7th International Conference on Water Resources and Arid Environments (ICWRAE 7): 367-376
4-6 December 2016, Riyadh, Saudi Arabia

Heavy Metals and Radionuclides Sorption and Removal from Ground Water by Graphene Oxide (GO) and its Derivatives

Khaled M. Naguib

Sanitary and Environmental Engineering Institute,
Housing and Building National Research Center, Egypt

Abstract: This research show the efficiency of graphene oxide (GO) for rapid removal of some of the most toxic andradioactive long-lived human-made radionuclides from contaminated water, even from acidic solutions (pH <2). The interaction of GO with actinides including Am(III), Th(IV), Pu(IV), Np(V), U(VI) and typicalfission products Sr(II), Eu(III) and Tc(VII) were studied, along with their sorption kinetics. Cation/GOcoagulation occurs with the formation of nanoparticle aggregates of GO sheets, facilitating theirremoval. In the presented work, new composite nanomaterials, based on graphene oxide and styrene, have beendeveloped for the retention purpose. ^{85}Sr and ^{137}Cs represent two of the main fission products being presentin radioactive wastes from nuclear power cycle. The graphene oxide samples were prepared from naturalgraphite using high intensity cavitation field in a pressurized (6 bar) batch-ultrasonic reactor.Graphene oxide (GO) and two magnetic grapheme oxide (MGO) composites with a different amounts ofmagnetite were synthesized, characterized and used insorption experiments. The effect of pH on sorption ofAm(III) and Pu(IV) isotopes as well as Co(II), Ni(II),Cu(II) and Pb(II) to GO and MGO was studied in equilibriumand kinetic experiments. The adsorption capacitiesvaried from 30 to 574 mg g^{-1} while rate constants rangedfrom 0.29 to 0.46 min^{-1} and increased in the followingorder Co, Cu, Pb and Ni. Large variations in the uptake ofstudied elements by adsorbents depending on initial andfinal pH of solutions were observed.

Key words: Grapheneoxide · Sorption · Radionuclide · Heavy metals.

INTRODUCTION

Naturally occurring radioactive materials (NORM) are abundant throughout the earth's crust. Human manipulation of NORM for economic ends, such as mining, ore processing, fossil fuel extraction and commercial aviation, may lead to what is known as "technologically enhanced naturally occurring radioactive materials" (TENORM). The existence of TENORM results in an increased risk for human exposure to radioactivity. TENORM-producing industries may cause workers to be occupationally exposed to ionizing radiation and may release significant amounts of radioactive material into the environment resulting in the potential for widespread exposure. These industries include mining, phosphate processing, metal ore processing, heavy mineral sand processing, titanium pigment production, fossil fuel extraction and combustion, manufacture of building materials, thorium compounds, aviation and scrap metal processing [1].

Treatment and decontamination of waste products and two-dimensional honeycomb network [2].

An advance in graphite-related materials promises to finally mitigate a long-standing problem for the resource development industries. Graphene oxide (GO), which is non-conductive,hydrophilic and easily suspended in water is able to clean radionuclide-contaminated liquids by agglomerating contaminants into solids.

There are realistically three strategies for ensuring that contaminated groundwater containing human-made radionuclides, among which the transuranic elements are the most toxic, is an essential task in the clean-up of legacy nuclear sites [3]. The recent accident that included radionuclide release to the environment at the Fukushima Daiichi nuclear power plant in Japan and the contamination of the water used for cooling its reactor cores, underscores the need for effective treatment methods of radionuclide-contaminated water [4].

Corresponding Author: Khaled M. Naguib, Sanitary and Environmental Engineering Institute,
Housing and Building National Research Center, Egypt.

Graphene and related materials such as GO, reduced GO and various nanocomposites have attracted great attentionsince the graphene discovery in 2004 [5]. Their unique properties and a wide range of physical and engineeringapplications in various fields as well as their high potential for the efficient removal of various pollutants including the most toxic long-lived radionuclides from contaminated solutions made them the most promising materials of thetwenty first century [6-8]. It is generally accepted that graphene is a flat single layer of sp2 hybridized carbon atoms, densely packed into an ordered radioactive materials don't cause harm to people or the environment:

- Separation,
- Isolation,
- Transmutation, a nuclear reaction by bombarding the material with neutrons or protons from an accelerator or a reactor to form isotopes with short half-lives.

The last approach, while highly effective, is developmental and prohibitively expensive to consider for anything less radioactive than spent nuclear fuel, so the only realistic options are separation and isolation. The role that GO can play in these options is separation [9].

The invention of a GO filtration system originated through an international collaboration led by the efforts of James Tour in the Nanomaterial's Research Lab at Rice University in Houston and StepanKalmykov in the Environmental Radioactivity Research Lab at Moscow State University. Although it is still in a stage of development, it is being introduced in a variety of systems configurations through the efforts of VSW Water Purity, LLC, in Grapevine, Texas. In this system, GO powder is suspended in water and coagulates when heavy metal ions are introduced to the solution. It is then easily separated by sedimentation or rough mechanical filtering.

The properties of GO suspended in solution make it a promising material in rheology and colloidal chemistry [10, 11]. The hydrophilic GO produces stable suspensions when dispersed in liquids and shows excellent adsorption capacities due to its relatively vast and highly accessible surface area, lack of internal surfaces, which usually cause slow cation-sorbent interactions and its significant negative charge [12-14].

Sample Preparation: Preparing samples for this experiment requires that certain precautions be taken. First, all samples should be prepared in the fume hood in order to contain any harmful fumes and or radioactive material. Lab coat, goggles and gloves taped to the sleeves of the lab coat are required as well.

In order to prepare a solution of 1 part per million (ppm) of uranium, a sample of uranium oxide (UO_2) will be used. Nitric acid (HNO_3) will break down the UO_2 and create a water soluble salt of uranyl nitrate (UO_2•(NO_3)$_2$). This salt will then be dissolved in deionized water to produce a 1ppm solution of uranium. Once the sample solution has been produced, it should be stored in a glass container with a cap. The cap of the container should be taped to ensure a good seal and to prevent a possible release of radioactive material. The container should also be labeled with its contents, the date of creation and the name of person who created it. This container should then be stored in a radioactive safety locker.

