exchange with carboxyl groups of carbon.

However, surface silanol groups are of primary importance in the modification of silica gel. They are more active and more easily enter into chemical reactions than siloxane ones, since the proton of the silanol group is weakly acidic and is capable to participate in exchange reactions [47]. This modification leads to obtaining sorbents with hydrophobic properties.

From the obtained data, it can be seen that the modification of commercial silica gel by C$_{18}$H$_{37}$ groups is carried out through the Si-C bond. In contrast to it, the proposed silica gel sample (D 102) is characterized by the presence of modification through the Si-O-C ether bond. This fact is reflected in the structural characteristics of the sorbents. The decrease in surface area and pore volume is most observed for silica gel modified with cetyl alcohol (D 102), indicating a higher amount of modifier. Despite this, both sorbents are characterized by a developed surface of 200–240 m^2/g and commensurate pores of 3.15–3.3 nm. In contrast to these sorbents, the carbon carrier modified by the C$_{22}$H$_{43}$N(CH$_3$)$_3^+$ cation has less developed surface and pore volume, but is characterized by the presence of mesopores (Table 2).
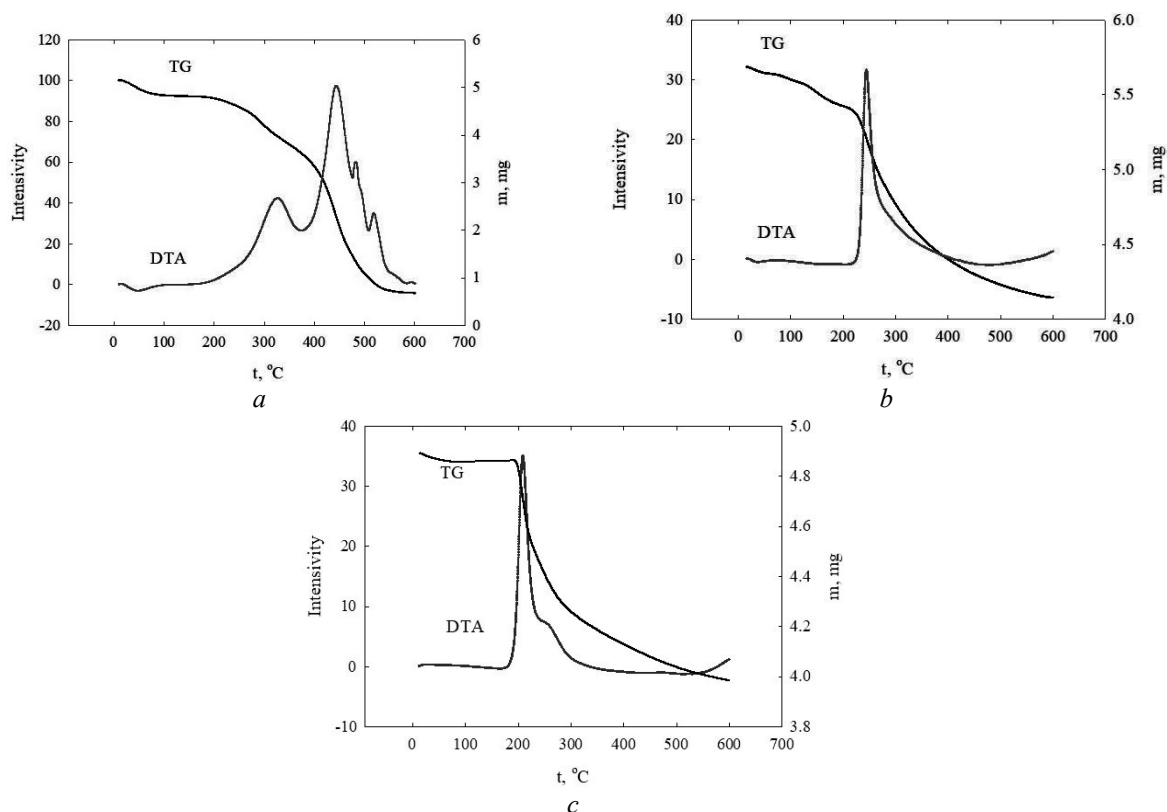
Table 2. Characteristics of sorbents: carbon modified with behenanthrimonium (D 101), silica gel modified with cetyl alcohol (D 102), and octadecylradical C$_{18}$H$_{37}$ (D 103), BAU activated carbon oxidized

