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SORPTION AND LIQUID CHROMATOGRAPHIC SEPARATION OF LIGHT FULLERENES C_{60} AND C_{70} WITH MULTIWALL CARBON NANOTUBES

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Isotherms for the sorption of light fullerenes (C_{60} and C_{70}) from toluene solutions with the use of multiwall carbon nanotubes (MWCNTs) were investigated. Both isotherms are of the Langmuir-type. The successful liquid chromatographic separation of light fullerenes from toluene solutions was accomplished using the above-mentioned sorbent.

Keywords: light fullerenes, C_{60}, C_{70}, isotherms of sorption, toluene solutions, chromatographic separation.

1. Introduction

One of the main (if not unique) methods of industrial fullerenes separation and purification is now the method of liquid chromatography. In this method, one typically uses an aromatic solvent — mobile phase, where the solubility of the fullerenes is relatively high [1–4] (e.g. benzene, toluene, chlorbenzene, m-, p-, or often o-xylene or o-dichlorbenzene, etc), however, some non-aromatic solvents e.g. CS_2, CCl_4, etc. can be used as well. Sometimes, the addition of a non-aromatic solvent with comparatively low fullerenes solubility (e.g. n-hexane, n-octane, 1-hexanol, acetonitrile, etc.) [1–5] to an aromatic solvent is also done to increase the efficiency of the separation. As a stationary phase — one can use different sorbents with relatively high affinity for the fullerenes (e.g. different activated carbons, modified (carbonized silicates, silochroms, aerosols, etc) [5–8]. Literature searches yielded no information about the use of single-wall or multiwall carbon nanotubes (MWCNTs) for the chromatographic separation of the light fullerenes, C_{60} and C_{70} as the main components of standard fullerenes mixture, produced by the most popular current method — electric arc erosion of carbon rods in a He atmosphere. Meanwhile, such a stationary phase seems to be reasonable enough, because carbon nanotubes:

— are absolutely inert and insoluble in any nondestructive solutions used for fullerenes separation,

— have considerable specific surface (m^2/gram),

— have high affinity for fullerenes (the main structural motif of carbon nanotubes and fullerenes is the same — carbon hexagons without any functional groups; carbon pentagons also are present in fullerenes and in the ends of carbon nanotubes),

— are relatively accessible, if we use MWCNTs, which are considerably cheaper than single wall ones and are produced in mass quantities.

So, the aim of preset work is:

— to investigate the isotherms for the sorption of light fullerenes (C_{60} and C_{70}) from toluene solutions with the use of MWCNTs,

— to execute liquid chromatographic separation of light fullerenes with the use of the above-mentioned MWCNTs, produced by Bayer corporation (Germany).

2. Materials

1. MWCNTs used in this study were produced by Bayer corporation (Germany). Their physical properties are as follows: external diameter 50–60 nm, internal diameter 5–15 nm, specific surface area 125±35 m^2/g (BET – theory), bulk density $\rho^b = 0.15 \pm 0.02$ g/cm^3, length 10–20 μm, temperature of phase transition 3652–3697 °C. Typical electronic photo of MWCNTs, produced by Bayer corporation (Germany) is represented in Fig. 1.

2. C_{60} and C_{70}fullerenes were produced by the "ILIP" corporation (Saint Petersburg) [6–8] with purities of 99.9 and 99.5 mass%, respectively. Liquid — phase chromatograms of these products are shown in Fig. 2 and 3. The condition of UHPLC-analysis hereinafter were the following: chromatograph – Shimadzu LC-20 Prominence, solvent – toluene, detector – light absorption at wavelength $\lambda = 335$ nm, column Agilent HC-C18(2).

3. The C_{70}-enriched fullerene mixture $C_{60} + C_{70}$ utilized in these separation studies was also produced by "ILIP" corporation [7–9]. This mixture had the following average composition: 90±3 mass% C_{70}, 10±3 mass% C_{60}, high fullerenes $C_{n>70} \leqslant 0.3$ mass%. The fullerene mixture, enriched by the C_{60} fullerene was not investigated, because one can produce the pure individual light fullerene C_{60}, using the cheaper and more traditional sorbent with high exploitation characteristics, e.g. active carbon Norrit Azo [7, 8]. A typical liquid — phase chromatogram of such fullerene mixture is also represented in Fig. 4.

4. Toluene ("pure for analysis", Rus. State Standard GOST — 5789-78) (boiling temperature (1 atm) $T^b = 110.6$ °C, refractive index $n_D^{20} = 1.4969$ rel.un.).