Preparation of a solution containing 0.5 ppm of ^{137}Cs and 0.5 ppm of ^{90}Sr, for a total of 1 ppm concentration of radioactive elements will use a slightly different technique. Strontium nitrate (Sr•(NO_3)$_2$) and cesium nitrate (Cs•NO_3) salts will be added directly to deionized water in order to create the solution. Once this has been accomplished, trace amounts of radioactive isotopes ^{137}Cs and ^{90}Sr will be added to the solution. Once the sample solution has been produced, it should be stored in a glass container with a cap. The cap of the container should be taped to ensure a good seal and to prevent a possible release of radioactive material. The container should also be labeled with its contents, the date of creation and the name of person who created it. This container should then be stored in a radioactive safety locker.

High resolution scanning electron microscopy (HRSEM) analysis was conducted on a FEI Nova Nano SEM scanning electron microscope equipped with an Everhart-Thornley detector, Through Lens detector and accelerating voltage 1-30 kV. The sample was deposited on the silicon chip substrate 5x5 mm.

Diffraction patterns were collected with diffractometerBruker D2 equipped with conventional X-ray tube (Cu Kα radiation, 30 kV, 10 mA). The primary divergence slit module width 0.6 mm, Soller Module 2.5,Airscatter screen module 2 mm, Ni Kbeta-filter 0.5 mm, step 0.00405°, a counting time per a step 1 s and the LYNXEYE 1-dimensional detector were used. The range of measurement is from 5° to 90° 2Theta.

Qualitative analysis was performed with the Diffrac Plus Eva software package (Bruker AXS, Germany) usingthe JCPDS PDF-2 database. For quantitative analysis of XRD patterns we used Diffrac-Plus Topas (BrukerAXS, Germany, version 4.1) with structural models

based on ICSD database. This program permits to estimate the weight fractions of crystalline phases and mean coherence length by means of Rietveld refinement procedure.

Characterization: GO and MGO were characterized by M?ssbauer spectroscopy, X-ray diffraction (XRD), Fouriertransform infrared spectroscopy (FTIR) andScanning electron microscopy (SEM) (Fig. 1). The M?ssbauerspectra were acquired at room temperature applying. The Mssbauerspectrometer in the transmission geometry using the 57Co(Rh) source. NormosDist software was used for analysis of spectra. The XRD analyses were conducted by means of a D8 (Bruker AXS) X-ray diffractometer.

SEM was used to observe the surface state and structure of the samples using the scanning electron microscope (High resolution FESEM Su-70 Hitachi). FTIR spectra were obtained with the ATR–FTIRPerkin Elmer spectrophotometerusing the MCD detector with a scan range of 4000–400 cm^{-1}.

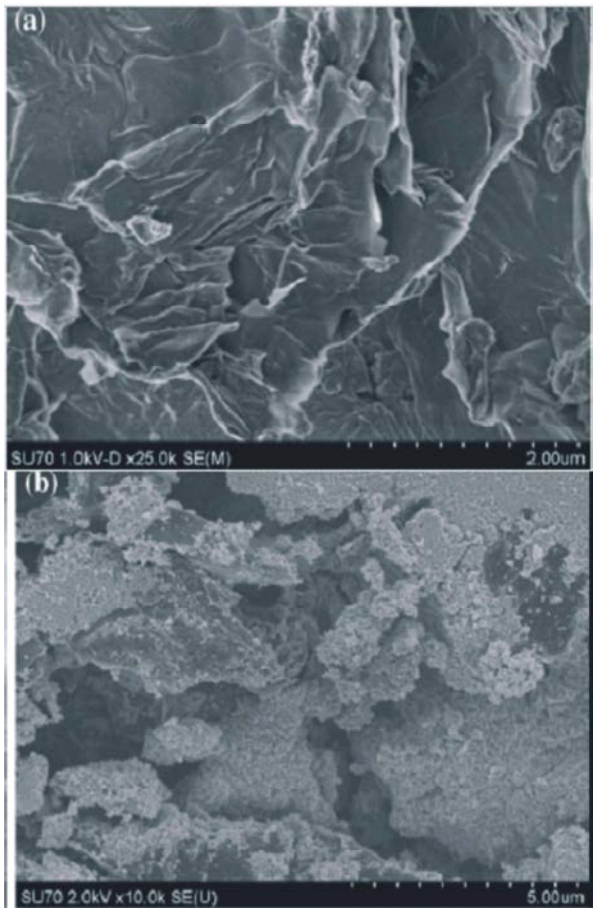


Fig. 1: SEM images of GO (a) and MGO composite (b)

Experimental: GO was prepared using the improved Hummer's method.10Large-flake graphite (10.00 g, Sigma-Aldrich, CAS 7782-42-5,LOT 332461-2.5 KG, Batch #13802EH) was suspended in a 9 : 1mixture of sulfuric and phosphoric acids (400 mL) and thenpotassium permanganate (50.00 g, 0.3159 mol) was added insmall portions over a 24 h period. After 5 d the suspension wasquenched with ice (1 kg) and the residual permanganate was reduced with H_2O_2 (30%aqueous, ~3 mL) until the suspensionbecame yellow. The product was isolated by centrifugation at319g0 for 90 min (Sorvall T1, ThermoFisher Scientific) andsubsequently washed with 10% HCl and water. The yellowbrownwater suspension (190.0 g) was isolated, correspondingto 10 g of dry product. For gravimetric analysis 50 mL of mainproduct was separated from main batch, washed as describedabove and reduced by excess N_2H_4. It isimportant to note thatthe product isolation process produced significant amountsof contaminated organic solvents that could be consideredenvironmentally hazardous. However, this process could bechanged or omitted in an industrial procedure and is usedhere only to allow characterization of starting material byremoval of water and manganese II–IV) oxides [15].

