Application of modified graphene oxide GO-MnO₂ in radiochemical determinations of selected analytes

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Abstract

Graphene oxide (GO) chemically modified with manganese oxide (GO-MnO₂) has been used as a sorbent in the radioanalytical determinations. The sorption of selected elements in dependence on pH has been evaluated in batch and column experiments. For the batch technique, the results of the experiments demonstrated that alkali metals were not removed from aqueous solutions over the entire pH range and removal of other elements strongly depends on acidity of the solution. Two examples: determination of Pt and Th in biological materials by radiochemical neutron activation analysis and separation of gamma-ray radionuclides from environmental samples have been described in details.

Keywords GO-MnO₂ · Platinum and thorium determination · RNAA · Gamma-emitters determination · Biological and environmental materials

Introduction

Several research studies described the development of new technologies used for chosen inorganic pollutants removal [1–4]. Discovery of graphene in 2004 opened new possibilities in analytical chemistry. Its a theoretical specific surface area (SSA) of 2630 m²/g makes graphene flakes making a beneficial choice in separation and preconcentration processes [5]. However, due to the difficulty in the dispersity of graphene in solutions, its application in analytical practice is hampered. As an alternative to graphene, the use of graphene oxide (GO) has been proposed. GO as a hydrophilic reagent, forms stable aqueous colloids [6]. Also, due to presence of oxygen-containing functional groups, such as hydroxyl, epoxy, carbonyl and carboxyl groups, GO can be easily functionalized using various chemical reactions. Such approaches, which add functionality to groups already present on the GO surfaces, make GO flakes a more versatile precursor for a wide range of applications [7–10]. In last

years, several papers concerning the separation and/or sorption of natural and artificial radioisotopes using GO have been published [11–22]. Many of them concerns the sorption of uranium [13–15, 19] from water samples, for its toxicity and causing real injury and increase the incidence of cancer. Other papers described the sorption of the artificial radionuclides—like Co-60 [16, 17], Tc-99 [18], Eu-152 [19], Sr-90 [19, 20]. Recently, a review of the application of GO and related sorbents in the nuclear decommissioning industry have been published [21].

From previous work carried out in the Laboratory, it appears that GO shows low selectivity. The modification of “pure” GO with manganese oxide should ensure sorbent specific selectivity for chosen elements/radionuclides.

Recently, several publications on radionuclide sorption have been appeared [23–29]. Most of them are dedicated for U [23–29], Am [24, 26] and Eu [23, 28] sorption/removal. Among different sorbents used for inorganic preconcentration and separation, manganese oxides and hydroxides play an important role. Manganese oxide (MnO₂) shows good properties for the sorption of heavy metal ions [30], radionuclides [31], Co-60 [32] and Ra-226 [33, 34] from waters. It should be pointed to its relatively low production cost, high surface area, mild oxidizing properties and good stability in acidic conditions. Recently, the application of graphene oxide modified with MnO₂ was found as the sorbent to

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simultaneous removal of thorium/uranium ions from aqueous solutions has been shown [22].

In the most of the cited publications, GO based sorbents were used for the removal of radionuclides from aqueous solutions in purification processes. In this work, GO-MnO₂ material has been applied in radiochemical determinations of Pt and Th in sample tissue. Also, its possibility for gamma-ray radionuclides separation and preconcentration from water samples prior to their determination by gamma-ray spectrometry has been shown.

Experimental

Reagents, standards, radioactive tracers

Sorbent GO-MnO₂ has been prepared by Faculty of Chemical and Process Engineering, Warsaw University of Technology, according to [22]. The obtained material used in all experiments has following parameters: 5% MnO₂ in 0.5% GO in water solution. All reagents used for sorbent preparation, batch and column experiments were of analytical reagent grade purity. 18 MΩ cm grade water from Milli-ORG Millipore Co purification system was used throughout. Standards used for ICP-MS and NAA were supplied by Perkin Elmer as stock standard solutions of 100 µg mL⁻¹ and 1 mg mL⁻¹.