FIG. 1. Typical electronic photo of carbon multiwall nanotubes, produced by Bayer corporation (Germany) (* 10^5)

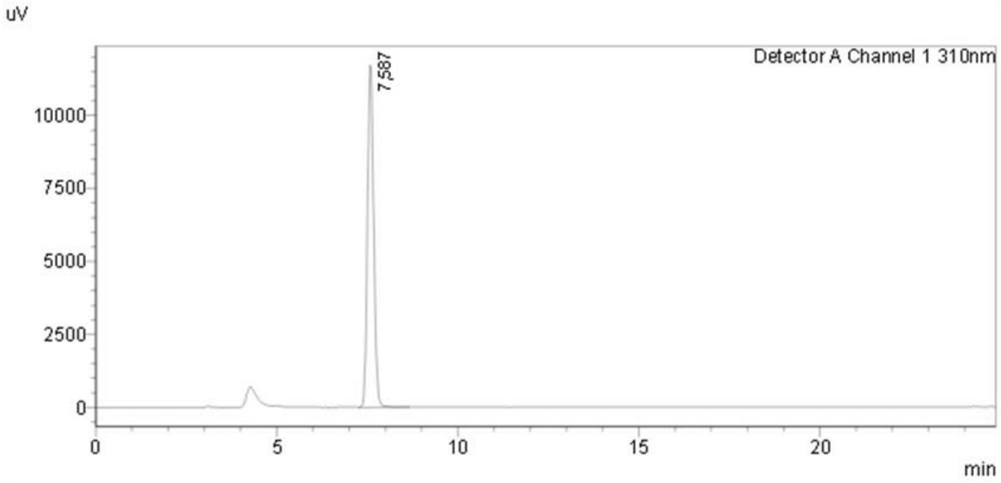

FIG. 2. Liquid — phase chromatograms of C_{60}

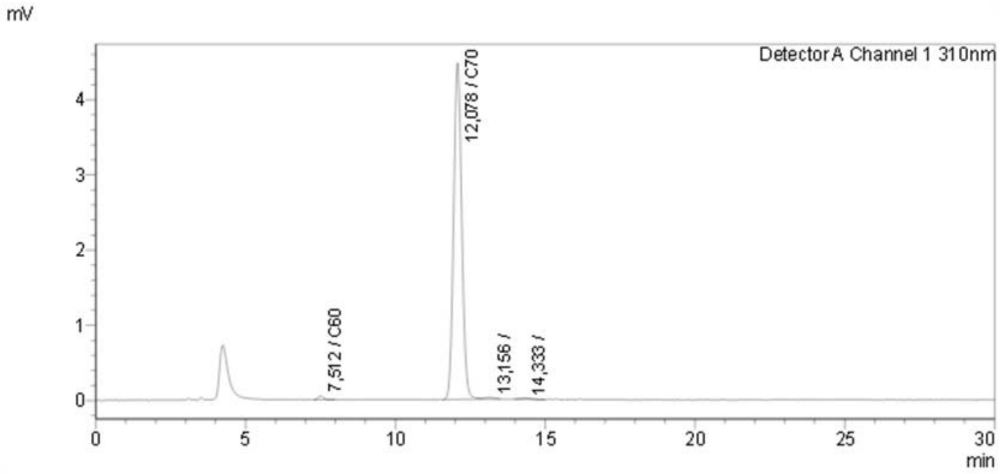

FIG. 3. Liquid — phase chromatograms of C_{70}

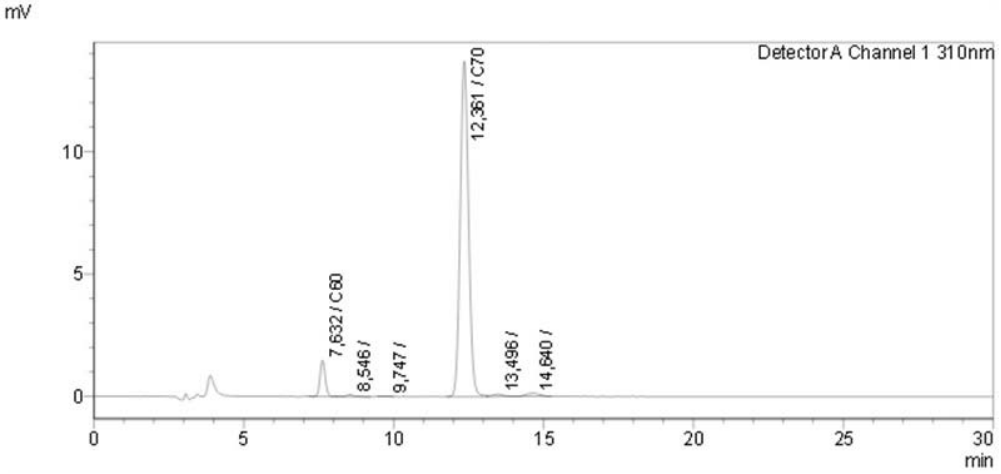

FIG. 4. Liquid — phase chromatograms of mixture $C_{60} + C_{70}$

3. Isotherms of sorption of light fullerenes

Experiment and discussion

The investigation of the isotherms for the sorption of individual light fullerenes — C_{60} and C_{70} separately, on Bayer MWCNTs, in toluene solutions was done using the static method. In preliminary experiments, it was established that 2–3 hours was long enough to realize sorption equilibrium — i.e. after this time, the concentration of fullerenes in the liquid solution ceased to change. So, the duration of the experiment was chosen as 4 h. The experiment was done at $25.0 \pm 0.1\,^{\circ}$C in a shaker-thermostat by the method of constant volumes. A determined mass of the sorbent was added to an aliquot of the fullerene-toluene solution with a determined concentration (20 ml), and after shaking for 4 h with an equal mass of the sorbent (0.15 g), the concentration of fullerenes in liquid solution was determined. According to the changes of fullerenes concentrations in liquid solution the concentrations of the remaining fullerenes in the sorbent were calculated. In this manner, the sorbent capacity was determined.

To measure the fullerenes concentration, we used light absorption in the near-UV and visual spectral region. These measurements were done using a UV–1800 spectrophotometer (Shimadzu), quartz cuvette (l = 1 cm), toluene as a solvent, spectral range ($\lambda = 250 - -750$ nm). To calculate the concentration of C_{60} and C_{70}, we hereafter use the following system of equations, which are the decision of Burger-Lambert-Beer equations in the maxima of light absorption wavelengths for C_{60} and C_{70} — 335.7 and 472.0 nm, respectively:

