Graphene oxide-polydimethylsiloxane based Lab-on-a-chip platform for heavy metals preconcentration and electrochemical detection

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Abstract

Herein we present the application of a novel graphene oxide – polydimethylsiloxane (GO-PDMS) composite in reversible adsorption/desorption including detection of heavy metals. GO-PDMS was fabricated by simple blending of GO with silicon monomer in presence of tetrahydrofuran, followed by polymerization initiated upon curing agent addition. We found GO concentration, curing agent concentration, pH and contact time among the most important factors affecting the adsorption of Pb(II) used as a model heavy metal. The mechanism of adsorption is based on surface complexation, where oxygen active groups of negative charge can bind with bivalent metal ions Me(II). In order to demonstrate a practical application of this material, we fabricated microfluidic Lab-on-a-chip platform for heavy metals preconcentration and detection. This device consists of a screen-printed carbon electrode, a PDMS chip, and a GO-PDMS chip. The use of GO-PDMS preconcentration platform significantly improves the sensitivity of electrochemical detection of heavy metals (an increase of current up to 30x was observed), without the need of modifying electrodes or special reagents addition. Therefore, samples being so far below the limit of detection (0.5 ppb) were successfully detected. This approach is compatible also with real samples (sea water) as ionic strength was found as indifferent for the adsorption process. To the best of our knowledge, GO-PDMS was used for the first time in sensing application. Moreover, due to mechanical resistance and outstanding durability, it can be used multiple times unlike other GO-based platforms for heavy metals adsorption.

Keywords

Graphene; polydimethylsiloxane; heavy metals; preconcentration; sensor; electrochemistry; nanocomposite

1. Introduction

Recent decades brought an incredible progress in the field of analytical chemistry allowing researchers to detect more compounds in a shorter time with a significantly lower limit of detection than ever before. Unfortunately, many of the hazardous compounds are present in nature in a very low concentration and as they interact with other compounds, their separation and detection are still challenging. One of the examples are heavy metals, considered as hazardous as they accumulate easily in live organisms, including animals and plants, as well

as due to their (bio)degradation which occurs to a very low extent. For example, cadmium can be accumulated in liver and kidney for more than 10 years seriously affecting human's health[1,2]. In the case of lead, its toxicity carries a risk of irreversible health effects. It can interfere with a number of body functions particularly the central nervous, hepatic, renal system and hematopoietic[3].

The presence of heavy metals in natural environments is caused both due to natural processes (i.e. aeolian process) and anthropogenic activities (rapid industrialization). For example, some common sources of lead contamination are leaded gasoline, industrial processes like coal combustion and lead smelting, lead-containing pipes, paints, solders and bearings[3,4]. Heavy metals from industrial wastes can migrate to water and soil leading to the pollution including inland and coastal ecosystems. As a result, heavy metals accumulate in live organisms, both plants and animals, posing a risk for consumers[5,6].

Analytical laboratories usually use atomic absorption spectroscopy (AAS)[7], flame atomic absorption spectrometry (FAAS)[8], energy dispersive X-ray fluorescence (EDXRF)[9] or mass spectroscopy (MS)[10] for heavy metals determination. Those techniques provide very good sensitivity and accuracy but on the other hand, generate a high single cost of analysis and require sophisticated equipment that can be used only by very well trained personnel. For this reason, there is a strong need of simple sensors development that can perform sensitive and accurate measurements but are cheaper and easier to use in the laboratory as well as in-field. Of special interest is the use of macro, micro and nanomaterials-based tools and strategies for heavy metals (HM) detection[11]. Various classes of sensors are already reported such as optical, electrochemical, ion-selective and piezoelectric. Most of them are based on electrochemistry either using (bio)sensing approach for example, interaction of HM with nucleic acids, proteins or enzymes[5,11-16].

Direct detection of heavy metals can be performed using Anodic Stripping Voltammetry, as certain metals are oxidized at specific voltage that can be used for their determination. Square wave anodic stripping voltammetry is very sensitive, as the accumulation step is performed so metals are reduced onto the working electrode surface[17,18]. This method is also compatible with screen-printed electrodes which are the most promising tools (transducers) in novel sensors due to the low cost, easy fabrication process and possibility to perform a surface modification, as well as integration with various devices and platforms. Although stripping voltammetry is one of the best electrochemical techniques for HM measurements, its sensitivity may be altered because many compounds may affect the final performance. Thus,

detection of heavy metals in complex samples such as seawater (due to high salt content and therefore matrix interference) might be more complicated and requires sample pretreatment or some preconcentration method to be included. Analytical techniques equipped with preconcentration step are more accurate as allow to detect heavy metals present in real samples at very low concentration (ppb). Preconcentration is based on the interaction between the target compound and adsorbent. In order to release the preconcentrated analyte, the elution buffer is used. This means that the final sample being detected is partially purified (does not contain compounds having no affinity to adsorbent) and contains a multiplied amount of target analyte. Due to that, a better sensitivity and limit of detection can be obtained[4,11, 19-21].

Various materials have been reported recently as effective adsorbents of heavy metals. One of the most common is activated carbon which is well known for its adsorption properties and can be obtained from cheap and abundant materials. For example, heavy metals adsorption using activated carbon made of palm shell[22], coir pitch[23], saffron leaves[24] or nut shell[25] is already reported. Activated carbon is suitable for further modification such as sulfurization. Tajar et al. used SO_2 for activated carbon sulfurization and observed an increased adsorption capacity towards Cd(II) comparing to unmodified activated carbon[25].

Simultaneously, graphene and its derivatives are especially attractive for scientists recently. Sitko et al. investigated the adsorptive properties of graphene oxide (GO) towards divalent metal ions. It was found that a strong adsorption occurs in a wide range of pH: 3–7 for Cu(II), 5–8 for Zn(II), 4–8 for Cd(II), 3–7 for Pb(II). All of the studied metals compete with each other to bind onto GO surface, with Pb(II) having the highest and Zn(II) the lowest affinity. The mechanism of the adsorption involves surface complexation of metal ions with the oxygen-containing groups on the surface of GO[26]. Same research group used GO/cellulose membranes to evaluate heavy metals adsorption in a more convenient way. The platform showed good adsorption performance as well as reusability up to more than 10 cycles of adsorption and desorption[27].

Another interesting approach reported by Wu et al. used 3D sulfonated reduced graphene oxide (3D-SRGO) with very high adsorption capacity of 234.8 mg/g towards Cu(II)[28]. Hallaj et al. used exfoliated graphene nanosheets for Cd(II) adsorption performed in ultrasonic bath[29].