Apparatus

Analytical and micro-analytical balances Sartorius MC5 and Sartorius BP221S, calibrated using national mass standards traceable to the international standards were used. The microwave digestion system (Anton Paar Multiwave 3000, USA) equipped with temperature and pressure regulation was used for digestion of the samples. ICP-MS instrument ELAN DRC II (Perkin Elmer) with crossflow nebulizer with Scott double-pass spray chamber and Ni cones was used. To perform gamma-ray spectroscopic measurements the following detector was used: 255 cm³ HPGe well-type detector (Canberra) with associated electronics (resolution 2.15 keV for 1332 keV ⁶⁰Co line, efficiency ca. 55%), coupled to a multichannel analyzer (Canberra) and spectroscopy software Genie-2000 (Canberra).

Batch and column experiments

In batch experiments, radioactive tracers or multielemental standards in aqueous solution at different pH at room temperature were used. Known amounts of resin (ca 1.2 mg) were brought with occasional shaking in contact with 10 mL of a solution of appropriate composition, containing equal volumes (10–100 µL) of radioactive tracers/multielemental

standards. After 24 h, sorbent was filtered off and the concentration of individual element/radionuclide was determined in an aliquot of the solution by gamma-ray spectrometry/ICP-MS and compared with that of initial solutions.

The sorption rate was investigated in batch mode. 10 mg of prepared sorbent was added to the series of samples. After appropriate time (varied from 1 to 60 min.) shaking was stopped and samples were centrifuged, measured and compared with the standards.

In column experiments, 2 mg of sorbent were placed on 30 mm syringe filter 0.45 µm. The test solutions were made by mixing a known amount of Pa-233 or Au-199 tracers into acidified water (pH-2), digested biological material and digested irradiated biological material. Obtained solutions were passed through syringe filter with GO-MnO₂. Retained tracers of Au-199 were measured on the filter; Pa-233 was eluted and measured in solution.

Results and discussion

Characterization of prepared sorbent

The graphene oxide and prepared sorbent were analyzed by SEM-EDX [35]. The EDX spectrum of GO-MnO₂ nanocomposite shows the existence of C, O and Mn, indicating the successful formation of nanocomposite with rather poor purity (presence of Mg, Zn, Cl was observed). The elemental composition GO-MnO₂ in normalized atomic % content is presented in Table 1. Stability of prepared sorbent was investigated as a function of time—no changes in sorption properties have been observed within 1 year of its preparation.

Table 1 Elemental composition of GO and GO-MnO₂ in normalized atomic % content

Element	GO-MnO ₂
C	39.18
O	49.91
Ca	1.83
Na	2.44
Cl	1.99
Mn	1.49
Si	1.11
K	0.60
Mg	0.60
S	0.45
Zn	0.25
Al	0.12
Ti	0.03

Adsorption experiments

Mn oxides participate in a wide variety of oxidation–reduction and cation-exchange reactions. They exhibit large surface areas and can be very chemically active. Figures 1, 2 and 3 present the percent of sorption of individual elements in dependence on acidity of the solutions.

As one can see, the sorption of individual elements strongly depends on the pH. In acidic solution ($\text{pH} = 1.5$), only few elements show the high affinity to prepared sorbent: Th (Pa-233), Au, Pd, Mo and Ni. In most publications

concerning the removal of elements on manganese sorbents, sorption at low pH was not observed [31, 34]. However, some exceptions have been described. Pan described efficient sorption of Th(IV) on GO-MnO_2 sorbents (different nanostructures) at solution pH 2–2.5 [22]. The pH dependence of the adsorption capacities of Th(IV) may be caused by the differential adsorption of hydrolyzed Th(IV) at various pH values and at a lower solution pH value, the high concentration of H^+ competes with Th(IV) for the same available sites on GO-Mn sorbents. In previous papers from the Laboratory, it was investigated that some transition

Fig. 1 Sorption of selected elements from aqueous solutions in $\text{pH} = 1.5$

Fig. 2 Sorption of selected elements from aqueous solutions in $\text{pH} = 6.5$

Fig. 3 Sorption of selected elements from aqueous solutions in pH = 9

metals show high affinity to MnO₂-Resin (Eichrom) in acidic solutions [36, 37]. Alkali metals are not retained on the resin under all pH range investigated. With increasing pH, higher sorption is observed for most elements (Fig. 2.). In an alkaline media, at pH = 9, practically all the elements (except Au, alkali metals, Mo and V) are retained on GO-MnO₂. It seems that prepared sorbent is appropriate for the selective separation of Pa-233 and some noble metals from acidic solutions. The dynamics of sorption on GO-MnO₂ is very fast—5 min of the contact the aqueous phase with the sorbent is sufficient to obtain the maximum of sorption.