Characteristics	D 101	D 102	D 103	BAU oxidized
Surface area, m^2/g	2.0	202.4	236.5	717
Pore volume, sm^3/g	0.018	0.32	0.39	0.35
Average pore radius, nm	17.2	3.15	3.3	5.0
Weight loss at every stage by	6.3	4.01	1.01	–
TG,%	22.68	23.57	17.50	
	57.76			

The number of grafted groups to the surface of the original matrix was estimated based on the thermogravimetric analysis data (Fig. 3). Silica gel-based sorbents are characterized by the presence of one pronounced exothermic peak at 209 °C (D 103) and 245 °C (D 102). Since the sorbents are essentially hydrophobic, losses at the first stage of heating correspond to the evaporation of adsorbed water and water molecules bound in polymers by hydrogen bonds and are insignificant. The main loss of sorbent mass (17.5 % for D 103 and 23.57 % for D 102)

obviously corresponds to the removal of grafted modifier groups.

For modified carbon cation exchanger, two exothermic peaks are observed at 330 and 450 °C. At the first stage, in the temperature range of 50–110 °C, hygroscopic and colloidal-bound moisture is released, which corresponds to a loss of 6 % of mass, further in the range of 300–330 °C the destruction of the C$_{22}$H$_{43}$N(CH$_3$)$_3^+$ cationic group occurs, and at the third stage decarboxylation and burning of the sorbent itself takes place.

Fig. 3. Thermograms of sorbent samples: *a* – carbon modified with behenanthrimonium (D 101), *b* – silica gel modified with cetyl alcohol (D 102), and *c* – with octadecylradical $C_{18}H_{37}$ (D 103)

The obtained information was used to estimate the number of grafted groups according to the following calculation:

$$n = \frac{\Delta m}{M}, \qquad (6)$$

$$m = \frac{\Delta m_s}{M_s}, \qquad (7)$$

where, Δm is the loss of modifier mass, M is the molar mass of the modifier, Δm_s is the loss of sorbent mass, M_s is the molar mass of the elementary unit of the sorbent.

For the commercial sample D 103 (Fig. 3 *b*), the relative value of n:m is about 1:19, which corresponds to 1 modifier group per 19 SiO_2 structural units. For silica gel modified with cetyl alcohol, this ratio is about 1:11 (Fig. 2 *a*), i.e., one modifier group corresponds to 11 SiO_2 molecules. The presence of a larger amount of modifier per unit of surface area is consistent with the data of the analysis of structural characteristics. For carbon cation exchanger D 101 modified with $C_{22}H_{43}N(CH_3)_3^+$ cation (Fig. 2 *a*), the calculation is more complicated, since it is difficult to consider the number of carboxyl and phenolic groups on the surface, as well as the oxygen of keto groups that do not participate in the process. If we assume that the amount of carboxyl and phenolic groups, to which the cation is grafted, are equal, then a rough estimate shows that one group of the modifier accounts for 61.45 C atoms.

All these sorbents were used to study the separation process of a mixture of C_{60}, C_{70} fullerenes in a column. The results are presented in Table 3.

As can be seen from the elution curves (Fig. 4), the retention time of the components of the mixture in the column is the same, and for samples D 101 and D 103, these indicators are proportional and amount to 180 minutes. Complete separation under the specified experimental conditions (column *d:h* = 1:35) is not achieved. For silica gel modified with D 102, the separation front has a blurred character, which is usually due to the resistance of the sorbent to the mass transfer of the separation components during elution. Apparently, this fact is caused by a larger number of modifier groups grafted to the sorbent matrix, in contrast to the sample modified

through the Si-C bond. In case of application for the separation of a commercial sorbent in a column with a diameter: height ratio of 1:35 (Fig. 5), the bulk is separated quickly when passing one column volume of toluene (BV). At the same time, for the proposed sample of silica gel modified with cetyl alcohol, quite high rates of separation of the mixture of C_{60} and C_{70} from solutions of low and high concentration are also observed when the parameters of the experiment are changed (Table 3). Thus, separation for C_{60} from a concentration of 0.1 g/l reaches 90.53 %, and from a concentration of 2 g/l it is 87.81 %. Due to the small surface area of carbon cation exchanger and mesoporosity, the cationic ion exchanger apparently does not show selectivity to larger fullerenes, unlike silica gels prone to microporosity, so such a matrix requires a different method of modification or changes in the separation parameters.