As can be seen, there are many materials with excellent adsorption properties but unfortunately, in most cases, the use of them requires membrane-based systems or centrifugal separation of the adsorbent from the solution. In some cases, such approaches are quite

impractical, especially taking into account the need of special equipment and additional work. In this case, the use of Graphene/Polymer composites might be more promising, as polymeric composites are more flexible and can be used for microdevices fabrication such as Lab-on-a-chip. Moreover, the use of elastomers provides mechanical resistance and durability, what is very important taking into account reusability of the preconcentration system[52].

Polymer composites consist of two components: nanofiller – a nanomaterial which is in-built in polymer structure; polymer – which defines the main physicochemical properties of the composite[30]. So far, various polymers were employed as matrices to fabricate graphene-based composite. Poly(vinyl alcohol)[31], epoxy[32], Polystyrene[33], Polypropylene[34], Poly(methyl metacrylate)[35], Polyimide[36] and Polycarbonate[37] are some of them.

The main advantage of graphene comparing with other carbon nanomaterials (such as Carbon Nanotubes) is a high surface-to-volume ratio. Graphene can tune many properties of polymers as well as enrich these with the new ones. Therefore, an access to many applications in the field of novel materials, electronics, biosensors and medicine is possible[38-50,57-58]. This applies as well to GO used in our work. For example, there are many reports of using GO as a nanofiller as it influences Young's modulus and composite's stiffness. The presence of reactive hydroxyl and epoxy group on its surface facilitate solubility and reactivity with the polymer matrix, unlike pure Graphene which tends to stack due to Van der Waals interactions[11,41-43].

There are several ways of Graphene/Polymer composite preparation. The most common are based on the use of GO that is simply blended with a polymer matrix and let for curing/polymerization afterward. In a case of more sophisticated modification, a proper graphene derivative is prepared first and then blended with polymer matrix[39,51].

The relative simplicity of Graphene/Polymer composite preparation is the main motivation of using it instead of particle- or membrane-based adsorption materials for heavy metals preconcentration. In this work, a GO-PDMS composite was developed with the purpose of Lab-on-a-Chip device fabrication. The use of Lab-on-a-chip platforms due to their small size and flexibility might be a solution to provide a preconcentration system of heavy metals combined with simultaneous detection. Apart from that, as flow-based devices, Lab-on-a-chip platforms can be fully automated so the parameters can be well controlled and less workforce is required.

In our previous work an rGO-PDMS composite was used for effective removal of polybrominated diphenyl ethers. The mechanism was based on π-π stacking between rGO

aromatic rings and PBDE[52]. In a case of heavy metals (or any bivalent metals) interaction with graphene is due to surface complexation, as metals have an affinity to oxygen groups richly present on GO surface, unlike rGO[53].

The developed device consist of three layers: GO-PDMS channel, where preconcentration is performed, PDMS channel, where detection is performed and screen-printed electrode where heavy metals are deposited and detected using anodic stripping voltammetry. As a proof of concept, we worked with Pb(II) as an example of the hazardous heavy metal being toxic and able to accumulate in water, soil and live organisms.

2. Experimental section

2.1 Reagents

Isopropyl alcohol, tetrahydrofuran, ethanol, acetone, 3-aminopropyltriethoxylane (APTES) and heavy metals standard solution TraceCERT® was purchased from Sigma. The screen-printed inks (carbon sensor paste C2030519P4 and silver-silver chloride paste C2130809D5) were purchased from Gwent Group, United Kingdom. Polycarbonate sheets were purchased from Vink Plastics S.L.U., Spain. Sylgard® 184 Elastomer kit containing silicon monomer and curing agent solution was purchased from Ellsworth Adhesives Iberica, Spain. Graphene Oxide stock solution (5 mg/mL) was purchased from Angstron Materials (Dayton, USA). All commercial reagents were of analytical grade and handled according to the material safety data sheets suggested by the suppliers.

2.2 System operation

Presented approach is based on a multilayer Lab-on-a-chip platform (LOC) that consists of a) screen-printed carbon electrode printed on polycarbonate sheet; b) PDMS microfluidic chip bonded with an electrode; c) GO-PDMS chips containing a network of serpentine channels, connected vertically with PDMS layer. Samples are passing through the LOC starting in GO-

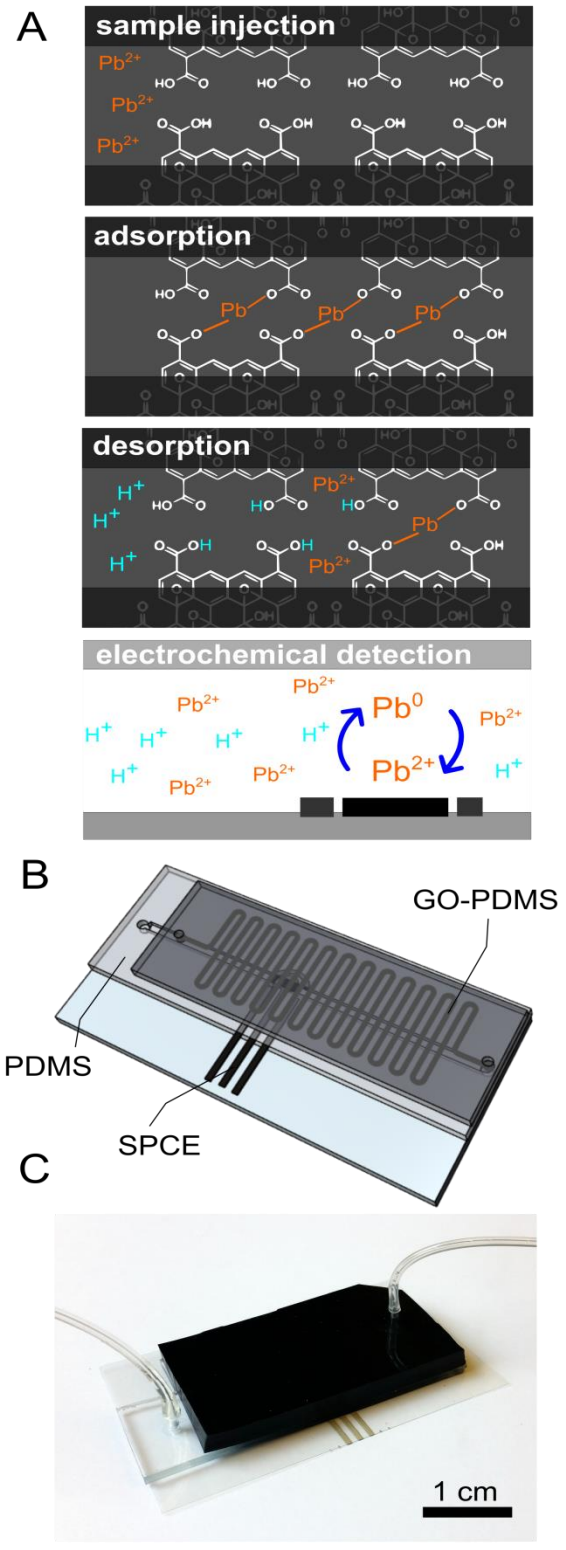

Fig. 1 LOC system for heavy metals preconcentration. A. Reactions occurring in the chip: Pb(II) is adsorbed to GO-PDMS; 0.1 M HCl is injected in order to perform desorption and detection. A sample is passing from GO-PDMS chip to PDMS electrochemical chip, where the SW-ASV is performed; B. Design of the platform; the scheme of the GO-PDMS chip and PDMS chip. C. Image of the full LOC device with polymeric tubes connected to the inlet and outlet.