$$C(C_{60}) = 13.10(D_{335.7} - 1.8051 D_{472.0})$$

$$C(C_{70}) = 42.51(D_{472.0} - 0.00810 D_{335.7})$$

Where: $C(C_{60})$, $C(C_{70})$ concentration of fullerenes C_{60} and C_{70} in mg/l, $D_{335.7}$, $D_{472.0}$ — optical density at l = 1 cm and λ = 335.7 nm and 472.0 mn, correspondingly [1–4]. Typical electronic spectrum of C_{60} and C_{70} are represented in Fig. 5.

Data obtained for the investigation of sorption isotherms in the C_{60} fullerene — Bayer MWCNTs — toluene and the C_{70} fullerene — Bayer MWCNTs — toluene systems are represented in Table 1 and in Fig. 6 and 7. Both isotherms are of the Langmuir-type. The graphics of the isotherms in Langmuir coordinates are also shown in Fig. 8 and 9.

One can see, that the static capacities of the sorbent for both light fullerenes are very similar and rather high — $C^s_{\max} \approx 21$ and 18 mg of C_{60} and C_{70} fullerenes per gram of sorbent, respectively. As a comparison, the capacity of traditional sorbent for C_{60} and C_{70} separation, carbon Norrit Azo, has capacities of $C^s_{\max} \approx 14$ and 8 mg of C_{60} and C_{70} fullerenes per gram of sorbent, respectively.

4. Liquid chromatographic separation of light fullerenes

Experiment and discussion

As a typical example, the chromatographic separation of light fullerenes from toluene solutions was done with Bayer MWCNTs as the sorbent. The column volume was ≈ 28 ml, height ≈ 56.5 cm (so, we used “thick” preparative column). The composition of the initial fullerene solution was as follows: $C_{60} \approx 1450$ mg/l, $C_{70} \approx 178$ mg/l ($C_{60} \approx 11$ mass%, $C_{70} \approx 89$ mass%), the volume of fullerene toluene solution was ≈ 33 ml. The mass of the sorbent was $m \approx 4.254$ g. So, we used dynamical capacity of the sorbent $C^s_{dyn.} \approx 12.6$ mg of total light fullerenes per gram of sorbent or approximately 2/3 of its average static capacity. The results of the separation are represented in Fig. 10.