Table 3. Separation of fullerenes in solution at the outlet of the sorption column

Concentration of initial toluene solutions	Column *d:h* = 1:35		Column *d:h* = 1:100	
Fullerene content, %	C_{60}	C_{70}	C_{60}	C_{70}
D 101	48.52	51.48	87.81	12.19
D 102	90.52	9.48	87.26	12.74
D 103	93.72	6.28	67.45	32.55
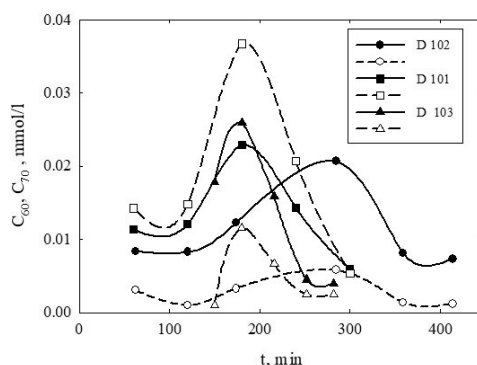
Fig. 4. Dependence of the concentration of the components of the mixture of C_{60} and C_{70} at the outlet of the column after elution with toluene on the duration of the separation (the ratio of the height of the sorbent layer to the diameter of the column is 1:35, the column is saturated with a solution of a mixture of fullerenes with a concentration of 0.1 g/L). Solid curves and dark dots correspond to C_{60}, and dashed curves and white dots to C_{70}. (■,□ – D101, ○,● – D102, Δ,▲ – D103)
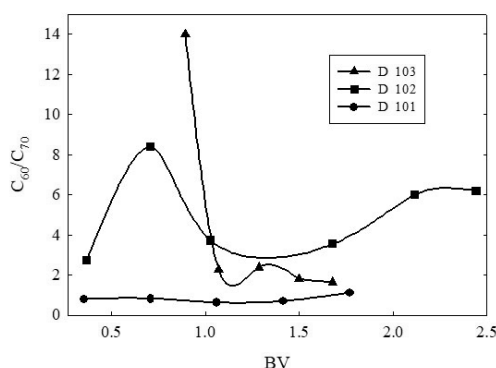
Fig. 5. Molar ratio of C_{60}/C_{70} mixture components in the eluate as a function of the number of column volumes (BV). Initial molar ratio of C_{60}/C_{70} = 2.6

CONCLUSIONS

The resulting sorbents show slightly lower separation values than commercially known ones, therefore, for sufficient purity of the final product, it is necessary to make a denser packing of the sorbent in the column, which approaches the conditions of a chromatographic column, and to use solvents with a lower eluent power. However, the advantage of the studied sorbents is their relative cheapness according to current market prices (estimated cost is 200–250 times lower). These sorbents can be manufactured using simpler methods that can be easily scaled. Modification of known commercial samples with alkyl radicals is carried out using a very expensive trialkylchlorosilane precursor. This reagent requires special manufacturing conditions (dry and highly pure solvents, multistage) and is toxic. The need for such measures is justified by the formation of the Si-C bond, which is hydrolytically very stable. The proposed sorbents are modified through an ionic bond (carbon) and Si-O-C bond (silica gel) and do not require expensive modifiers and special conditions for the process. They are less hydrolytically stable, but under the conditions of separation of fullerenes using dried non-aqueous solvents, this does not play a significant role. Apparently all ion exchange group of carbon sorbent are full with big cation of modifier result in decreasing total surface area. To improve characteristic of this type of sorbent it could be use another approach of modification. An alternative way to improve separation can be to use it as an adsorbent matrix for modifying oxide compounds of tetravalent elements [25–29].