Sorption experiments were carried out in plastic vials forwhich sorption onto the vial walls was negligible under the experimental conditions. In the sorption experiments, solutionsof the radionuclides nitrates (each radionuclide experimentwas done separately) were added to GO suspensionand then the pH was measured using a combined glass pHelectrode (InLab Expert Pro, Mettler Toledo) and adjusted byaddition of small amounts of dilute $HClO_4$ or NaOH. Afterequilibration, the GO suspension was centrifuged at 40 000g0for 20 min (Allegra 64R, Beckman Coulter) to separate radionuclidessorbed onto the GO. The sorption was calculated fromthe difference between the initial activity of the radionuclidesand that measured in solution after equilibration. The initialtotal concentration of radionuclides in the kinetic experimentsand pH-dependence tests was 2.15×10^{-7} M for $^{233}U(VI)$,1.17×10^{-9} M for $^{239}Pu(IV)$, 5.89×10^{-14} M for 234Th(IV),3.94×10^{-10} M for $^{241}Am(III)$, 3.43×10^{-12} M for 152Eu(III),3.77×10^{-7} M for $^{237}Np(V)$, 1.91×10^{-7} M for 95mTc(VII) and1.24×10^{-7} M for $^{90}Sr(II)$. The concentration of the GOsuspension was 0.077 g L^{-1} in 0.01 M $NaClO_4$. In all cases thetotal concentration of ions was much less than the solubilitylimit and the GO/radionuclide ratio correspond to a very highunder-saturation of GO sorption sites [15].

For desorption tests, $HClO_4$ was added to the suspensions todecrease pH and after different time intervals the concentrationof radionuclides in solution was measured. Tomeasure the sorptioncapacity of GO towards different radionuclides, the sorptionisotherms were obtained using 0.038 g L^{-1} GO suspension in0.01 M NaClO4 in case of U(VI), Sr(II), Am(III) and 0.38 g L^{-1} GOsuspension in 0.01 M $NaClO_4$ in case of Eu(III). The concentrationof the cations was varied at constant pH values [15].

XPS was performed on PHI Quantera XPS with Al source.TGA Q50 (TA Instruments) was used for TGA; B10 mg ofhomogenized sample was investigated. Temperature wasincreased at a rate of 20 °C min^{-1} to 150 °C, held at 150 °Cfor 1 h and then the temperature was raised at a rate of

$10^{o}Cmin^{-1}$. FTIR analysis was performed in reflection geometryusing Nicolet FTIR Infrared Microscope Samples for FTIR,Raman and XPS were drop-cast onto glass substrates and driedunder vacuum for 48 h to form detachable free-standinggraphene oxide paper. To trace the changes that occur with GOupon interaction with cations, the sample was equilibrated withEu(III) to prepare it for IR and XPS examinations. Experimentalconditions were similar to those described for the isotherm experiments, using 0.38 g L^{-1} GO suspension in water. Concentration ofEu was determined to be 1 mM by gravimetric analysis of sourceEuCl3 salt (Aldrich, CAS 13759-92-7) that was dried with SOCl2 andsubsequently dried under vacuum [15].

To demonstrate the performance of GO compared to othersorbents for radionuclide removal, experiments were conductedwith a simulated liquid nuclear waste containing highconcentrations of complexing agents. The concentrations ofactinides was equal to 8 x 10^{-8} M for ^{233}U(VI) and 3 x 10^{-9}Mfor^{239}Pu(IV). Sorbent concentrations were 0.5 g L^{-1} of GO,commercial bentonite

(SC ‘‘Khakassiyabentonite’’, Russia)and granular activated carbon (Sigma-Aldrich). For HRTEM,GO aggregates were deposited onto a carbon-coated TEM gridand analyzed using HRTEM (JEOL-2100F) at an acceleratingvoltage of 200 kV. EDX analysis was performed with a JED-2300analyzer. The CCC was determined by addition of aliquots ofsolutions with cations, i.e. Na^{+}, Ca^{2+} and Eu^{3+}, to GO suspension.

After the addition of the certain portion of solution thatled to CCC, GO precipitated and was observed by the unaidedeye after B1 h of equilibration[15].

Preparation of Sorption Materials: The graphite was exfoliated with the effect of high intensity ultrasound and delaminated grapheme nanosheets were used for graphene oxide [16] preparations by improved Hummers method [17]. H_2SO_4(60 ml), H_3PO_4 (10 ml), graphene (1 g) and $KMnO_4$ (3 g) were mixed in a round-bottom flask. The mixturewas then heated to 40 °C and stirred for 6 h, affording a pink, dense suspension. The suspension was then poured onto a mixture of ice and 30% H_2O_2 (200 ml) and the pink suspension quickly turned bright yellow.

The product was purified by dialysis (Spectra/Por 3 dialysis membrane) and centrifuged. Purified GO productwas obtained as a brown, honey-like suspension. The oxidation was quantitative when the theoretical yieldwas assumed to equal the starting graphite mass. The elemental analysis of prepared GO showed an overallcomposition of C 48.8%, H 2.1% and O 49.1% (impurities from natural graphite: SiO_2 1%, K_2O_3.2%, CaO0.6%, TiO_2 1.3%, CuO 1.5%,ZnO1.5%). The content of carboxylic group -COOH in the graphene oxide wasincreased by reaction with monochloroacetic acid [18].

Graphene oxide polystyrene composite was synthesized using direct emulsion polymerization of styrene inthe presence of graphene oxide at 90 °C [19]. Hydrothermal conditions were maintained in stainless steelstirred autoclave. The graphene oxide was dispersed in 400 ml distilled water. After that argon gas was usedfor 10 minutes to purge oxygen from the solution. Styrene (30 ml) and divinylbenzene (1 ml) were added intosolution. The solution was under constant stirring and heating until the reaction temperature reached to91°C, after that 12 ml solution of sodium 4-styrenesulfonate (4.00 g of sodium 4-styrenesulfonate in100.0 ml water) was added. After 3 min the 24 ml solution of sodium 4-styrenesulfonate (4.00 g of sodium4-styrenesulfonate in 100.0 ml water) and 1 ml of the solution of potassium per sulfate and sodiumbicarbonate (1 g $K_2S_2O_8$ and 3.5 g $NaHCO_3$ in 100 ml water) was added. The reaction mixture iscontinuously stirred and heated. After 85 min a mixture of 6 ml styrene, 0.15 ml divinylbenzene, 24 ml ofwater, 24 ml solution of sodium 4-styrenesulfonate and 3 ml of the solution of potassium persulfate andsodium bicarbonate were added; heating and stirring continuous next hour. The obtained sample was centrifuged 10 minutes at 10 000 rpm. The main fraction was filtered off and dried at 60 °C.