One can see the following:

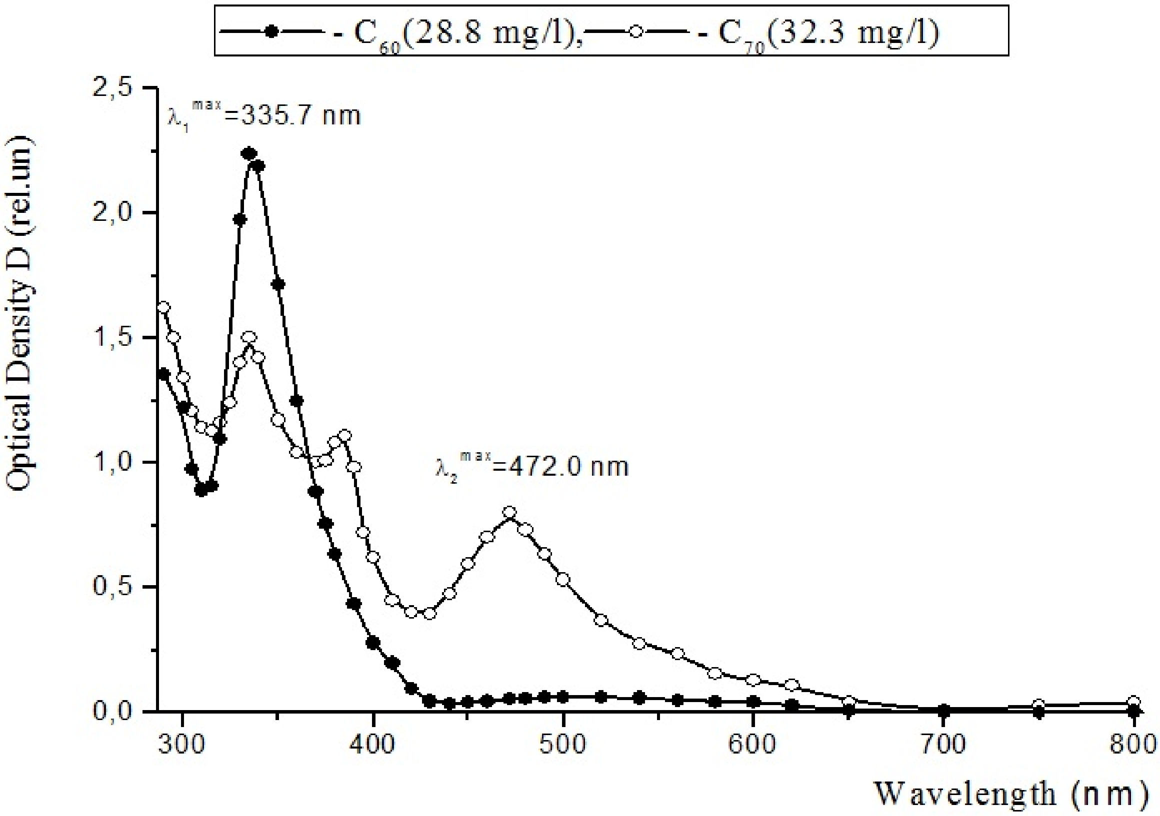

FIG. 5. Electronic spectrum of C_{60} and C_{70}

TABLE 1. Sorption isotherms for the C_{60} fullerene – Bayer MWCNTs – toluene and the C_{70} fullerene – Bayer MWCNTs – toluene systems at 25 °C

System	Concentration in liquid phase $C^l(g/l)$	Concentration in solid phase $C^s(mg/g\ sorbent)$	Degree of sorbent filling $\theta = C^s/C^s_{\max}$ (rel.un.)
C_{60} fullerene – Bayer MWCNTs – toluene	0.00	0.0	0.00
-“-	0.12	10.7	0.52
-“-	0.26	18.7	0.91
-“-	0.47	20.0	0.97
-“-	0,65	20.4	0.99
C_{70} fullerene C_{70} – Bayer MWCNTs – toluene	0.00	0.0	0.00
-“-	0.13	9.3	0.51
-“-	0.30	13.3	0.73
-“-	0.48	16.0	0.88
-“-	0.67	17.3	0.95
-“-	0.86	18.0	0.99