PDMS layer where heavy metals are

adsorbed to graphene oxide molecules via surface complexation. This allows performing a preconcentration of the heavy metals using the sample of desired volumes and pump (peristaltic or syringe) as a driving unit of the given flow rate. After this step, desorption buffer is introduced (0.1 M HCl), so previously adsorbed heavy metals are released from the surface and move to the detection chip where the process of electrochemical deposition is already going on. As the same buffer is used for desorption and detection, those steps occur subsequently. As a result, sensitive electrochemical detection with inbuilt preconcentrated platform can be performed (Fig.1.).

2.3 Fabrication and assembling of Lab-on-a-Chip platform

2.3.1 Fabrication of the microfluidic mold. The microfluidic mold was fabricated following the same procedure as in[52,54]. The design of the LOC platform is shown in Fig. 1 and the dimensions of the microfluidic channels of GO-PDMS in Fig. 2. GO-PDMS chips contain channels with extra curvatures in the initial part. This support the diffusion as the laminar flow is rendered impossible.

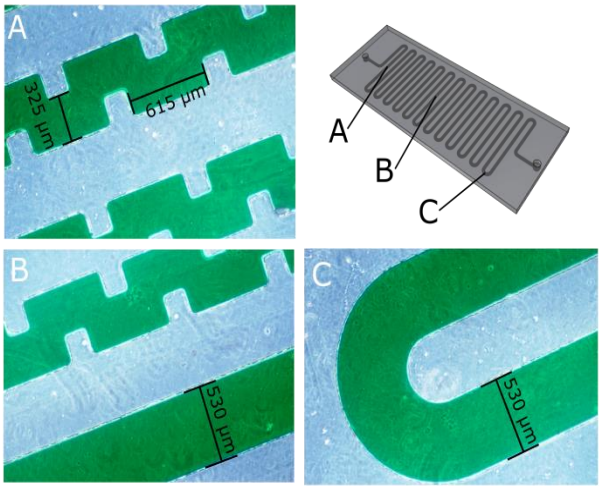

Fig. 2 Microfluidic channels of the GO-PDMS chip. Using a mold dedicated to GO-PDMS chip, a PDMS chip was fabricated to ensure transparency. A green ink was introduced to visualize the geometry of the channels which dimensions were measured using optical microscope (4x magnification). A- inlet section of the chip, B- middle section , C – outlet section.

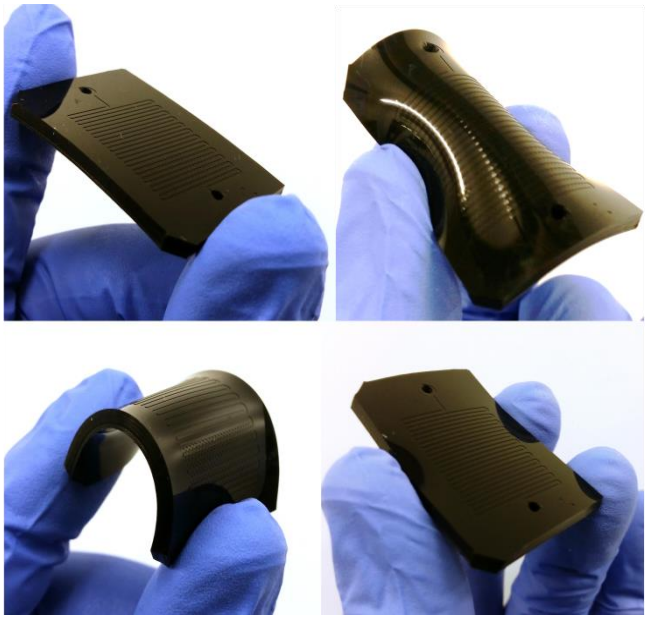

Fig. 3 GO-PDMS chip. Despite the high content of GO, the composite maintains typical physical properties of PDMS like mechanical durability and elasticity.

2.3.2 Fabrication of the GO-PDMS composite. GO-PDMS was prepared according to the following protocol. 40 mL of 5 mg/mL GO solution was mixed with 15 mL of tetrahydrofuran (THF) and sonicated (QSonica sonicator) for 20 minutes. Meanwhile, 20 g of silicon monomer solution was mixed with 10 mL of THF. Both parts were stirred together and sonicated another 1 hour (90% amplitude, pulse mode). After that, a composite was placed on

the hotplate with magnetic stirring and stirred for 24 hours at 70 ºC until the whole solvent evaporates. This can be visually inspected as the composite containing solvent is brownish-opaque while the well-prepared one is glossy and translucent. After cooling down, a curing agent solution (silicon resin) is added, following the mass ratio 10:1 (silicon monomer : curing agent). The material is stirred vigorously for about 10 minutes and air bubbles are removed using a vacuum. As polymerization occurring, PDMS is cross-linked with GO molecules. Afterwards, the GO-PDMS is poured onto silicon mold with the shape of serpentine channels (50 cm total length, 530 µm width, 100 µm height, 27 cm^2 active surface) and kept at room temperature for 1 hour, protected in a plastic petri dish. Then the composite is transferred onto 70 ºC hotplate for about 3-4 hours until completely polymerized (Fig. 3).

2.3.3 PDMS preparation. A monomer solution was mixed with a curing agent solution (silicon resin) in the mass ratio 10:1. After intensive stirring for 5 minutes, an excess of air bubbles was removed using a vacuum. Afterward, PDMS was poured onto Si wafer mold with a given design of microfluidic chip and kept on the hotplate, 70 ºC, for 3 hours until completely polymerized.

2.3.4 Screen-printed electrodes. Screen-printed carbon electrodes (SPCE) were fabricated by screen-printing technology using a screen-printer (DEK 248, UK). Electrochemical measurements were carried out using computer-controlled Autolab PGSTAT-12 (302 N-High performance) (potentiostat/galvanostat) with general-purposes electrochemical software operating system (GPES version 4.9.007, from Eco Chemie B.V., Utrecht, The Netherlands).