Sorption Experiments: The sorption properties of produced nanomaterials were evaluated by batch sorption

experiments, based onthe contact of solid material with tracer solution. The volume of the solution was 1.5 ml and the mass of thesorbent was 0.01 g. The salts CsCl and $SrCl_2$ were used as carrier for radionuclides ^{137}Cs and ^{85}Sr,respectively. In the case of the kinetics experiments the concentration of CsCl or $SrCl_2$ was 2*10^{-6} mol/L.

These solutions were spiked by ^{137}Cs or ^{85}Sr. The contact time was 24 hours unless otherwise specified.

Sorption experiments were carried out at 24°C under atmospheric conditions. After the adsorption ofradionuclides, the suspension was filtered and an aliquot of the supernatant was measured on the gammaspectrometer (EMPOS MC1256) using NaI(Tl) detector. The volume of measured aliquot was 0.5 ml.

The sorption experiments were described by the distribution coefficient (*K*d) and percentage of the sorption.The definition of K_d is following:

$$K_d = \frac{C_{mass}}{C_{volume}} \cdot \frac{V}{m} [ml/g], \quad (1)$$

Wherec_{mass} is the concentration of the sorbate adsorbed onto the solid phase, c_{volume} is the concentration ofthe sorbate in solution, V [ml] is the volume of the liquid phase and m [g] is the mass of the sorbent.

Langmuir (2) and Freundlich isotherm (3) were utilized for evaluation of the sorption data. Thecation exchange capacity was determined by Langmuir isotherm:

$$qe = \frac{KL \cdot qmax \cdot ce}{1 + KL \cdot ce} [mg/g], \quad (2)$$

Whereq_{max} is the maximum sorbate uptake (mg/g), *K*L is the coefficient (L/mol), *c*e is the equilibriumconcentration of the solute (mg/L) and *q*e is the adsorbed amount of the sorbate on the sorbent (mg/g).

Freundlich isotherm is defined as

$$qe = qF \cdot ce^{1/n} [mg/g], \quad (3)$$

WhereK_F ((mg/g)/(mg/L)$^{1/n}$) and n are characteristic constants related to the adsorption capacity and theadsorption intensity, respectively. The experimental data were fitted in program SciDAVis 0.2.4 that uses thenonlinear least-squares Marquardt-Levenberg algorithm for fitting.

RESULTS AND DISCUSSIONS

Sorption kinetics and pH dependences an important characteristic of the toxic element removal istheir reaction kinetics of with GO. Data on the sorptionkinetics have indicated fast adsorption of all elements. Theamount of adsorbed Co^{2+}, Cu^{2+}, $Pb^{2+}$and Ni^{2+}After5 min varied from 70 to 90%. The equilibrium at90–100% level was observed after 10–60 min of contacttime. The pH of liquid-phase decreased from 5.4 ± 0.1 to3.3 ± 0.1. Kinetic data were fitted to the pseudo-first-orderkinetic model: qt = qe $(1–e^{-kadt})$, where qt and qe are thestudied element concentrations (μ mol g^{-1}) at time t andequilibrium, respectively, while k_{ad} (min^{-1}) is thepseudofirst-order rate constant. The kinetic parameters showedthat obtained data well fitted the pseudo-first-order equation.

The rate constants ranged from 0.29 to 0.46 min^{-1} andincreased in the following order: Co, Cu, Pb and Ni. Speciationof metals was not investigated during this studywhile it was reported that under close and identical conditionsin the pH range from 3 to 5.4 the studied elementscould exist as cations Co^{2+}, Cu^{2+}, Pb^{2+} and Ni^{2+} in thecontact solutions [20-23]. Thus, we believe that pHdepended species of elements could not affect the sorptionkinetics. However, the sorption kinetic data followed wellthe electronegativity of elements (according to Allen'sscale)—the rise of rate constants corresponds to theincrease in electronegativity.

Studies of pH dependences indicated that about 100%of Ni was sorbed to GO at the initial pH of 3 to 8 after 24 hof contact time. Adsorption of Co graduallyincreased from 80 to 100%, while the amount of adsorbedCu and Pb was decreased at pH of 7 and 8. For all elements the maximum adsorption was observed at initial pH values of 5and 6. The pH values remained stable for 24 h in sorptionexperiments with MGO and Cu or Co at initial pH = 5.4 ± 0.1. Our preliminary data have indicated themaximum adsorption capacity of GO for Pb, Ni, Co and Cuof 573, 264, 253, 285 mg g^{-1}, respectively, while theadsorption capacity of MGO for the studied elements wasfound to be 567, 127, 30, 133 mg g^{-1}, respectively. Thepublished data revealed wide variations of reported values,e.g.[Wu *et al*] showed that GO can possess a much higherabsorption capacity of 117.5 mg g^{-1} for Cu(II) than that ofactivated carbon [20-24]. It has been demonstrated that GOhad a high adsorption capability up to 1119 mg g^{-1} towardPb(II) ions in aqueous solutions [25, 26]. It was pointed outthat the adsorption capacity of

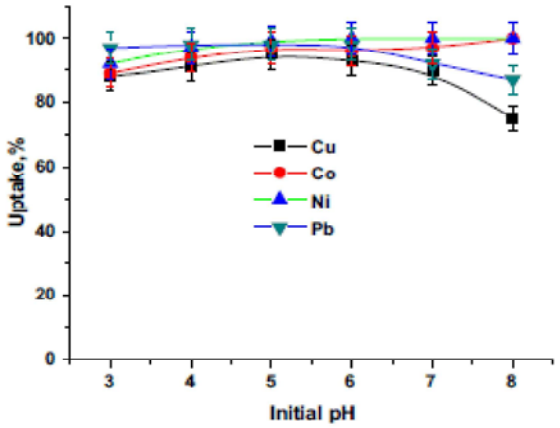


Fig. 2: Sorption of Cu, Co, Ni, Pb to GO depending on initial pH,C(Cu, Co, Ni, Pb) = 100 lmol L^{-1}, contact time 24 h

