

Adsorption Capacity of Foils Prepared From Water Suspension of Graphene Oxide and Graphene Oxide/Fullerene C₆₀ in Respect to Radioactive Uranyl Nitrate.



Public Health

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ABSTRACT

Hybrid products were prepared by oxidation of graphene and joint oxidation of graphene and fullerene C₆₀ in various weight ratios, which allowed preparation of foils of diverse morphologies. The prepared initial matrices can be used for further treatment, such as fluorination, bromination, embedding of metals with catalyst effects, preparation of composite materials in combination with other polymers or nano fibers, or in form of lamellar fibers by freeze drying. They can be widely used as adsorbing/absorbing materials with new physicochemical properties (electric, optical etc.)

A pilot experiment performed in this work has proved adsorption capacity of the prepared foils in respect to radioactive uranyl nitrate by means of a liquid scintillation spectrometer HIDEX 300 SL which measured total alpha and beta activity of filtrate and spare solution of uranyl nitrate. Adsorption capacity of the foils depended not only on the weight ratio of graphene oxide and fullerene C₆₀ but also on the method of preparation of the foils and on their morphology.

I. Introduction

In our previously published works [1, 2] we described a method of oxidation of fullerene C₆₀, graphite and a mixture of graphite and fullerene C₆₀. Identification of the prepared compounds focused on their functional groups, structure and thermal stability using FT IR, DSC, TGA, XRD methods and mass spectroscopy. The resulting products, with the exception of fullerene alone, were transformed into foils (membranes). Quality of the foils prepared from our products was influenced by the method of filtration and drying. Fast drying at 50-60°C caused point-like cracking of the foil due to swift evaporation of adsorbed water. Another factor is treatment of the initial suspension (sonification, centrifugation). Foils of the best quality were obtained after the suspension was repeatedly (min. 5 times) centrifuged at 2500 rev./min. every time for 10 minutes and subsequently dried on a silicon foil which was evaluated as a highly suitable base to slip off foils up to ca. 50 µm thick.

The work [3] also mentioned the possibility to influence foil thickness by composition of the filtered suspension, concentration and filtration rate. If the suspension is exposed to sonification the result is influenced by its duration, temperature and output power of the device [4]. Properties of the foils can be affected by some specific treatments, such as washing of the foils with solutions of MCl₂ (Ca, Ba, Mg) when carbon layers connect in a plane and across with di-aldehyde [5]. Further, the foils may be also impregnated e.g. with Ti, Ag, Cu₂O [6] or the space between the layers may be expanded [7] etc.

Graphene, graphene-oxide (hereinafter GO) and GO with a composite, e.g. with Fe₃O₄ [8], are used as adsorbents for separation of heavy metals (Hg, Cd, Cu, Cr, As), organic matters, tetracycline antibiotics, waste colorants, aniline, methyl orange, naphthalene, 1-naphthol, fluorides, halogen derivatives, etc. [8, 9, 10, 11].

GO can be used as a molecular sieve for selective separation of hydrogen, CH₄, SF₆, He etc. [12, 13], as well as an ion sieve for desalination of sea water or filtration in biomedicine [14]. GO selectively intercalates methanol between its layers from the mixture H₂O/CH₃OH [15]. There is also a promising application for GO because it significantly reduces content of toxic and radioactive substances in contaminated water in acidic environment, specifically Am^{III+}, Th^{IV+}, Pu^{IV+}, Np^{V+}, U^{VI+}, Sr^{III+}, Eu^{III+} and Tc^{VI+}. In comparison with bentonites and active carbon, the adsorption capacity of GO is 15 times higher [16].

Mutual adsorption (biofunctionalization) between graphene, GO and biomolecules, e.g. DNA, enzymes and proteins, is very important and it can be used in biomedicine [17, 18]. At the same time, this property can influence toxicity of graphene and GO because adsorption on a biomolecule is one of the key factors affecting cytotoxicity. This is directly associated with biodistribution, biodislocation and accumulation of GO in organs which, on the other hand, may be used for efficient transport and medications and gene-derivatives [19].