Модифікований силікагель і катіоніт на основі активованого вугілля для розділення фуллеренів

В.А. Діамант, Л.М. Рожденственська, К.О. Куделко

Інститут загальної та неорганічної хімії ім. В.І. Вернадського Національної академії наук України
просп. Академіка Палладіна, 32/34, Київ, 03141, Україна, carbon.h.4@gmail.com

Фуллерени є цікавими об'єктами досліджень з огляду їхнього перспективного використання як нанорозмірної добавки до покриттів, плівок, адсорбентів, а також до активних компонентів в медицині, фармації, косметології. У цій роботі проведено модифікування комерційних адсорбентів - силікагелю та катіонообмінного сорбента на основі активованого вугілля доступними та недорогими лінійними вуглецевими радикалами. Як останні обрано бегентримоніум хлорид ($C_{22}H_{45}(CH_3)_3N^+Cl^-$) та цетиловий спирт ($C_{16}H_{33}OH$). Отримані адсорбенти порівнювали з комерційним зразком силікагелю, який модифіковано лінійним вуглеводневим радикалом $-C_{18}H_{37}$. Адсорбенти охарактеризовано методами ІЧ спектроскопії, термогравіметрії, основні характеристики пористої структури визначені методом низькотемпературної адсорбції-десорбції азоту. Модифікування адсорбентів на основі силікагелю призводить до зниження питомої площі поверхні до 202.4 та 236.5 $м^2/г$ та загального об'єму пор до 0.32 та 0.39 $см^3/г$, що практично в 2 рази менше вихідного матеріалу. Збільшення долі мікропор сприяє кращим показникам розділення великих молекул. Модифікування катіонообмінного сорбента на основі активованого вугілля великим за розміром катіоном призводить до суттєвого зниження питомої площі поверхні, а також збільшення розміру пор з переважним утворенням мезопор.

Показано, що модифікування силікагелю здійснюється як через силанольні, так і через силоксанові групи, на відміну від комерційного зразку силікагелю. Оцінено наближена кількість груп модифікатора на поверхні вихідної матриці SiO_2, яка складає 1 група модифікатора ~ на 11 молекул SiO_2.

Для вивчення поведінки адсорбції фуллеренів C_{60}, C_{70} та їхніх сумішей на адсорбентах були проведені експерименти в колонках зі змінними геометричними параметрами та вихідних концентрацій розчинів. Результати показали, що модифіковані силікагелі є адсорбентами для розділення суміші фуллеренів зі співвідношенням 65/35. Найкращу роздільну ефективність показав силікагель модифікований цетиловим спиртом $C_{16}H_{33}OH$. За допомогою адсорбента можливе розділення C_{60} – 90.52 % з менш концентрованого розчину та 87.26 % з більш концентрованого розчину. Для підвищення чистоти продукту необхідно пропускання розчину через сорбент 2–3 рази.

Конкурентна спроможність запропонованих модифікованих силікагелів, разом з економічною ефективністю, простотою модифікування, та можливістю розділення фуллеренів характеризують ці

адсорбенти як матеріали для практичного застосування. Зважаючи на значно меншу собівартість та простіші методики виготовлення, запропоновані адсорбенти можуть бути застосовані для розділення у промислових масштабах.

Ключові слова: *фуллерени, C_{60}, C_{70}, розділення, силікагель, активоване вугілля, бегентримоніум хлорид, цетиловий спирт*