GO was much higher ascompared to the reported sorbents including nanomaterialse.g., carbon nanotubes [26]. Impressive adsorption capacitieshave been reported for the GO composites, e.g.,sorption capacity of GO decorated with Fe_3O_4, sorptioncapacity of sulfonated magnetic GO composite and magneticmn-doped Fe(III) oxide nanoparticle implanted grapheme for Cu(II) varied from 18.3 to 129.7 mg g^{-1}, whilefor Pb(II) it ranged from 274.7 to 673 mg g^{-1} [26-30]. They reported that the maximum adsorption capacity at pH of 7 ofmagnetic GO composite for Cu(II) was 59.44 mg g^{-1} andfor Pb(II) was 151.17 mg g^{-1} were lower than thatobtained in this study. Thus, the synthesized sorbentsshowed a similar or higher adsorption capacity as comparedto the values reported in the recent publications withthe exception of the GO adsorption capacity for Pb. The GOadsorption capacity of [than 1 g per g reported in previouspublications for Pb was not reached in this study. Nevertheless,much higher adsorption capacities of all studiedelements were found in sorption experiments with MGOwhich is important from the practical point of view.

Radionuclide Interaction with GO: The kinetics of radionuclide removal at pH ~3.5 by GO arepresented, indicating that steady state conditionswere achieved within 5 min even at very low GO concentration(<0.1 g L^{-1} by carbon). The fast sorption kinetics are likely dueto GO's highly accessible surface area10,22 and its lack of internalsurfaces that usually contribute to the slow kinetics of diffusion incation–sorbent interaction. The fast kinetics are importantfor practical applications of GO for removal of cationic impuritiesincluding $Th_{(IV)}$, $U_{(VI)}$, $Pu_{(IV)}$ and $Am_{(III)}$.Fig. 3B and C show pH sorption edges for $Th_{(IV)}$, $Pu_{(IV)}$,$Am_{(III)}$, $Eu_{(III)}$, $U_{(VI)}$, $Sr_{(II)}$, $Tc_{(VII)}$ and $Np_{(V)}$. All of the radionuclidesdemonstrate typical S-shaped pH-edges for cations,except for Tc, that exists as the pertechnetate anion. This explains its higher sorption at low pH whenthe GO surface is protonated and positively charged. Sorptionof most of the cations is quantitative over a broad pH range; for$Th_{(IV)}$ and $Pu_{(IV)}$ complete sorption is achieved at pH > 1.5and for $Am_{(III)}$ and $Eu_{(III)}$ complete sorption occurs at pH > 2.3.

This suggests that GO would be useful in the remediation ofcontaminated natural waters. The position of the pH sorptionedge is correlated to the formal cation charge. The sorption ofU(VI) decreases at high pH (>7), possibly due to $U_{(VI)}$ carbonatecomplexation. This was demonstrated earlier for mineralsorbents.23,24Further experiments demonstrated that the reversibility ofsorption for Pu(IV) and U(VI) was quantitative.

When the pH was decreased, a newsteady state was achieved in o10 min, as shown in the inset.

GO has a high sorption capacity towards $U_{(VI)}$, $Sr_{(II)}$, $Am_{(III)}$and $Eu_{(III)}$cations as determined from the sorption isothermsshown in Fig. 3. Even at a GOconcentration as low as 0.038 g $^{L-1}$,the saturation limit is not reached. The Langmuir sorptionformalism (Equ1) is:

$$C_{sorb} = Q_{max}KLaC_{sol}/(1 + KLaC_{sol}) \quad (1)$$

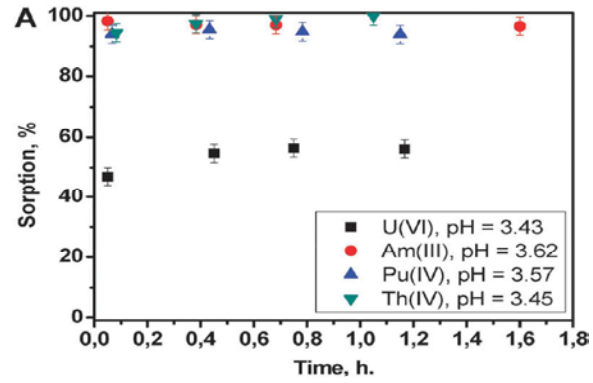
and the Freundlich sorption formalism (Equ 2) is:

$$C_{sorb} = KFrC_{soln} \quad (2)$$

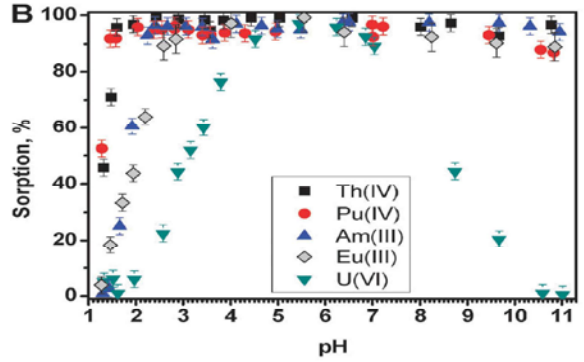
whereC_{sorb} is the equilibrium concentration of radionuclidesadsorbed on GO, C_{sol} is the equilibrium concentration of radionuclidesin aqueous solution, Qmax is the maximum sorption capacity, KLa is a constant representing the strength with whichthe solute is bound to the substrate and KFr and n are empiricalcoefficients. In several cases the use of the Langmuir formalism(Equ 1) does not give as good a fit for the isotherm descriptionas the Freundlich formalism (Equ 2). This is the case forAm(III), for which sorption saturation is not reached under theexperimental conditions. The values of the parameters for theLangmuir and Freundlich formalisms that are presented in Table 1 were calculated from experimental data, though the GOsurface is far from saturation.