2.3.5 LOC device assembling. Chips of GO-PDMS and PDMS were cut out from the mold and inlet/outlet was made using biopsy puncher (1.5 mm diameter). In order to get rid of impurities, samples were washed in miliQ water, followed by isopropanol and dried on the hotplate 70 ºC for 10 minutes. In order to reduce the hydrophobicity of the surface, oxygen plasma treatment (Harrick Plasma) was performed. The same treatment was performed on screen-printed electrodes which surface was previously modified using APTES and commonly known protocol[55].

Assembling was performed by placing PDMS layer onto electrode and GO-PDMS onto PDMS. The outlet of the GO-PDMS layer was centered in the same position as the inlet of PDMS layer. Bonded device was kept in 70 °C on the hotplate for another 30 min so as to

strengthen the bonding. Polymeric tubes were connected to the inlet and outlet of LOC platform as well as to the pump.

2.4 Electrochemical detection of heavy metals

During preliminary experiments, commercial Bismuth electrodes were used for the sensitive detection of heavy metals (Gwent Group, United Kingdom). Measurements were performed by dropping 150 µL of the sample onto the electrode surface. As a detection technique, square wave anodic stripping voltammetry (SWASV) was used. Parameters were as follows: deposition potential -1.2 V, deposition time 230 s, equilibration time 10, Frequency 25 Hz, step potential 0.006 V, amplitude 0.03 V, potential range from -1.4 V to 0.0V. 0.1 M HCl was used for detection. Each measurement was repeated 3 times.

In the final approach, microfluidic chips with integrated home-made SPCE electrodes were connected to the Autolab PGSTAT-12 with a specially adapted electrical edge connector. The same electrochemical technique was used with slightly different parameters: deposition potential -1.2 V, deposition time 120 s, equilibration time 30 s, Frequency –25 Hz, step potential 0.006 V, amplitude 0.03 V, potential range from -1.4V to 0.0V. Unless otherwise indicated, 0.1 M HCl was used for detection and the flow rate was 0.5 mL/min. Each measurement was repeated 3 times.

2.5 Adsorption studies

All the parameters regarding GO-PDMS composition, as well as the influence of the external factors were optimized toward an adsorption ability of the standard solution containing 250 ppb of Pb^{2+} in water. A sample of this concentration has a pH=7 so further adjustments were not performed. In selected tests where the effect of pH was tested 1 M HCl or 1 M $NH_3 \cdot H_2O$ was used for adjustment.

As a proof of concept, using a biopsy puncher, a cylindrical shape GO-PDMS pieces were cut out. Their surface area was about 0.5 cm^2. Depending on the experiment, a different number of GO-PDMS pieces were immersed in 1 mL of Pb^{2+} standard solution in 2 mL Eppendorf tubes and shake for 2h (unless otherwise stated) with 500 rpm on thermoshaker in a constant temperature of 25 °C.

After the incubation, 100 µL of the sample was collected and mixed with 900 µL of HCl so as to obtain a final concentration of 0.1 M HCl. In a case of the highly concentrated Pb^{2+} samples which are out of the linear detection range, further dilutions were applied accordingly.

In each case, a control experiment was run, using the same type of Eppendorf, same initial concentration, but no GO-PDMS placed in it. This was used for the relative adsorption calculation.

Adsorption was expressed as a relative decrease of the concentration in comparison to the control samples. Concentration was calculated using a calibration curve (Electronic Supplementary Information (ESI)). A general formula was as follows:

$A_{Pb2+} = [(C_0 - C_1)/C_0]*100\%$

Where C_0 is the initial concentration of the Pb^{2+} (250 ppb usually), C_1 is the concentration of Pb^{2+} measured after the experiment.

In order to study the recovery of the GO-PDMS composite, desorption experiments were performed. Samples after standard adsorption assay were washed 3-times with miliQ water in order to remove an unbound and excessive Pb^{2+} solution. After drying, a given desorption buffer was added (usually 0.1 M HCl). Standard desorption experiments took 2 hours, using shaker similarly as for the adsorption studies. Measurements were performed analogically providing adequate dilutions. A relative desorption was calculated using the following formula:

$D_{Pb}{}^{2+} = [C_D/(C_0 - C_1)]*100\%$

Where C_D is the concentration of the Pb^{2+} found in a sample after recovery experiment. As it can be seen, desorption is calculated as regards of previously adsorbed metal. This means, that a % of desorption can be higher than % of adsorption.

2.6 On-chip preconcentration of heavy metals

Experiments with LOC device were performed using peristaltic pump as a driving unit. A LOC device consists of screen-printed electrode, PDMS chip and GO-PDMS chip. All elements are connected through the microfluidic channels. Sample containing metals to be adsorbed is passing through GO-PDMS. The direction of the flow (1 mL/min) is changed every 30 s so as to ensure the best catchment of the metals from a given sample. Unless otherwise stated, a dynamic incubation with the metal-containing solution took 30 minutes. Afterwards, a sample is withdrawn from the chip and 0.1 M HCl is introduced with the flow rate of 1 mL/min. Similarly as during preconcentration, the flow is moved back and forward. Once desorption is finished, the flow rate is slowed down to 0.5 mL/min and moved towards electrode. At this moment an electrochemical deposition is already going on. After 120 s, an electrochemical stripping is performed.

3. Results and discussion

3.1 Optimization of the GO-PDMS performance

GO-PDMS is made of Graphene Oxide suspension mixed with silicon monomer followed by silicon curing agent addition. PDMS itself is neutral and does not have a negative charge that could attract bivalent metals to its surface. But an important factor is a curing agent, playing a role of catalyser, allowing silicon monomers to polymerize. We evaluated the influence of the composite composition on adsorption. As it shows in Fig. 4A, the more curing agent added, the lower adsorption is observed.

As mentioned before, in this approach dependence between adsorbent mass and adsorption yield is not relevant. Thus, an effect of the total adsorptive surface was studied. It can be seen the increase of adsorption proportional to the increase of GO-PDMS surface (proportional to the number of cylindrical GO-PDMS pieces immersed in the tested solution). In this proof of concept test (Fig. 4B) a maximum adsorption was achieved for the surface of 15 cm^2 of GO-PDMS (using 10 mg/g GO in PDMS).

Another crucial factor is the concentration of GO in PDMS. It can be seen (Fig. 4C) that if the concentration of GO is lower than 2 mg/g PDMS the adsorption actually does not occur. Most probably at this point, all the GO reacts with PDMS so there are no free oxygen groups that could interact with bivalent metals. For higher concentration, there is a significant increase of adsorption ability having the maximum for GO=10 mg/g PDMS. Further increase of the GO content does not improve adsorption performance as probably the inhibition of the polymerization is more likely to occur. We have observed very inconsistent results for highly concentrated GO-PDMS. For this reason, a 10 mg/g PDMS was maintained as the best concentration to be used.