REFERENCES

1. Hammond G., Kuck V. *Fullerenes: synthesis, properties, and chemistry of large carbon clusters*. (Washington: ACS, 1992).
2. Hirsch A. *The chemistry of the fullerenes*. (Germany: Wiley-VCH Verlag GmbH, 1994).
3. Acquah S., Penkova A., Markelov D., Semisalova A.S. The beautiful molecule: 30 years of C_{60} and its derivatives. *ECS J. Solid State Sci. Technol.* 2017. **6**(6): 3155.
4. Chaudhery M., Rüstem K. *Use of nanomaterials for environmental analysis in modern environmental analysis techniques for pollutants*. (Elsevier, 2020).
5. So-Ryong C., Ernest M., Mark R. Possible applications of fullerene nanomaterials in water treatment and reuse in nanotechnology applications for clean water. *Micro and Nano Technol.* 2009: 167.
6. Kamat P., Haria M., Hotchandani S. C_{60} cluster as an electron shuttle in a Ru(II)-polypyridyl sensitizer-based photochemical solar cell. *J. Phys. Chem. B.* 2004. **108**(17): 5166.
7. Mize S. *Nanotechnology opportunity report*. (London: CMP-Cientifica, 2002).
8. Ros T., Prato M. Medicinal chemistry with fullerenes and fullerene derivatives. *Chem. Commun.* 1999. **21**(8): 663.
9. Bottero J.-Y., Rose J., Wiesner M. Nanotechnologies: tools for sustainability in a new wave of water treatment processes. *Integr. Environ. Assess. Manage.* 2006. **2**(4): 391.
10. Kausar A. Potential of polymer/fullerene nanocomposites for anticorrosion applications in the biomedical field. *J. Compos. Sci.* 2022. **6**(12): 394.
11. Shan C., Yen H., Wu K., Lin Q., Zhou M. Functionalized fullerenes for highly efficient lithium ion storage: Structure-property-performance correlation with energy implications. *Nano Energy*. 2017. **40**: 327.
12. Sapurina I., Sapurina I., Mokeev M., Lavrentev V., Zgonnik V., Trchová M., Hlavatá D., Stejskal J. Polyaniline complex with fullerene C_{60}. *Eur. Polym. J.* 2000. **36**(11): 2321.
13. Saim S., Kuo K.C., Stalling D.L. Supercritical fluid extraction of fullerenes C_{60} and C_{70} from carbon soot. *Sep. Sci. Technol.* 1993. **28**(8): 1509.
14. Scrivens W.A., Bedworth P.V., Tour J.M. Purification of gram quantities of C_{60}. A new inexpensive and facile method. *J. Am. Chem. Soc.* 1992. **114**(20): 7914.
15. Nawrocki J., Rigney M., McCormick A., Carr P.W. Chemistry of zirconia and its use in chromatography. *J. Chromatogr. A.* 1993. **657**(2): 229.
16. Schafer W.A., Carr P.W. Chromatographic characterization of a phosphate-modified zirconia support for bio-chromatographic applications. *J. Chromatogr. A.* 1991. **587**(2): 149.
17. Wang L., Shi C., Pan L., Zhang X., Zou J. Rational design, synthesis, adsorption principles and applications of metal oxide adsorbents: a review. *Nanoscale*. 2020. **12**(8): 4790.
18. Da'na E. Adsorption of heavy metals on functionalized-mesoporous silica: A review. *Microporous Mesoporous Mater.* 2017. **247**: 145.
19. Cheng Y., Chuah G.K. The synthesis and applications of α-zirconium phosphate. *Chin. Chem. Lett.* 2020. **31**(2): 307.
20. Dzyazko Y.S., Rozhdestvenska L.M., Palchik A.V. Ion-exchange properties and mobility of Cu^{2+} ions in zirconium hydrophosphate ion exchangers. *Sep. Purif. Technol.* 2005. **45**(2): 141.
21. Dzyazko Yu.S., Rozhdestvenskaya L.M., Pal'chik A.V. Recovery of nickel ions from dilute solutions by electrodialysis combined with ion exchange. *Russ. J. Appl. Chem.* 2005. **75**(3): 414.
22. Maji S., Ghosh A., Gupta K., Ghosh A., Ghorai U., Santra A., Sasikumar P., Ghosh U.Ch. Efficiency evaluation of arsenic(III) adsorption of novel graphene oxide@iron-aluminium oxide composite for the contaminated water purification. *Sep. Purif. Technol.* 2018. **197**: 388.
23. Myronchuk V., Zmievskii Y., Dzyazko Y., Rozhdestveska L., Zakharov V., Bildyukevich A. Electrodialytic whey demineralization involving polymer-inorganic membranes, anion exchange resin and graphene-containing composite. *Acta Periodica Technologica*. 2019. **50**: 163.

24. Perlova O.V., Dzyazko Yu.S., Pal'chik A.V., Ivanova I.S., Perlova N.O., Danilov M.O., Rusetskii I.A., Kolbasov G.Ya., Dzyazko A.G. Composites based on zirconium dioxide and zirconium hydrophosphate containing graphene-like additions for removal of U(VI) compounds from water. *Appl. Nanosci.* 2020. **10**: 4591.