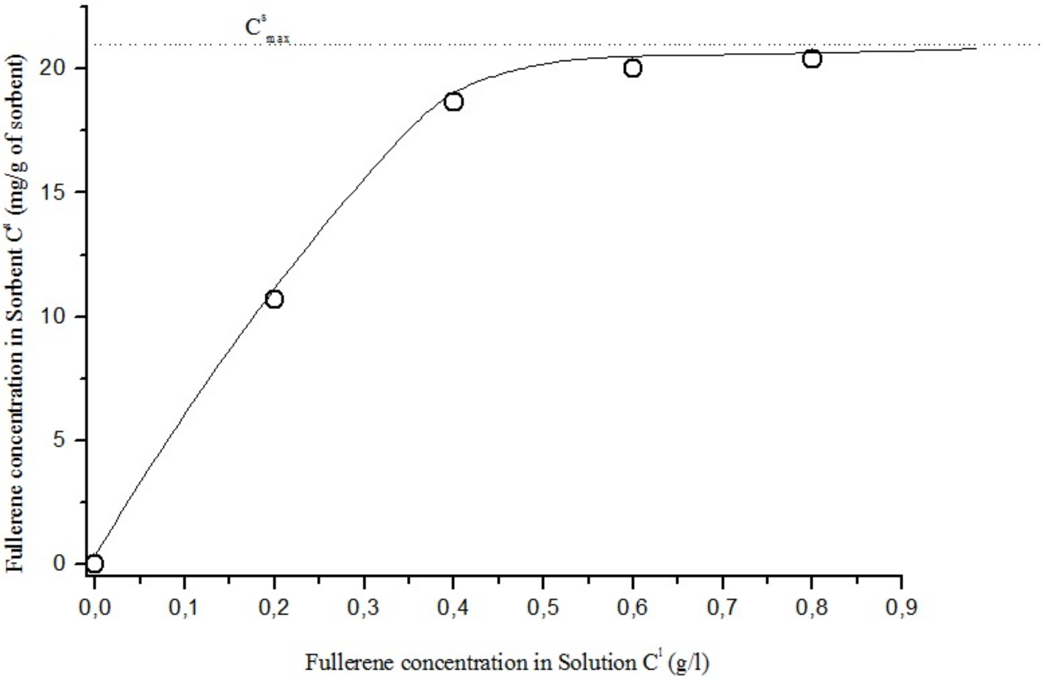

FIG. 6. Sorption isotherms in the C_{60} fullerene – Bayer MWCNTs – toluene system in normal coordinates

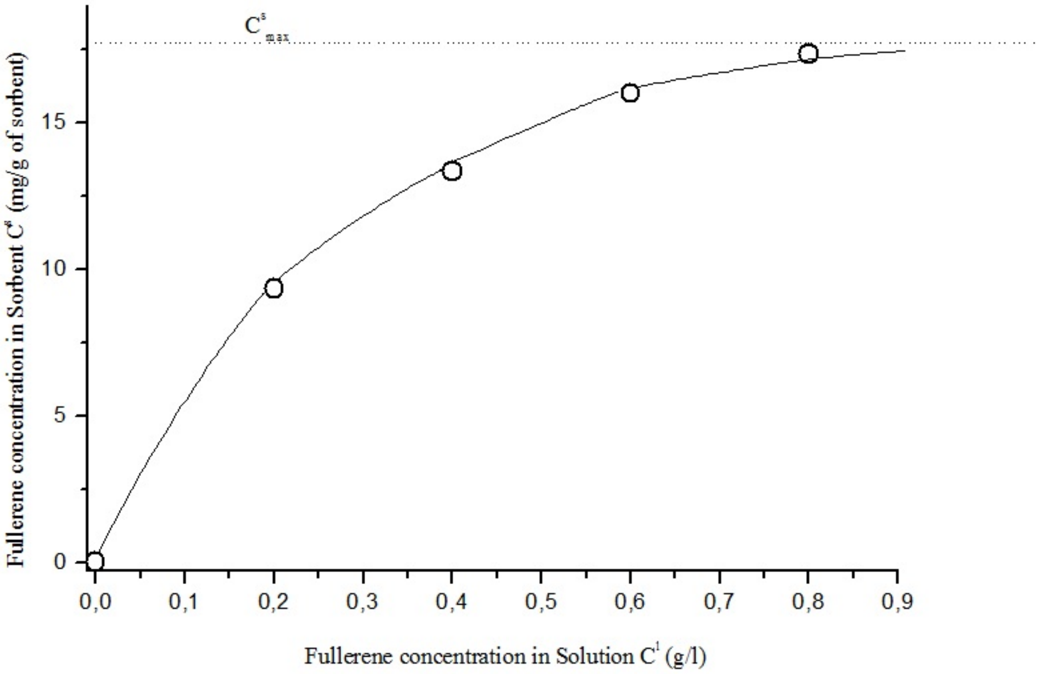

FIG. 7. Sorption isotherms in the C_{70} fullerene – Bayer MWCNTs – toluene system in normal coordinates