The dependence on the ionic strength was also checked and no influence on the sorption behavior was observed. Obtained results have been verified by column experiments. Due to small dimensions of the GO-MnO₂ particles, there were great difficulties with column preparation. The intermediate solution applied in this work was usage of 30 mm syringe filter 0.45 μm to keep sorbent. The presence of impurities in GO-MnO₂ [35] does not interfere with the use of the prepared sorbent for analytical purposes.

Possible application of GO-MnO₂ in radiochemical separations

Determination of platinum in human tissues by RNAA

Platinum which has been used broadly in medicine, especially plays an important role in oncology. Platinum derivatives are effectively used both in monotherapy and combination therapy. [38]. The first platinum compound used for medical purposes was cisplatin—licensed for medical use in

the seventies of the last century. The presence of molecules containing Pt in tissues is variable and not correlated with the introduced dose. The prolonged retention of platinum are observed, which may be relevant to long-term toxicity. Therefore, there is a need to elaborate analytical methods that can be used to determine Pt at different concentration levels in tissue samples with a mass of single mg. Recently, inductively coupled plasma mass spectrometry (ICP-MS) has been applied in platinum determination in body fluids [39]. Neutron activation analysis is considered as a complementary method to ICP-MS [40]. In the case of platinum, the instrumental version of NAA usually can not be applied because of short half-lives of radionuclide ¹⁹⁷Pt, as well as, low energies of their gamma ray photopeaks, which are completely masked by high activity of major and trace elements present in the human tissue samples. In addition, radiochemical separation of Pt after irradiation is also very difficult due to radiation hazard. The activity measurement of formed radionuclide ¹⁹⁹Au is widely used for the determination of platinum with NAA in the analysis of tissue samples with high content of sodium, potassium, and phosphorus. because ¹⁹⁹Au is of longer half-life (3.14 days) and emits the gamma ray photons of considerably higher energy (159.6 keV) However, even then the determination of Pt via ¹⁹⁹Au by the instrumental version of NAA can be hampered.

In this work, tissue samples (blood, liver, muscles) with added platinum have been irradiated together with platinum standards and blank in Polish nuclear reactor Maria. After appropriate cooling, samples were digested in the mixture HNO₃ and H₂O₂. Next, GO-MnO₂ was added to dissolved sample solution, shaken for 6 h in room temperature, and

then the sample solution was passed through the syringe filter 0.45 μm ; or GO-MnO₂ was loaded onto the syringe filter and next sample was passed through filter. The filters with retained radionuclides were measured by gamma spectrometry. In both cases recovery of formed Au-199 on the sorbent was about $75 \pm 3\%$. The recovery is relatively low but it is sufficient for this kind of samples. Body tissues and fluids contain high content of some elements like sodium, potassium and bromine, which are the main source of radioactivity of these samples. Application of RNAA with separation of ¹⁹⁹Au on GO-MnO₂ allows to shorten the cooling time c.a. 3 times.

Thorium determination by RNAA in biological samples

In the case of human tissues, thorium content was investigated because of its high specificity for the skeleton, long biological half-life and dose associated with subsequent progeny [41, 42].

²³²Th can be determined via ²³³Pa [formed in nuclear reactor in the ²³²Th(n, γ)²³³Pa reaction]. In the case of NAA, neutron irradiated sample (biological and environmental) was digested and obtained solution was acidified to pH 1.5 and introduced onto the filter with GO-MnO₂. Next 5 mL of 8 M HNO₃ were passed through the column. Adsorbed protactinium was recovered from the resin by eluting with 5 mL of concentrated H₂O₂ and measured by gamma-ray spectrometry. Recovery of ²³³Pa was at $81 \pm 3\%$. Table 2 contains the results of thorium determinations in certified reference materials.

In the above examples, both formed radionuclides (Au-199 and Pa-233), due to their nuclear properties, could be measured directly after irradiation and appropriate cooling

time. However, in the case of irradiated biological samples with very low content of Pt and Th, the measurements uncertainty could be significant, due to high background from P-32, Br-82, K-42 and Na-24. Application of GO-MnO₂ in the separation of chosen radionuclide from irradiated matrix, reduces analysis time. Moreover, RNAA usually ensures the better accuracy of the obtained results comparing to INAA [36, 37, 43].