This contribution focuses on demonstration of adsorption capacity of the prepared foils in respect to radioactive uranyl nitrate.

II. Experimental part

1. Preparation and characterization of foils

Graphite: PM – very fine crystalline powder graphite, mesh 0.025mm, Supplier: Koh-I-Noor Netolice, Czech Republic

Fullerene C₆₀: 99.5% purity, SES Research, Houston USA

Sulfuric acid, nitric acid, potassium permanganate, hydrogen peroxide: Supplier: Sigma –Aldrich

Detailed methods used for oxidation of fullerene C₆₀, graphite

and a mixture of graphite-fullerene C_{60} , formation of water suspension and preparation of foils were described in our previous publications [1, 2]. The weight ratios and representation of the individual components used for oxidation are provided in Table 1.

Tab. 1 Weight representation of the individual components used for oxidation

Ratio /weight (g)		NaNO ₃ (g)	KMnO ₄ (g)	H ₂ SO ₄ (ml)	Product No.
Graphite	C ₆₀				
-	1/(0,7)	1	2	18	I. C ₆₀ -C ₆₀
1/(1,5)	-	2	4,5	31	II. GO
1/(1,1)	1/(1,1)	3	7	52	III. GO-C ₆₀
2/(1,5)	1/(0,7)	3	7	52	IV. GO-C ₆₀
3/(1,75)	1/(0,55)	3	7	52	V. GO-C ₆₀

Identification of the prepared compounds focused on their functional groups, structure and thermal stability using FT IR, DSC, TGA, XRD methods and mass spectroscopy. The results were described in detail in the mentioned publications [1, 2]. The tests of adsorption capacity were performed on foils prepared from products No. III -V as indicated in Table 1. Microscopic images show the fine morphology of selected foils – see Fig. 1

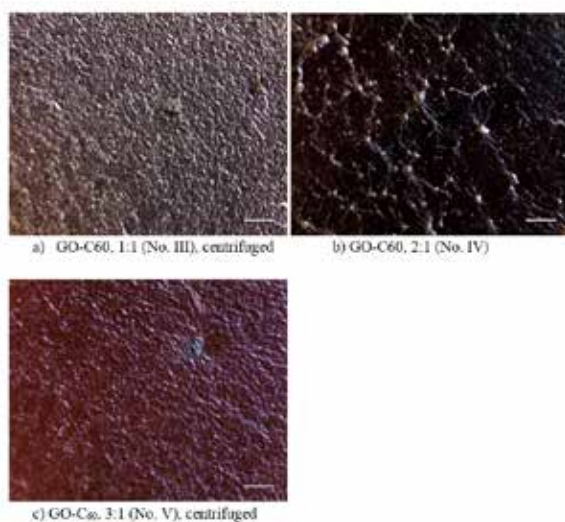


Fig 1. Morphology of selected foils (50x magnification, the line = 1mm, view of the front side of the foil, naturally dispersed light)

Structure of the prepared foils was investigated in our previous work [1, 2] with scanning electron microscopy. The mentioned method showed fine and partly deformed lamellar structure – see Fig 2.

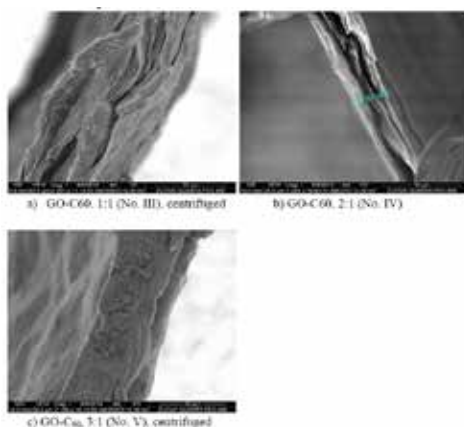


Figure 2 SEM image of foil sections made of the products No. III -V

Specific weights of selected foils:

GO-C₆₀ (No III.): $\rho = 0.1436 \text{ g/cm}^3$

GO-C₆₀ (No IV.) $\rho = 0.228 \text{ g/cm}^3$

GO-C₆₀ (No V.) $\rho = 0.810 \text{ g/cm}^3$

2. Tests of adsorption capacity of GO-C₆₀ foils

Uranyl nitrate - liquid activity etalon of natural uranium, type ERX, supplied by Eurostandard CZ, s.r.o.