Table 1: Sorption of Cs and Sr on polystyrene and GO-polystyrene.

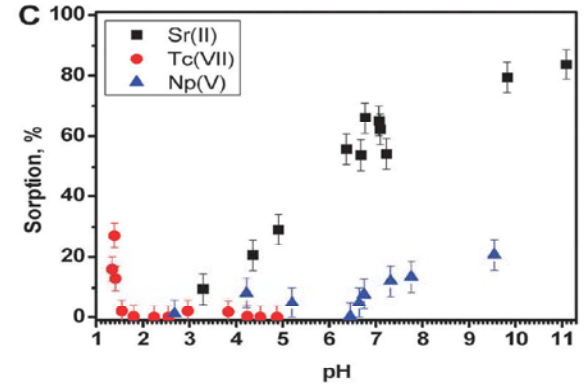
	Cs(I)		Sr(II)	
	%(Cs)	pH	%(Sr)	pH
Polystyrene	5	3.4	16.6	3.2
GO-polystyrene	90.2	4.8	98.4	5.3



(A) Kinetics of U(VI), Am(III), Th(IV) andPu(IV) sorption onto GO indicating that steady state conditions are reachedwithin 5 min.



(B) pH-sorption edges for Th(IV), U(VI), Pu(IV), Eu(III) and Am(III).



C) pH-sorption edges for Sr(II), c(VII),Np(V) at steady state. The concentrations are listed in the Experimental section.

Fig. 3: Radionuclides removal by GO.

Data presented in Table 1 demonstrated thatthe sorption of Cs(I) and Sr(II) on polystyrene (it was prepared by the samemethod like the composite material only without adding of GO) and on the composite materialGO-polystyrene. The results demonstrated that sorption of selected radionuclides is on the pure polystyrene very low - only 5.0 % for Cs(I) and 16.6 % for Sr(II). On the otherside, the sorption on GO-polystyrene is very high - 90,2 % for Cs(I) and 98,4 % for Sr(II). Therefore the modification of polystyrene by GO increases the sorption properties.

Figure 4 demonstratedthat the sorption kinetics of GO-polystyrene is very fast for bothradionuclides. The Cs(I) reach maximum after 2 hours, the Sr(II) reach maximum after 1 hour. The pH of equilibrium solution for Cs(I) was around 5.0 and for Sr(II) pH was around 5.5.

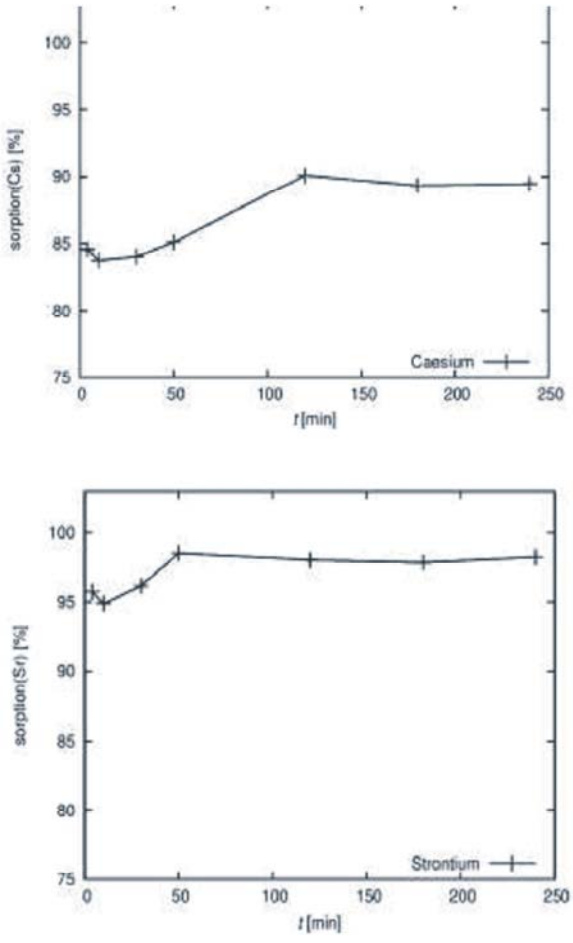


Fig. 4: Dependence of the sorption of Cs(I) (left) and Sr(II) (right) on contact time; V =1.5 ml; m=0.01 g; temperature 24 ºC.

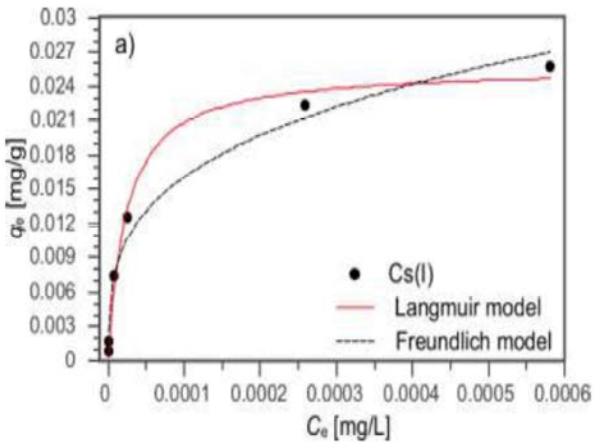


Fig. 5: Experimental data and Langmuir and Freundlich isotherms of Cs(I); V =1.5 ml; m=0.01 g; temperature24 ºC.

Table 2: Parameters for Langmuir and Freundlich models of Cs(I) adsorption on GO-polystyrene attemperature 24 ºC.