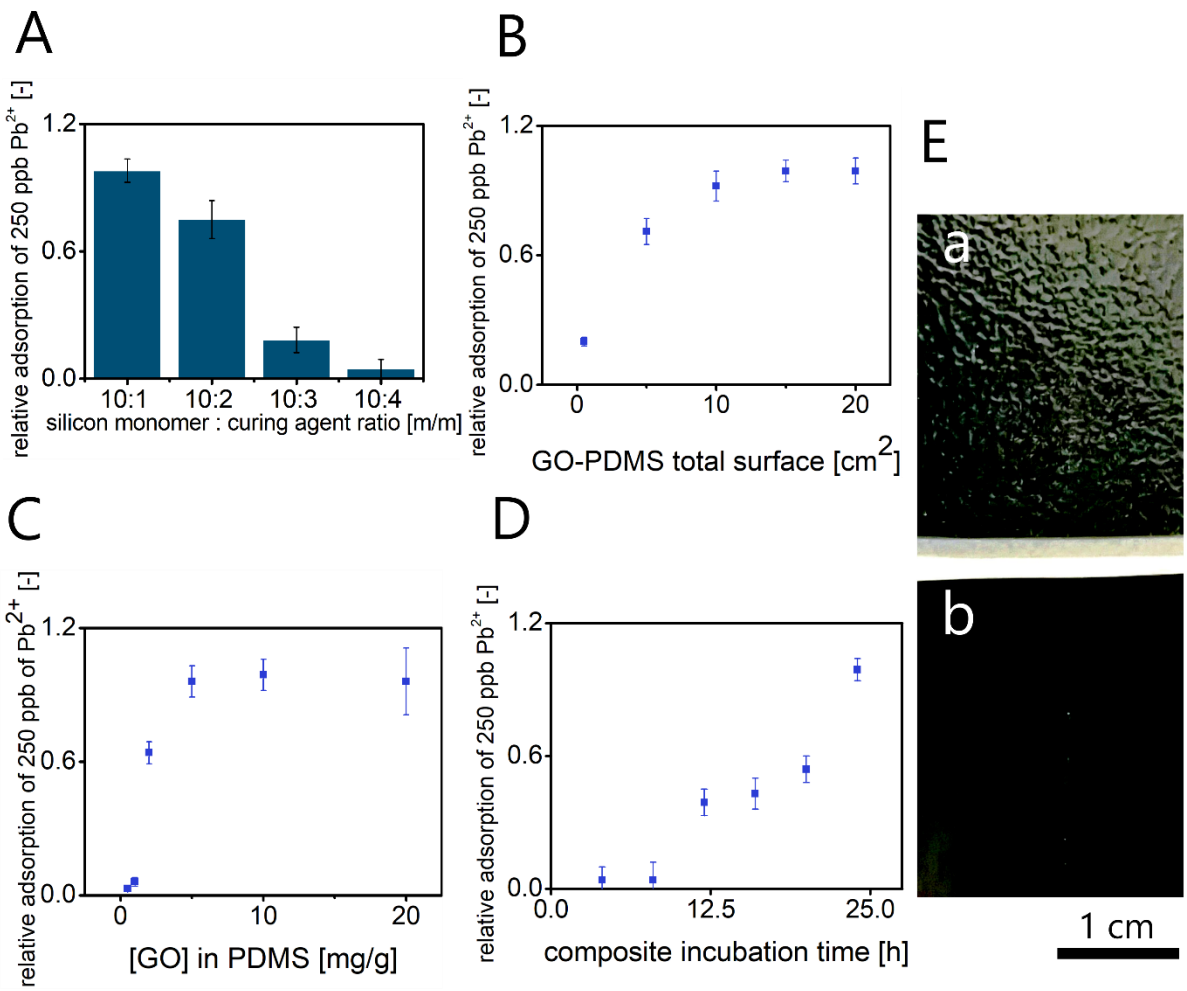

Fig. 4 GO-PDMS parameters affecting adsorption ability. A. Mass ratio of silicon monomer:curing agent; B. Total surface of GO-PDMS in contact with sample; C. GO concentration in PDMS; D. Effect on composite incubation time (solvent evaporation); E. Composite quality a. example of 12 h evaporation with visible inhomogeneity, b. example of 24 h evaporation with visible, homogenous GO-PDMS.

During the composite preparation, PDMS and GO are dissolved in THF and stirred on the hotplate until the solvent is evaporated. This process has an important influence on the GO-PDMS performance. If there is no full evaporation, a GO, as hydrophilic, is more likely to agglomerate within water droplets. Such composite is not homogenous, neither translucent and its surface shows an irregular distribution of GO as well as air bubbles. It was found that a mandatory time for an efficient adsorption is at least 24h incubation on the hotplate (Fig. 4D). A shorter time, but with the increased temperature (>100 °C) led to possibly partial reduction of the GO (a significant blacking of the composite is observed; data not shown), thus this approach was not furtherly considered.

3.2 Optimization of external factors affecting adsorption

3.2.1 Initial pretreatment. Although the process of GO-PDMS composite synthesis is quite simple and does not involve many chemicals, it is important to perform an initial treatment of the material before running an adsorption experiment, so as to ensure the lack of contamination that would possibly affect adsorption ability.

We found alkaline-treatment as the most efficient, allowing reaching nearly double adsorption yield comparing to acid or isopropanol treatment. If the GO-PDMS is contaminated with acid residues, in presence of base a neutralization reaction occurs. On the other hand, any cation possibly blocking the active surface of GO will be released because it reacts with negatively charged OH^- groups. One of the possible sources of contamination is PDMS itself, as it may contain traces of metals. Although in a very low concentration, during the 24h incubation (GO-PDMS preparation) some metal traces can react with oxygen active groups of GO leading to the decrease of available surface of the adsorbent. Apart from that, it was observed that the oxygen plasma treatment does not cause any change in the adsorption ability (Fig. 4A).

3.2.2 Initial concentration. As it can be predicted, lower initial concentration results in higher adsorption yield at a certain point of time. We evaluated the adsorption performance of GO-PDMS in the range 62.5-2000 ppb (Fig. 5B). It can be seen that a full adsorption is observed for the concentrations ≤250 ppb, while for the 2000 ppb almost does not occur. This can be explained mainly by the adsorbent surface capacity insufficient for such amount of metal. Moreover, highly concentrated Pb^{2+} samples were adjusted to the neutral pH=7 (so as to not introduce another variable in the experiment). This means the presence of some extra NH_4^+ ions that may interact with Pb creating an ammonia complex $Pb(NH_3)^{2+}$, $Pb(NH_3)_2^{2+}$, $Pb(NH_3)_3^{2+}$, as suggested in[56]. Nevertheless such a big concentration (2000 ppb) is practically never present in real conditions.