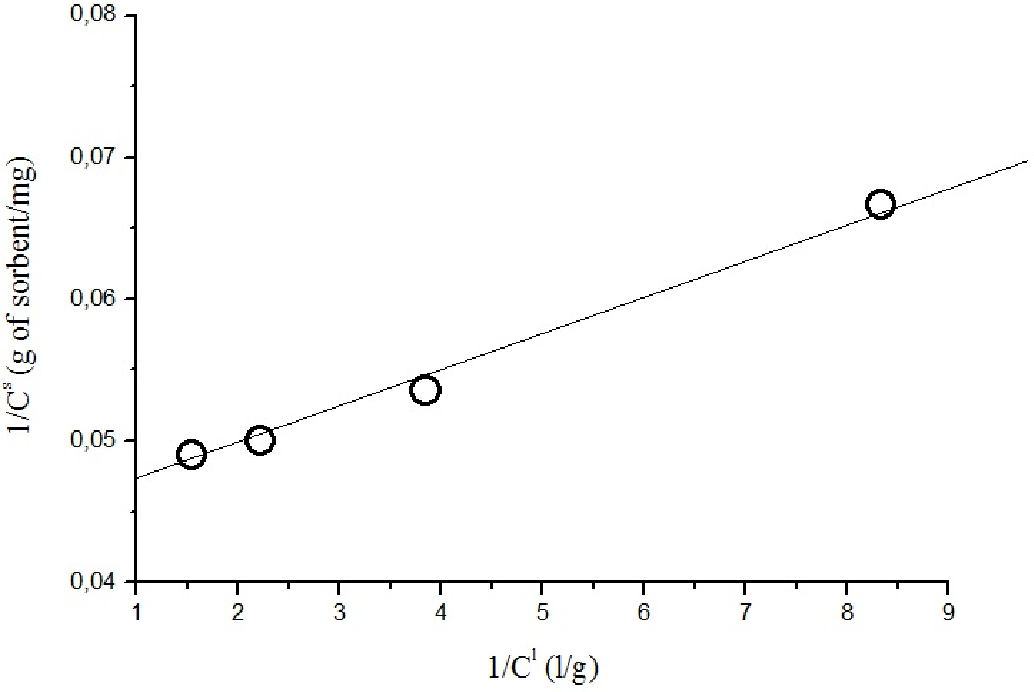

Fig. 8. Sorption isotherms in the C_{60} fullerene – Bayer MWCNTs – toluene system in Langmuir coordinates

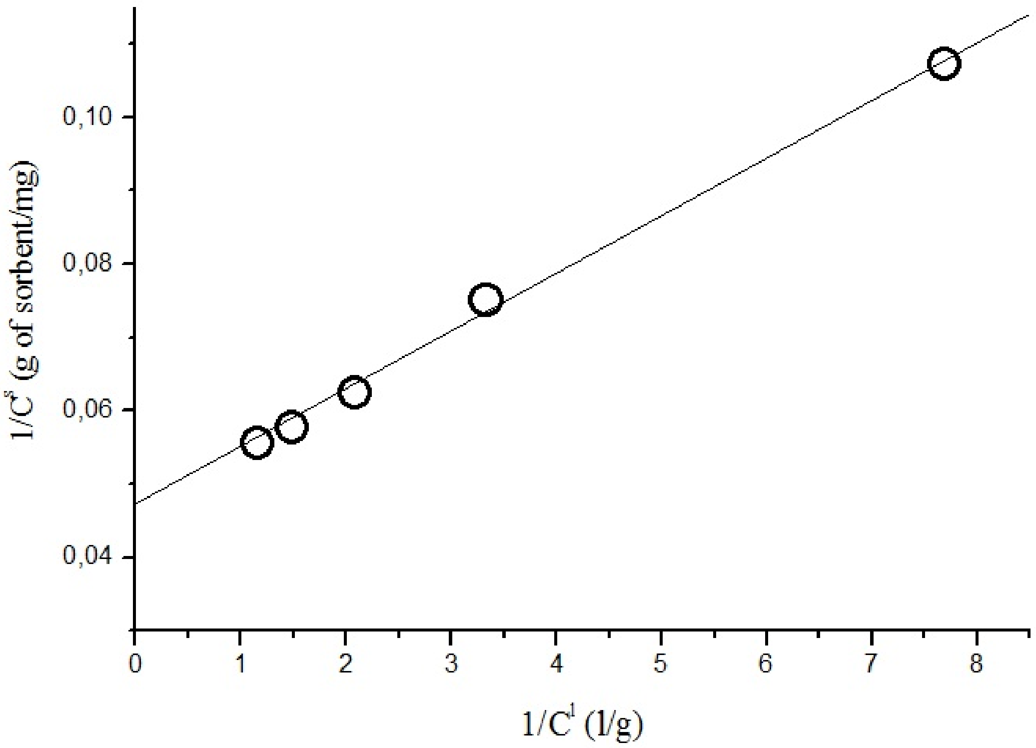

Fig. 9. Sorption isotherms in the C_{70} fullerene – Bayer MWCNTs – toluene system in Langmuir coordinates