Langmuir model			Freundlich model		
*Q*max[mg/g]	*K*L [L/mol]	R2	*K*F [(mg/g)/(mg/L)1/n]	n	R2
0,026	43032	0,990	0,243	3,39	0,977

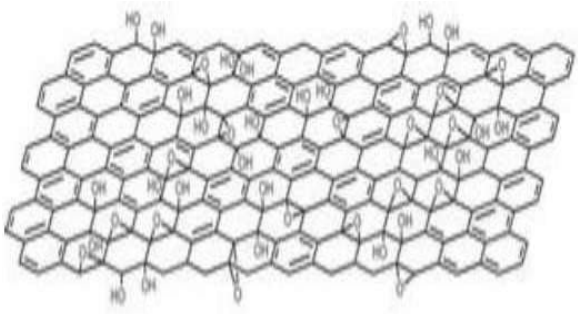
Fig. 5 demonstrated thatthe experimental data and Langmuir and Freundlich isotherms of Cs(I). Also data presented in Table 2demonstrated thatthe parameters of Langmuir and Freundlich models of Cs(I) adsorption on GO-polystyrene. Ascan be seen in Table 2, the adsorption of Cs(I) on GO-polystyrene can be better fitted by Langmuir model(R2=0.990) compared to Freundlich model (R_2=0.977). The maximum adsorption capacities (*q*max) ofGO-polystyrene calculated from Langmuir model at pH 4.0 and temperature 24 ºC were 0.026 mg/g for Cs(I).

How Graphene Oxide Works: The amphiphilic GO produces stable suspensions when dispersed in liquids6 and shows excellent sorption capacities. Previously it was shown that GO enables effective removal of Cu,10 Co and Cd,11 Eu,12 arsenate13 and organic solvents.14 The surface of GO is functionalized with epoxy, hydroxyl and carboxyl moieties; the formation and composition of GO has been extensively studied.7,8 The surface moieties are well-suited for interaction with cations and anions.

The fast sorption kinetics are likely due to GO's highly accessible surface area7, 8 and its lack of internal surfaces that usually contribute to the slow kinetics of diffusion in cation–sorbent interaction. The fast kinetics are important for practical applications of GO for removal of cationic impurities. GO has a high sorption capacity towards U, Sr, Am and Eucations as determined from the sorption isotherms. Even at a GO concentration as low as 0.038 g/L, the saturation limit is not reached.

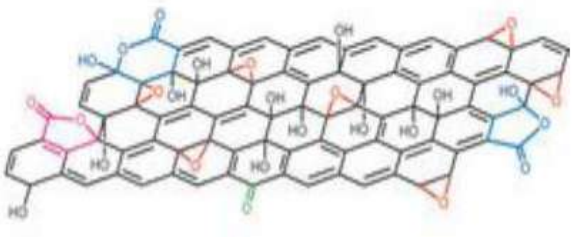
Low-valence ions such as in calcium and iron also adsorb onto GO's surface, but, unlike high-valence ions, they don't destabilize the suspension. That itself leads to the formation of stable complexes, completely immobilizing the cations. Thus for low-valence ions, adsorption is reversible and insignificant. Conveniently, anions such as chloride and carbonate, being negatively charged, are not attracted by GO, so neither of these species interferes with radionuclide adsorption.

b) Lerf-Klinowski model



a) The chemical structure of a single sheet of Graphene Oxide according to the Lerf–Klinowski model [15, 16].

a) Updated chemical structure proposed by Gao and colleagues



b) An updated chemical structure proposed by Gao and colleagues [17].

Fig. 6: Explain how graphene oxide works

The selectivity of heavy radioactive ion absorption by GO against lighter ions, the ones that yield water salinity, not only allows more effective concentration of radioactive materials into solids, the volume of which is the only price-determining factor in the radionuclide recycling process, but also allows their use in non-desalinated water, where many other sorbents fail.

CONCLUSION

This research hopes to find a less expensive and easier way of cleaning up radioactive accidents and leaks by demonstrating an ability of the GO to effectively and efficiently filter radionuclides from water sources such as rain water runoff or holding tank water.

GO demonstrated high sorption affinity towards the most toxicradionuclides from various solutions. GO is found to be muchmore effective when compared to bentonite clays or activated carbon in actinide removal from liquid nuclear wastes. TheGO-containing radionuclide could be easily coagulated andprecipitated. The simplicity of industrial scale-up of GO, itshigh sorption capacity and its ability to coagulate with cationsmakes it a promising new material for responsible radionuclidecontainment and remova Nanocomposite material GO-polystyrene have been successfully prepared by the direct emulsion polymerization of styrene in the presence of GO. The results (Table 1) demonstrates that GO-polystyrenehas enhanced sorption properties for Cs(I) and Sr(II) than polystyrene alone. The SEM demonstratesthe morphology of GO-polystyrene – spherical polystyrene particles with diameter of 100-200 nm covered byGO. The Langmuir isotherm better fit experimental data than Freundlich isotherm as illustrated in Fig. 3.The maximum sorption capacity of Cs(I) was determined from Langmuir isotherm – 0,026 mg/g.

The obtained data on the sorption kinetics have indicatedfast adsorption of CO^{2+}, Cu^{2+}, Pb^{2+} and Ni^{2+} after 5 min.

The equilibrium at the 90–100% level was reached after10–60 min of contact time. The kinetic studies have shownthat obtained data well fitted the pseudo-first-order equation.

Results obtained in this study have indicated that ahigher level of GO oxidation can provide a higher magnetiteloading and ensure insignificant pH variations andbetter sorption parameters for MGO. High variations in theuptake of studied elements depending on the pH requireadditional studies of sorption mechanisms.