25. Perlova O.V., Dzyazko Yu.S., Pal'chik O.V., Martovyi I.S. Hydrated titanium dioxide modified with potassium cobalt hexacyanoferrate (II) for sorption of cationic and anionic complexes of uranium (VI). *Appl. Nanosci.* 2022. **12**(3): 651.

26. Rozhdestvenska L.M., Chaban M.O., Dzyazko Yu.S., Palchik O.V., Dzyazko O.G. Formation of lithium-selective sorbent in nanoreactors of the support based on titanium dioxide. *Appl. Nanosci.* 2022. **12**(4): 1112.

27. Chaban M.O., Rozhdestvenska. L.M., Palchyk O.V., Dzyazko Y.S., Dzyazko O.G. Structural characteristics and sorption properties of lithium-selective composite materials based on TiO_2 and MnO_2. *Appl. Nanosci.* 2019. **9**(5): 1037.

28. Dzyazko Y.S., Ponomareva L.N., Vol'fkovich Y.M., Sosenkin V.E., Belyakov V.N. Conducting properties of a gel ionite modified with zirconium hydrophosphate nanoparticles. *Russ. J. Electrochem.* 2013. **49**: 209.

29. Dzyazko Y.S., Ponomareva L.N., Volfkovich Y.M., Sosenkin V.E. Effect of the porous structure of polymer on the kinetics of Ni^{2+} exchange on hybrid inorganic-organic ionites. *Russ. J. Phys. Chem. A*. 2012. **86**(6): 913.

30. Maltseva T.V., Kolomiets E.O., Dzyazko Yu.S., Scherbakov S. Composite anion-exchangers modified with nanoparticles of hydrated oxides of multivalent metals. *Appl. Nanosci.* 2019. **9**(5): 997.

31. Dzyazko Y., Zakharov V., Kolomiiets Y., Kudelko K. Composite ion-exchanges for the recycling of liquid waste of dairy industry. *Ukr. Chem. J.* 2020. **86**(5): 38.

32. Bashir A., Ahad S., Malik L.A., Qureashi A., Manzoor T., Dar G.N., Pandith A.H. Revisiting the old and golden inorganic material, zirconium phosphate: synthesis, intercalation, surface functionalization, and metal ion uptake. *Ind. Eng. Chem. Res.* 2020. **59**(52): 22353.

33. Ambrożewicz D., Ciesielczyk F., Nowacka M., Karasiewicz J., Piasecki A., Maciejewski H., Jesionowski T. Fluoroalkylsilane versus Alkylsilane as hydrophobic agents for silica and silicates. *J. Nanomaterials.* 2013. **2013**: 631938.

34. Akhavan B., Jarvis K., Majewski P. Hydrophobic plasma polymer coated silica particles for petroleum hydrocarbon removal. *ACS Appl. Mater. Interfaces.* 2013. **5**(17): 8563.

35. Cashin V.B., Eldridge D.S., Yu A., Zhao D. Surface functionalization and manipulation of mesoporous silica adsorbents for improved removal of pollutants: a review. *Environ. Sci. Water Res. Technol.* 2018. **4**(2): 110.

36. Patent US 5310532 Tour J.M., Scrivens W.A., Bedworth P.V. Purification of fullerenes. 1994.

37. Patent US 5662876 Tour J.M., Scrivens W.A., Bedworth P.V. Purification of fullerenes. 1997.

38. Patent US 5904852 Tour J.M., Scrivens W.A., Rawlett A.M. Process for purifying fullerenes. 1999.

39. WO N 9204279 Boltstren N.N., Oychenko V.M., Oleynik S.V. Method of production of fullerene C_{60}. 1992. [in Russian].

40. RU N 2259942 Rasnetsov L.D., Shvartman Y.Yu., Karnatsevich V.L. Installation for removing fullerene soot. 2005. [in Russian].

41. Kui S., Yik C., Ka M., Wibowo C. Separation of fullerenes C_{60} and C_{70} using a crystallization-based process. *AIChE J.* 2010. **56**(7): 1801.

42. Mchedlov-Petrossyan N. Fullerenes in liquid media: an unsettling intrusion into the solution chemistry. *Chem. Rev.* 2013. **113**(7): 5149.

43. RU N 2224714 Boltstren N.N., Oychenko V.M., Oleynik S.V. Method for producing fullerene C_{60}. 2004. [in Russian].

44. Patent RU Patent 2327635 Boltstren N.N., Oychenko V.M., Oleynik S.V. Method for producing fullerene C_{60}. 2008. [in Russian].