- We produced more than 85 mass% of C_{70} fullerene (in relation to the entered C_{70} — dotted line in Fig. 10, nearly 3 column volumes),

- Thus, the average concentration of produced C_{70} ($3 \rightarrow 8$ column volumes) was more than 99 mass%,

- The losses of both fullerenes C_{60} and C_{70} were negligible (< 3 mass%).

So, the chromatographic separation was thus deemed successful.

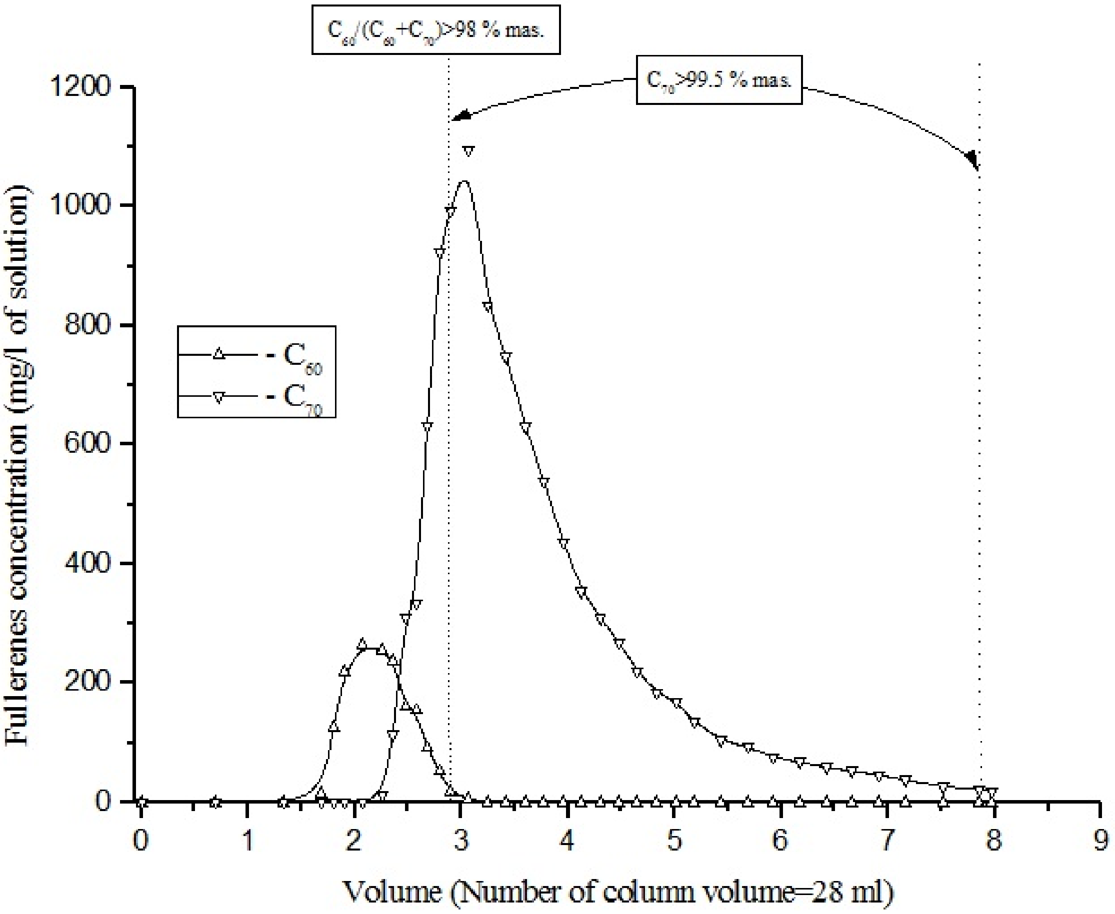

FIG. 10. Chromatographic separation of light fullerenes C_{60} and C_{70} with the help of the sorbent Bayer Multiwall Carbon Nanotubes from toluene solutions

A similar experiment was performed using mixed sorbent Bayer MWCNTs/granules of fluorine plastic (IV) in equal volume (1/1 v/v). We used a “thick” laboratory little column and a dynamical capacity of the mixed sorbent $C^{s}_{dyn.} \approx 12.6$ mg of total light fullerenes per gram of Bayer MWCNTs without taking into account the fluorine plastic (which was used to allow free flow of the solution through the sorbent in the column, and simultaneously, for the consolidation of the sorbent). The initial mixed fullerene solution was the same. The results of the separation are also represented in Fig. 11. In this case, chromatographic separation was also successful and very close to the above-mentioned results, however this separation was realized more quickly ($4 \rightarrow 6.5$ column volumes) and the concentration of the separated fullerenes were lower.