REFERENCES

1. Vearrier, D., J.A. Curtis and M.I. Greenberg, 2009. Clin Toxicol (Phila). May; 47(5): 393-406. doi: 10.1080/15563650902997849. Review.
2. Romanchuk Ayu, A.S. Slesarev, StN Kalmykov, D.V. Kosynkin and J.M. Tour, 2013. Graphene oxide for effective radionuclide removal. Phys. Chem. Chem. Phys., 15: 2321-2327.
3. National Research Council, Ground Water and Soil Cleanup, National Academy Press, Washington, D.C., 1999.
4. Special Fukushima Review session. Goldschmidt 2011 Earth, Life and Fire, Prague, Czech Republic, August 14–19 (abstract published in Mineral Magazine 2011, 75(3)).
5. Novoselov, K.S., A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva and A.A. Firsov, 2004. Electric field effect in atomically thin carbon films. Science, 306: 666–669.
6. Mauter, M.S. and M. Elimelech, 2008. Environmental applications of carbon-based nanomaterials. Environ. Sci. Techn., 42(16): 5843-5859.
7. Zhu, Y., S. Murali, W. Cai, X. Li, J.W. Suk, J.R. Potts and R.S. Ruoff, 2010. Graphene and graphene oxide: synthesis, properties and applications. Adv Mater, 20: 1-19.
8. Ivanovskii, A.L., 2012. Graphene-based and graphene-like materials. Russ .Chem. Rev., 81:571-605.
9. Joshua Paul Concklin, May 2014, Radioactive Element Removal from Water Using Graphene Oxide (GO), An Undergraduate Research Scholars Thesis.
10. Kosynkin, D.V., G. Ceriotti, K.C. Wilson, J.R. Lomeda, J.T. Scorsone, A.D. Patel, J.E. Friedheim and J.M. Tour, 2012. ACS Appl. Mater. Interfaces, 4: 222-227.
11. Behabtu, N., J.R. Lomeda, M.J. Green, A.L. Higginbotham, A. Sinitskii, D.V. Kosynkin, D. Tsentalovich, A.N.G. Parra Vasquez, J. Schmidt, E. Kesselman, *et al*., 2010. Nat. Nanotechnol., 5: 406-411.
12. Stankovich, S., D.A. Dikin, G.H.B. Dommett, K.M. Kohlhaas, E.J. Zimney, E.A. Stach, R.D. Piner, S.T. Nguyen and R.S. Ruoff, 200. Nature, 442: 282-286.
13. Marcano, D.C., D.V. Kosynkin, J.M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L.B. Alemany, W. Lu and J.M. Tour, 2010. ACS Nano, 4: 4806-4814.
14. Dimiev, A., D.V. Kosynkin, L.B. Alemany, P. Chaguine and J.M. Tour, 2012. J. Am. Chem. Soc., 134: 2815-2822.
15. Anna, Yu. Romanchuk, Alexander S. Slesarev, Stepan N. Kalmykov, Dmitry V. Kosynkinz and James M. Tour, 2013. Graphene oxide for effective radionuclide removal.
16. Brynych Vojtìch, Kolαøovα Markéta, Pospìchovα Jana, Tolasz Jakub, Štengl Vαclav, Oct 14th - 16th 2015, Brno, Czech Republic, EU, Nanocon 2015.
17. Hummers, W.S. and R.E. Offeman, 1958. Preparation of Graphitic Oxide, J. Am. Chem. Soc., 80(6): 1339-1339.

18. Štengl, V., S. Bakardjieva, M. Bakardjiev, B. Štíbr and M. Kormunda, 2014. Carborane functionalized graphene oxide, a precursor for conductive self-assembled monolayers, Carbon N.Y., 67: 336-343.
19. Sunkara, H.B., J.M. Jethmalani and W.T. Ford, 1994. Synthesis of crosslinkedpoly (styrene-co-sodium styrenesulfonate) latexes, J. Polym. Sci. Part A Polym. Chem., 32(8): 1431-1435.
20. Wu, W., Y. Yang, H. Zhou, T. Ye, Z. Huang, R. Liu and Y. Kuang, 2013. Highly efficient removal of Cu (II) from aqueous solution byusinggraphene oxide. Water Air Soil Pol., 224: 1372-1378.
21. WenbaoJis, W. and S. Lu, 2014. Few-layered graphene oxides as superior adsorbents for the removal of Pb(II) ions from aqueous solutions. Korean J. Chem. Eng., 31(7): 1265-1270.
22. Xing, H.T., J.H. Chen, X. Sun, Y.H. Huang, Z.B. Su, S.R. Hu, W. Weng, S.X. Li, H.X. Guo, W.B. Wu, Y.S. He, F.M. Li and Y. Huang, 2015. NH2- rich polymer/graphene oxide use as a novel adsorbent for removal of Cu(II) from aqueous solution. Chem. Eng. J., 263: 280-289.
23. Sheng, G., S. Yang, J. Sheng, D. Zhao and X. Wang, 2011. Influence of solution chemistry on the removal of Ni(II) from aqueous solution to titanate nanotubes. Chem. Eng. J., 168: 178-182.
24. Sitko, R., E. Turek, B. Zawisza, E. Malicka, E. Talik, J. Heimann, A. Gagor, B. Feist and R. Wrzalik, 2013. Adsorption of divalent metal ions from aqueous solutions using graphene oxide. Dalton Trans, 42: 5682-5689.
25. Sun, Y., Q. Wang, C. Chen, X. Tan and X. Wang, 2012. Interaction between Eu(III) and graphene oxide nanosheets investigated by batch and extended X-ray absorption fine structure spectroscopy and by modeling techniques. Environ Sci. Technol., 46: 6020-6027.
26. Li, J., S. Zhang an C. Chen, 2012. Removal of Cu(II) and fulvic acid by graphene oxide nanosheets decorated with Fe3O4 nanoparticles. ACS Appl Mat Interf, 4(9): 4991-5000.
27. Hu, X.J., Y.G. Liu and H. Wang, 2013. Removal of Cu(II) ions from aqueous solution using sulfonated magnetic graphene oxide composite. Sep Purif Technol., 108: 189-195.
28. Nandi, D., T. Basu, S. Debnath, A.K. Ghosh, A. De and U.C. Ghosh, 2013. Mechanistic insight for the sorption of Cd(II) and Cu(II) from aqueous solution on magnetic mn-doped Fe(III) oxide nanoparticle implanted graphene. J. ChemEng Data, 58(10): 2809-2818.
29. Kumar, S., R.R. Nair, P.B. Pillai, S.N. Gupta, M.A.R. Iyengar and A.K. Sood, 2014. Grapheneoxide-MnFe2O4 magnetic nanohybrids for efficient removal of lead and arsenic from water. ACS Appl Mat Interf, 6: 17426-17436.
30. Zhang, Y., L. Yan and W. Xu, 2014. Adsorption of Pb(II) and Hg(II) from aqueous solution using magnetic CoFe2O4-reduced grapheme oxide. J. MolLiq, 191: 177-182.