45. Atwood J., Koutsantonist G., Rastont C. Purification of C_{60} and C_{70} by selective complexation with calixarenes, *Letters to Nature.* 1997. **368**: 229.

46. Yashin Y., Yashin A. High performance liquid chromatography. Status and prospects. *Ross. Chem. J.* 2003. **XLVII** (1): 64. [in Russian].

47. Krokhina O., Postnov V. Mineral-carbon sorbents for chromatographic separation of fullerenes. *Vestnik of St. PSU.* 2010. **4**(2): 79. [in Russian].

48. Ohta H., Jinno K., Saito Y., Fetzer J.C., Biggs W.R., Pesek J.J., Matyska M.T., Chen Y.-L. Effect of temperature on the mechanism of retention of fullerenes in liquid chromatography using various alkyl bonded stationary phases. *Chromatographia.* 1996. **42**: 56.

49. Patent RU 2105715C1 Trikhleb V.A., Trikhleb L.M. Method for producing carbon cation exchanger. 1998. [in Russian].

50. Cashin V., Eldridge D., Yu A., Zhao D. Surface functionalization and manipulation of mesoporous silica adsorbents for improved removal of pollutants: a review. *Environ. Sci.: Water Res. Technol.* 2018. **4**(2): 110.

51. Çiçek B., Kenar A., Nazir H. Simultaneous determination of c60 and C_{70} fullerenes by a spectrophotometric method. *Fullerene Sci. Technol.* 2001. **9**(1): 103.

52. Anikina N., Shchur D., Zaginaychenko S., Zolotarenko A., Milto K., Krivushchenko O. Determination of the ratio of fullerenes C_{60} and C_{70} by absorption spectroscopy. In: *Proceedings of IX International Conference "Hydrogen Material Science and Chemistry of Metal Hydrides"*, Ukraine, September 5–11, 2005: 857. [in Russian].

53. Patent UA 48455 Trefilov V.I., Shchur D.V., Zaginaychenko S.Yu., Duboviy A.G., Pishuk V.K., Tarasov B.P., Shulga Y.M., Rogozinsky A.A. Method for producing fullerenes from solutions in toluene. 2004. [in Ukrainian].

54. Patent UA 66463 Lytvynenko Yu.V. An apparatus for preparing fullerene nanostructural materials. 2004. [in Ukrainian].

55. Sadegh K., Javad F., Fatemeh M., Maryam F. Detection and quantification of food colorant adulteration in saffron sample using chemometric analysis of FT-IR spectra. *RSC Adv.* 2016. **6**: 23085.

56. Electronic Supplementary Material (ESI) for RSC Advances. *The Royal Society of Chemistry*. 2018.

57. Sun D.-H., Lu P., Zhang J.-L., Liu Y.-L., Ni J.-Z. Synthesis of the $Fe_3O_4@SiO_2@SiO_2$–Tb(PABA)3 luminomagnetic microspheres. *J. Nanosci. Nanotechnol.* 2011. **11**: 9774.

58. Musić S., Filipović-Vinceković N., Sekovanić L. Precipitation of amorphous SiO_2 particles and their properties. *Braz. J. Chem. Eng.* 2011. **28**(1): 89.

59. *Profiles of drug substances, excipients and related methodology*, 1st Edition Editor: Harry Brittain Hardcover. Academic Press, 2012. **37**: 464.

60. Tran T., Anh-Pham T., Phung M., Thoa-Nguyen T., Tran V. Synthesis of amorphous silica and sulfonic acid functionalized silica used as reinforced phase for polymer electrolyte membrane. *Adv. Nat. Sci.: Nanosci. Nanotechnol.* 2013. **4**(4): 045007.

61. Okuno M., Zotov N., Schmücker, M., Schneider H. Structure of SiO_2–Al_2O_3 glasses: Combined X-ray diffraction, IR and Raman studies. *J. Non-Cryst. Solids.* 2005. **351**(12–13): 1032.

62. Jesionowski T., Krysztafkiewicz A. Preparation of the hydrophilic/hydrophobic silica particles. *Colloids Surf., A*. 2002. **207**: 49.