3.2.3 Contact/incubation time. A general assumption that an increase of contact/incubation time causes an increase of heavy metals adsorption was confirmed. As it is shown in Fig. 5C, during the first 15 minutes of the process, adsorption occurs very quickly. After that, the process significantly slows down and the maximum occurs after less than 3 hours so the further adsorption is no longer observed. It is important to take into account that the incubation time depends on the amount of adsorbent, volume of the sample as well as initial concentration. Thus, in different conditions, other values can be obtained. Nevertheless, it does not affect the kinetic profile of the adsorption process, where most of the lead present in the sample is adsorbed at the beginning of the process.

3.2.4 pH. The major mechanism of metals adsorption to GO is surface complexation. Thus, ionic composition and metals present in the solution affect the adsorption efficiency, kinetics as well as affinity. We have analyzed the effect of pH on Pb^{2+} adsorption in the range 2-12 (Fig. 5D). It can be observed that adsorption grows gradually together with the increase of the pH reaching maximum at pH=7. At pH 11-12 a significant decrease of adsorption is observed. This is in accordance with the works of Dowlatshahi et al.[24] and Gaya et al.[22] where the highest adsorption of Pb^{2+} was observed in pH=7. On the other hand, Sitko et al. reported pH=4 as the optimal for Pb^{2+} [26] and pH=5 when GO is immobilized onto cellulose membrane[27]. This may suggest that in our case, the presence of PDMS in composite affects the adsorption performance and shifts its maximum toward higher pH. That may result from the number of oxygen functional groups that is lower where GO is entrapped within PDMS.

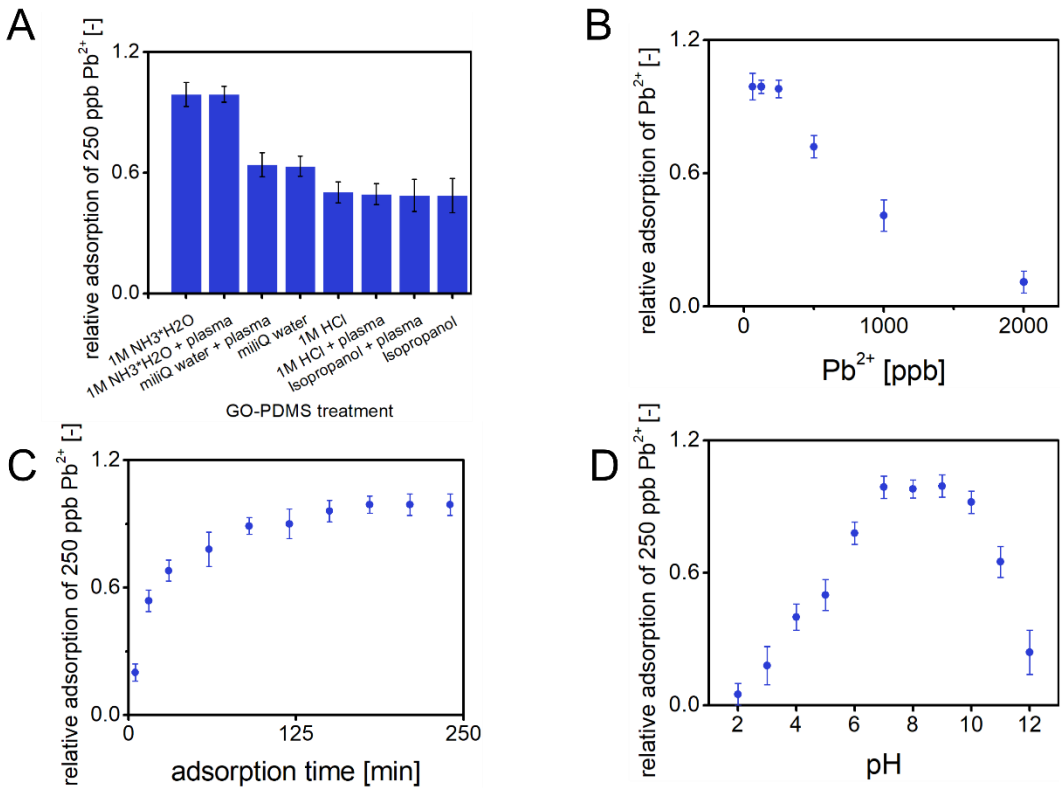

Fig. 5 Selected parameters affecting adsorption ability. A. Initial treatment of the GO-PDMS surface; B. Initial concentration of Pb^{2+}; C. Contact time between GO-PDMS and Pb^{2+}; D. pH of the Pb^{2+} solution.

Such behaviour can be explained taking into account two issues: protonation of the oxygen functional group of GO and the form in which metal is present in the solution. In highly alkaline solution metals precipitate as $Me(OH)_m^{n-}$ hydroxides which have no longer affinity to GO surface due to a negative charge. Lower pH maintains metals predominantly in cationic

form (Me^{2+}) thus, they are chemically active. Highly acidic pH, on the other hand, means that oxygen groups of GO are protonated so metals compete with hydrogen ions to be adsorbed. According to literature, for the pH <3.9 GO has a low negative charge, while for the pH>3.9 the charge is getting highly negative and from this point, the best conditions for metal adsorption shall have occurred[27, 53].

3.3 Desorption

The ability of GO-PDMS to reversibly adsorb and desorb metals is very crucial from the point of practical application of this material (preconcentration and detection). In principle, any acidic solution should cause metal's desorption as H^+ ions compete with bivalent metals, such as Pb^{2+} to be bonded with GO surface so the metal displacement reaction can be observed. For the desorption of bivalent ions from carbon materials, various chemicals were reported until now. For 3D-SRGO HNO_3 pH<1 was found as the most efficient leaching solutions[28]. 0.1 M HNO_3 was used by Sitko et al. for Pb desorption from Graphene oxide/cellulose membranes[27]. Hallaj et al. studied the desorption of Cd^{2+} from exfoliated graphene nanosheets and found 0.1 M HCl as more efficient (99.12% of recovery) comparing with 0.1 M HNO_3 (78.7% of recovery)[29]. HCl had also the best desorption performance (comparing with H_2SO_4 and HNO_3) in the case of Cd^{2+} desorption from the sulfurized activated carbon[25]. In our case, HCl in different concentrations was tested (Fig. 6A). We found that 1 M HCl desorbs Pb^{2+} more effectively than 0.1 M. However, adjusting the proper time of desorption allow to match an appropriate reagent for the desorption. The maximum recovery for 1 M HCl was 98.96% while for 0.1 M HCl 98.58%. In our case 0.1 M HCl is more attractive as it can be used directly for electrochemical detection of heavy metals in LOC platform. This means that within one step a desorption and subsequent detection might be performed.