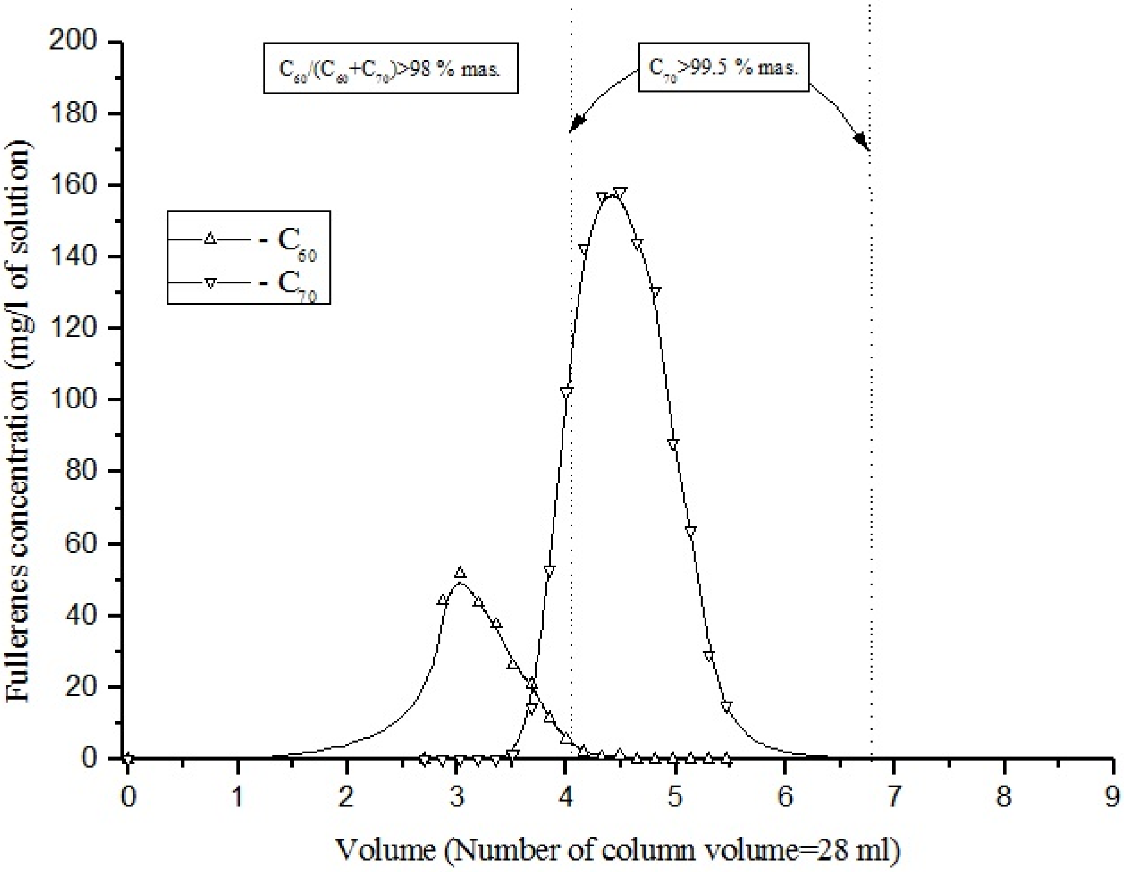

FIG. 11. Chromatographic separation of light fullerenes C_{60} and C_{70} with the help of the mixed sorbent Bayer MWCNTs/granules of fluorine plastic from toluene solutions

5. Conclusions

Isotherms for the sorption of light fullerenes (C_{60} and C_{70}) from toluene solutions with the use of MWCNTs were investigated. Both isotherms were of the Langmuir-type. The static capacities of the sorbent, for both light fullerenes, are very similar and rather high. Successful liquid chromatographic separation of light fullerenes has been achieved using the above-mentioned sorbent from toluene solutions. The results showed that Bayer MWCNTs are a reasonable and effective material for the separation and purification of light fullerenes.

Acknowledgements

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