Separation of long-lived gamma emitters from water samples prior to gamma-ray spectrometric measurements

In the case of the accidental contamination of a water with gamma-ray radionuclides, after acidification with nitric acid to pH 1, the samples are measured directly in Marinelli beakers. In normal conditions, the accurate measurements of long-lived gamma radionuclides in waters required their preconcentrations from the large volume of sample. Batch experiments show, that the most of gamma-ray radionuclides could be separated on GO-MnO₂ in alkaline media. Co-60, Am-241 and Eu-152 are retained quantitatively, whereas Ba-133 is absorbed at around 85%, regardless of the time of contact with sorbent. Cesium-137 and potassium K-40 are not retained in all conditions. In this work, water sample was adjusting pH to 9 by the addition of ammonia. Next, GO-MnO₂ was added to sample solution, shaken for 1 h in room temperature, and then the sample solution was passed through the syringe filter 0.45 μm ; standards containing known amounts of radionuclides were prepared in the same way. The filters with retained radionuclides were measured by gamma ray spectrometry. Proposed procedure has been validated using three water samples (distilled, potable water and sea water) with Ba-133, Am-241, Co-60, Eu-152, Cs-137 and K-40. Table 3 shows the sorption on long-lived gamma radionuclides in dependence on sample content; the data show that the sorption of Ba-133, Am-241, Co-60 and Eu-152 is independent on ionic strength. Barium-133 chemically resembles radium-226 very closely and can be used as an analogue for Ra-226 and Ra-228 isotopes. It can be assumed that Ra-226 will also be retained on the prepared sorbent. Ra-226 emits gamma radiation ($E = 186 \text{ keV}$) with a low abundance what limits the use of gamma-ray spectrometry for its accurate determination. Preconcentration of radium isotopes on GO-MnO₂ and their subsequent elution using hydrochloric acid prior to inductively coupled plasma

Table 2 The determination of Th in selected certified reference materials

Material	Obtained results (mg kg ⁻¹)	Certified value (mg kg ⁻¹)	Recovery (%)
Virginia tobacco leaves (CTA-VTL-2)	0.310 ± 0.031	0.378 ± 0.031	82
Mixed polish herbs (INCT-MPH-2)	0.122 ± 0.018	0.154 ± 0.013	79

Table 3 Sorption of long-lived gamma emitters in dependence on sample content

	Cs-137 (%)	Ba-133 (%)	Co-60 (%)	Eu-152 (%)	Am-241 (%)
Distilled water	0	85	99	100	100
Potable water	0	87	99	100	100
Sea water	0	86	100	100	100

Contact time 60 min., pH = 9

mass spectrometry (ICP–MS); as a complementary to radio-analytical methods allows radium to be determined with high accuracy in a relatively short time of analysis.

Conclusions

GO-MnO₂ sorbent is characterized by greater selectivity in relation to the pure graphene oxide. Presented examples show the possibility of practical application of GO-MnO₂ in radioanalytical determinations of selected elements/gamma-emitters. Sorption of some elements at pH below 4 is particularly interesting and requires further research. In the case of using prepared sorbent for RNAA, an unquestionable advantage of its using is the simplicity of the radio-chemical separation procedure. After the irradiation, sample is digested, obtained solution is loaded onto the syringe filter with sorbent and the filter is measured by γ -ray spectrometry. Simple procedure reduces a radiation hazard or a contamination hazard associated with analysis of irradiated samples. In the case of the determination of long-lived gamma emitters in waters, application of GO-MnO₂ for their preconcentration, significantly shortens the analysis time. As one can see, a significant problem is the relatively low recovery of the analyte. This is probably due to the way of preparing the syringe filter loaded with GO-MnO₂. The used syringe filters do not ensure quantitative separation of the nanoparticles. So the greatest challenge is the proper preparation of the GO-MnO₂ bed of ultra low mass or the thin disk containing sorbent.

Compliance with ethical standards

Conflict of interest Ewelina Chajduk declares that she has no conflict of interest. Paweł Kalbarczyk declares that she has no conflict of interest. Halina Polkowska-Motrenko declares that she has no conflict of interest. Leszek Stobiński declares that she has no conflict of interest.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

Informed consent Informed consent was obtained from all individual participants included in the study. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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