Liquid scintillation spectrometry was performed with Hidex 300 SL (made by Hidex Oy, Mustionkatu 2, FIN-20750 Turku, Finland). This liquid scintillation spectrometer uses the TDCR method (Triple to Double Coincidence Ratio) to determine activity of the samples. The device allows determination of absolute activity of the sample with a LSC method (Liquid Scintillation Counting). In comparison with other LSC devices the TDCR method enables to determine quench correction in the sample without necessity of an external standard. The device is controlled from a connected PC with MikroWin 2000 software.

Foils with diverse ratios GO-C₆₀ (products No. III -V indicated in Table 1) were used for testing of adsorption capacities. Sorption efficiency was determined with a radio carrier and it was expressed as a mass distribution coefficient Dg .

$$Dg = \frac{A_s}{A_f} \times \frac{V}{m} \text{ [mL/g]},$$

where Dg is the mass distribution coefficient, A_s – activity intercepted by the foils GO-C₆₀, A_f – activity of the filtrate, V – volume of filtered solution, m – weight of the foil GO-C₆₀. Dg values of the foils were reduced to take into account contribution of the underlying filter.

Water solution of uranyl nitrate (50 ml, volume activity 1 Bq/ml) was filtered on the GO-C₆₀ foil with an underlying filter (micro-fiber filter made of glass fibers, Sartorius Stedim Biotech). In order to subtract the contribution of the underlying filter the solution of uranyl nitrate was also filtered through the filter alone. The liquid scintillation spectrometer HIDEX 300 SL was subsequently used to measure alpha and beta activities of the filtrate and of the stock solution of uranyl nitrate. The filtered solution contained naturally occurring uranium isotopes ²³⁸U, ²³⁴U and ²³⁵U in a radioactive balance with daughter products, particularly ²³⁴Th and ²³⁴Pa. Uranium was selected for the measurement thanks to easy identification of alpha particles with the HIDEX spectrometer.

The obtained mass distribution coefficients Dg for the individual tested foils GO-C60 (1:1 – No. III, 2:1- No. IV, 3:1 – No. IV) are shown in the diagram in Figure 3.

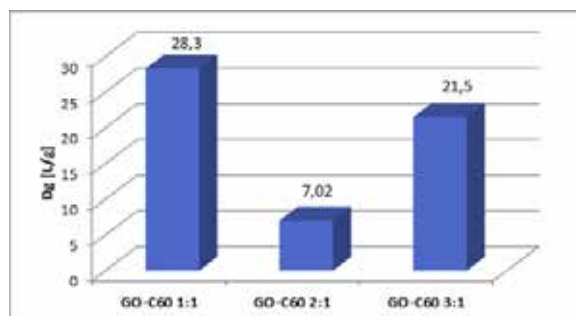


Fig 3. Dependence of the mass distribution coefficients on the used foils made of the products No. III, IV and V

III. Conclusion and discussion

In the pilot experiment the prepared GO-C₆₀ films indicated satisfactory deposition to be used as radiotracers from aqueous solution. We can conclude that the values of mass distribution coefficients D_g are associated with representation of C₆₀, specific weight of the foils and obviously also with foil morphology – see Figs. 1 and 2. The visibly different morphology of the foil made of the product No. IV, which demonstrated the lowest D_g, is probably associated with the fact that the obtained suspension for preparation of the foil was not centrifuged, as it was the case with the products No. III and V. As the objective of the work was to determine whether the foils have any adsorption capacity towards uranyl nitrate at all, it is not relevant to infer any exact reasons of different D_g values. It is obvious that this study should continue and it should focus on a bigger set of different samples, which would provide more information about how the adsorption capacity depends on physical properties, ratio of GO:C₆₀ and method of preparation of the suspension.

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