3.4 GO-PDMS reusability

One of the most important requirements for an adsorbent is its reusability. We performed several cycles of adsorption and desorption within different days (Fig. 6B). To highlight the importance of surface pretreatment we compared GO-PDMS pre-treated with $NH_3 \cdot H_2O$ with GO-PDMS rinsed only with miliQ water (after the desorption process). It can be clearly seen that the pre-treated surface shows a full adsorption capacity and can be re-used at least several times without the loss of performance. Same happens in the case of desorption ability. In the case of non-treated GO-PDMS after the first adsorption-desorption cycle, the material loose nearly 50% of adsorption capacity and it cannot be well recovered.

It is worthy to mention that the important advantage of this composite is a big resistance toward chemical and physical factors. PDMS provided mechanical strength and durability (Fig. 3), as well as it is not affected by concentrated acid or bases treatment. This shows the opportunity to use this device for multiple uses rather than single applications. Apart from that, GO-PDMS chains are able to diffuse from the bulk to the surface of the composite. This means that the composite might be considered as a self-healing to a certain degree[59].

Although a good approach to surface recovery was showed, to extend the viability of GO-PDMS it should be stored under protected atmosphere, like i.e. vacuum bags. This will protect the surface from the macroscopic impurities that are easily attracted due to the hydrophobicity of the PDMS.

3.5 Adsorption in seawater and interferences

We evaluated the effect of seawater (sample preparation described in Electronic Supplementary Information (ESI)) as an example of real sample and high ionic strength solution simultaneously (Fig. 6C). It was found that 250 ppb Pb added to samples was nearly fully adsorbed to GO-PDMS surface (>98.5%). In case of desorption, 96.9% and 98.1% of adsorbed Pb was recovered for 100% and 50% seawater solution respectively. This is in accordance with other works where the adsorption process was indifferent to ionic strength using GO as an adsorbent[27,53].

Although the capacity of GO-PDMS is big enough to adsorb spiked Pb as well as other metals present in real samples, such complexed matrix might be difficult to analyse using SW-ASV. As it shows in Fig. 6C spiked seawater (before adsorption) shows significant background current that results from the presence of various ions, salts and organic compounds. The peak of Pb is shifted and slightly flattened. This reduce the sensitivity of technique, as if more than one HM is present in sample, there is a big risk of peaks overlapping. However, after the adsorption and subsequent desorption we can observe the peak of Pb with much lower baseline, therefore with lower background current. This means that the use of GO-PDMS platform allow to purify sample from the possible impurities that affect measurements. This applies especially to either negatively-charged or neutral compounds that cannot be bonded to GO-PDMS via surface complexation but may non-specifically affect the process of electrochemical detection.

We also tested the difference between the adsorption of single metal Pb(II) and the mixture of Pb(II) and Cu(II). The results are shown in Table S2. of Supporting Information. It was found that both metals are fully adsorbed when alone, but the mixture of 100 ppb

Cu(II)+Pb(II) shows that lead has higher affinity to GO surface comparing to copper. This is in accordance with other works, as the adsorption of metals is correlated with the first stability constant of the associated metal hydroxide or acetate[26,27,60].

3.6 Lead preconcentration in LOC device

3.6.1 The effect of the flow rate. The flow rate is one of the most important factors affecting any process in a microfluidic chip. However in the range of the flow rates that we evaluated (0.2-2 mL/min) the differences were not that significant (data not shown), thus we used 1 mL/min as a standard flow rate for the experiments. The use of higher flow rate was impossible as the generated pressure was too high leading to the disruption of the bonding between chips layers.

Inherently the crucial factor is the contact time and this depends on the flow rate. In the case of 1 mL samples and the flow rate of 1 mL/min within 1 minute, the whole sample will

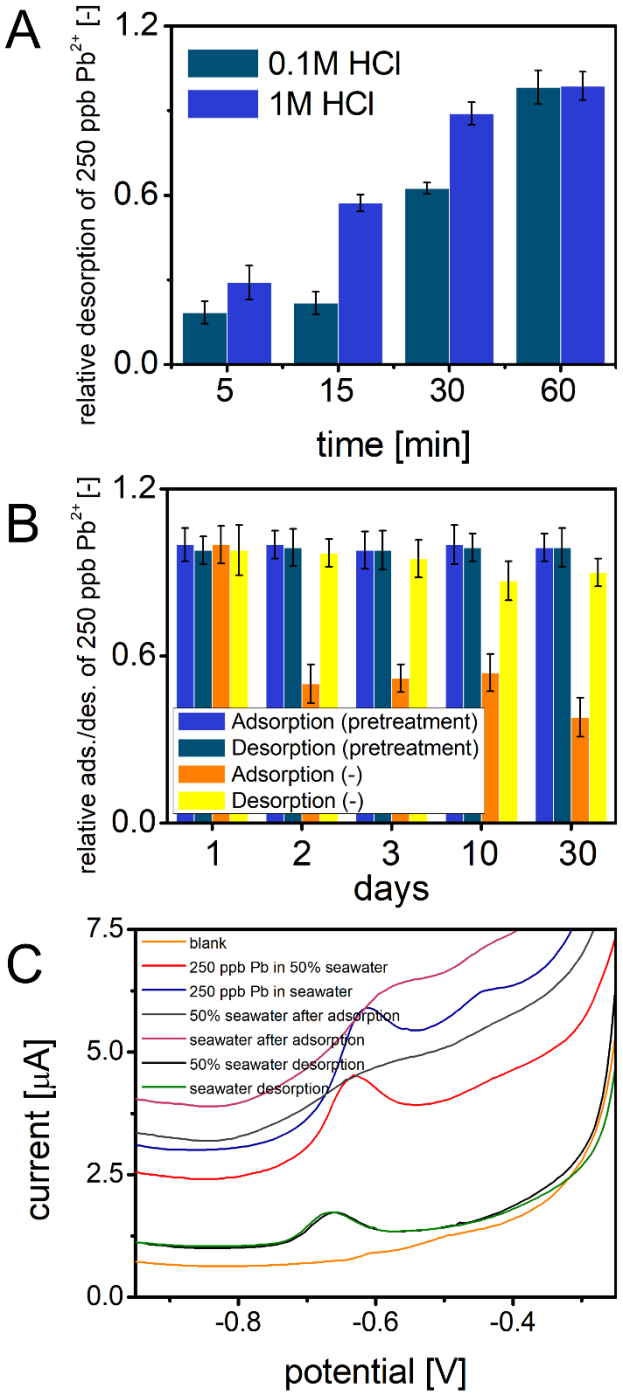

Fig. 6 A. Desorption of Pb^{2+} from GO-PDMS Surface using 0.1 M and 1 M HCl; B. Adsorption/desorption cycles performed in different days using non-treated and pre-treated ($NH_3 \cdot H_2O$) GO-PDMS; C. Effect of sea water (ionic strength) on adsorption and recovery.

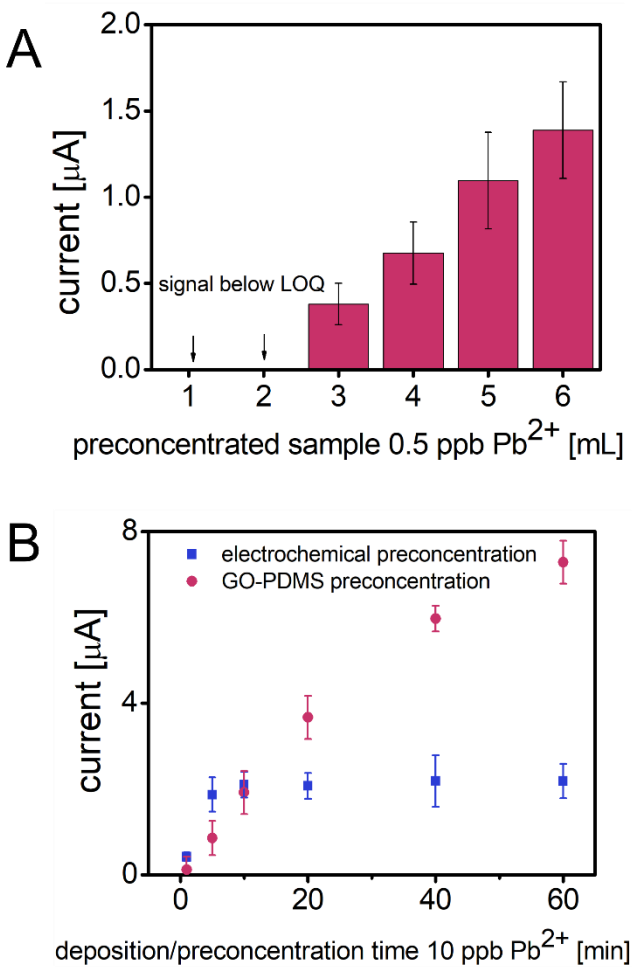

Fig. 7 On-chip preconcentration and detection of the Pb(II). A. The effect of the volume to be adsorbed (0.5 ppb Pb^{2+}) using the constant flow rate 1 mL/min and t=30 min; B. Comparison of the electrochemical and GO-based preconcentration of 10 ppb Pb(II). Samples tested for electrochemical preconcentration were directly diluted in 0.1 M HCl and measurement was performed in different deposition time (1-60 min) using only a PDMS chip and the flow rate of 1 mL/min. In the case of GO-PDMS preconcentration experiment in flow was performed as described before using different incubation time in GO-PDMS chip (1-60 min). Afterwards, a desorption and subsequent detection were performed using a standard protocol (1 mL of 0.1 M HCl for 30 min at 1 mL/min).

pass through the chip. This is not sufficient to ensure full adsorption, thus we decided to perform the back and forward operation, where the direction of the flow rate is changed every 60 s. This means that the same sample is in a dynamic contact with the GO-PDMS chip for a longer time. Thanks to this, a significant improvement on adsorption ability was achieved (Fig. 7A). The volume of the sample to be introduced can be tuned, so as to achieve the best preconcentration performance. In that case, the flow direction was changed in the proportional interval of the time, so as to ensure that all the volume will be in contact with a chip (for example, for 2 mL of the sample, a flow direction is changed every 120 s.

3.6.2 Desorption. Similarly, like in preliminary experiments, a 0.1 M HCl was chosen for the desorption as well as for the subsequent electrochemical detection. As low concentrated HCl need more time to desorb ions from GO-PDMS surface than 1 M HCl, a dynamic incubation was performed and the time of 30 minutes was applied.

3.6.3 Justification of the approach. Square wave anodic stripping voltammetry is a technique used for the detection of heavy metals (see more in Electronic Supplementary Information (ESI)). This technique includes the preconcentration step itself, as during the deposition step, ions are reduced onto the electrode surface and due to the flow rate, a sample being in contact with an electrode is consistently renewed. This allows to significantly improve the sensitivity and the limit of the detection but this approach has some limitations. In the case of our electrodes, if the deposition time is longer than 600 s, further increase of the signal is not observed anymore (Fig. 7B). This is related with the electrodes properties beside other phenomena, as the level of current is still below the saturation. On the other hand, the use of very long deposition time may reduce the electrodes viability, especially taking into account samples of the increased ionic strength (high background current). Due to that, the use of GO-PDMS might be an interesting way to perform preconcentration, as the only limitation is the adsorption capacity, while the other parameters can be tuned (time, flow rate, initial concentration). For instance, a 6-fold preconcentration of the sample (Fig. 7A) practically leads to the 6-times improvement of detection performance (LOD=0.07 ppb; LOQ=0.28 ppb).

Among recently published works on Pb(II) sensors, our results appeared as comparable. Wang et al. developed a graphene FET aptasensor for lead detection in blood with the LOD=0.0375 ppb[61]. Xuan et al. used micro-patterned reduced graphene oxide in square wave anodic stripping voltammetry for Pb(II) determination obtaining an LOD=0.4 ppb[62]. Using a

novel magnetic ion imprinted polymer Dahaghin et al. adsorbed and detected Pb(II) with the LOD=0.48 ppb[63]. Hong et al. used a microfluidic device to perform the electrochemical detection of Pb(II) with LOD=0.3 ppb[64].

Conclusions

In this work, a simple and versatile LOC platform for heavy metals preconcentration and detection was designed and developed. This is the first report of the application of GO-PDMS composite toward heavy metals adsorption. This composite can be characterized by physical and mechanical properties of PDMS having simultaneously exposed oxygen functional groups originated from GO. This allows performing adsorption of bivalent metals through the mechanism of surface complexation. An opposite process – desorption – occurs in presence of 0.1 M HCl. The same reagent is used for the electrochemical detection, as the device has screen-printed electrodes inbuilt. Thanks to the use of this platform, samples containing Pb^{2+} in the level below the limit of detection (0.5 ppb), can be preconcentrated and detected successfully, reaching a current value nearly 30 times higher than without using GO-PDMS for preconcentration. Moreover, the platform can be reused for a multiple time and subsequent cycles of adsorption/desorption can be performed without the loss of adsorption capacity. PDMS, as well as GO-PDMS, can be very easily adapted to any kind of design of the microfluidic device. Application of the presented GO-PDMS is not limited only to preconcentration and electrochemical detection of heavy metals, as various types of sensors can be combined with the microfluidic LOC device.

Conflicts of interest

There are no conflicts to declare.

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