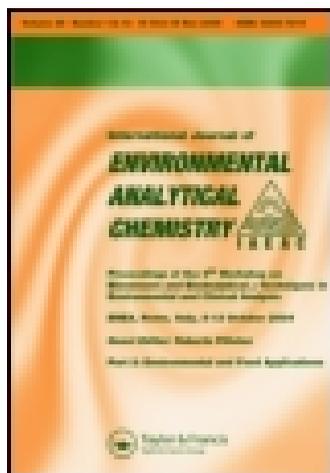


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Graphene oxide-packed micro-column solid-phase extraction combined with flame atomic absorption spectrometry for determination of lead (II) and nickel (II) in water samples

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A sensitive and simple method has been established for simultaneous preconcentration of trace amounts of Pb (II) and Ni (II) ions in water samples prior to their determination by flame atomic absorption spectrometry. This method was based on the using of a micro-column filled with graphene oxide as an adsorbent. The influences of various analytical parameters such as solution pH, adsorbent amount, eluent type and volume, flow rates of sample and eluent, and matrix ions on the recoveries of the metal ions were investigated. Using the optimum conditions, the calibration graphs were linear in the range of 7–260 and 5–85 $\mu\text{g L}^{-1}$ with detection limits ($3S_b$) of 2.1 and 1.4 $\mu\text{g L}^{-1}$ for lead and nickel ions, respectively. The relative standard deviation for 10 replicate determinations of 50 $\mu\text{g L}^{-1}$ of lead and nickel ions were 4.1% and 3.8%, respectively. The preconcentration factors were 102.5 and 95 for lead and nickel ions, respectively. The adsorption capacity of the adsorbent was also determined. The method was successfully applied to determine the trace amounts of Pb (II) and Ni (II) ions in real water samples. The validation of the method was also performed by the standard reference material.

Keywords: heavy metals; graphene oxide; micro-column; solid-phase extraction; flame atomic absorption spectrometry; preconcentration

1. Introduction

Water pollution due to the indiscriminate disposal of toxic heavy metal ions has been a rising worldwide environmental concern. Since heavy metals do not degrade biologically like organic pollutants, their presence in industrial effluents or drinking water is a public health problem due to their absorption and therefore possible accumulation in living organisms [1]. Lead (II), a typical hazardous heavy metal ion, commonly exists in the wastewater streams of various industries, such as acid mining, battery manufacturing, printing, and painting. The presence of lead in water may damage the kidney, nervous system, reproductive system, liver, and brain due to its accumulation in the human body [2,3]. Nickel (II) is a non-biodegradable toxic heavy metal ion present in wastewater. Trace amounts of nickel are beneficial to human organism as an activator of some enzyme systems; however, over-absorption of nickel causes cancer of lungs, nose and bones, extreme weakness, dermatitis, headache, dizziness, and respiratory distress [4,5]. The main source of nickel pollution in the water derives from industrial production

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processes such as nickel plating, porcelain enamelling, batteries, and furnaces used to make alloys or from power plants and trash incinerators [6]. The permissible limits of lead and nickel in drinking water are 10 and 20 $\mu\text{g L}^{-1}$, respectively [7]. Thus, the accurate determination of lead and nickel ions has become increasingly necessary to study problems associated with environmental water pollution.

Atomic absorption spectrometry (AAS), inductively coupled plasma–atomic emission spectrometry (ICP-AES), inductively coupled plasma–mass spectrometry (ICP-MS), and X-ray fluorescence (XRF) spectrometry are the most sensitive techniques for the determination of trace levels of heavy metals [8–11]. However, in these determinations, low concentration levels of analytes and high levels of matrices are the main problems. In order to overcome these limitations, a separation/preconcentration step prior to analysis is required [12]. Solid-phase extraction (SPE) is a preferred technique for the trace metal ions preconcentration by the researchers because of its advantages including simplicity, minimal cost, rapidity, low consumption of reagents, high preconcentration efficiency, and the ability to combine with different detection techniques whether in online or offline mode [13,14]. In the SPE procedure, the choice of the appropriate sorbent is a critical factor to obtain full recovery and a high preconcentration factor (PF). Various solid-phase adsorbent materials like activated carbon [15], carbon nanotubes [16], Amberlite XAD resins [17], synthetic polymers [18], polyurethane foam [19], silica gel [20], alumina [21], and zeolites [22], have been successfully used for this purpose. However, the development and application of novel adsorbents have attracted more and more interests.

Up to now, many carbonaceous materials such as activated carbons [15,23], as well as carbon nanostructures including fullerenes [24], carbon nanotubes [16,25], carbon nanohorns [26], carbon nanocones/disks [27], and even graphene [28–31], have been investigated as adsorbents in SPE techniques due to their large specific surface areas, high adsorption capacity, and good chemical stability. Graphene, a new two-dimensional carbon nanomaterial, receives extensive research interest because of its large surface area, unique electrical, thermal, mechanical, and optical properties [32–34]. Although it was discovered just a few years ago, graphene and its derivatives have attracted tremendous research interests not only in electronics and energy fields [35] but also in environmental applications [36]. Unlike carbon nanotubes, both sides of the planar sheets of graphene are available for molecule adsorption. So, the ultrahigh specific surface area (theoretical value $\sim 2630 \text{ m}^2/\text{g}$) of graphene-based material is responsible for its high adsorption capacity and high chemical activity [32,34]. Graphene oxide (GO), one of the most important derivatives of graphene, is a lamellar flexible material with a wide range of reactive oxygen-containing functional groups, e.g. epoxides, hydroxyl, ketones, and carboxyl groups [37]. Each fundamental layer of GO consists of planar, graphene-like aromatic domains with a dense two-dimensional carbonaceous skeleton containing a larger number of sp^3 hybridised carbon atoms and a smaller number of sp^2 carbons [38]. GO can be readily obtained from the strong oxidation of natural graphite in large scale. The preparation of this sorbent is not only very simple but also cheap in comparison with other commercially available solid-phase materials [39]. Moreover, GO is strongly hydrophilic, negatively charged material and readily disperses in aqueous solution to form a stable suspension [37]. Thus, all these exceptional properties serve GO sheets great promise as an excellent sorbent for removing positively charged contaminants in wastewater treatment as well as for preconcentration purposes in SPE technique [36,40–43]. To date, new analytical methods based on GO as a solid phase have been developed for determination of trace heavy metal ions in water samples including GO-based dispersive micro-SPE combined with energy-dispersive XRF spectrometry [40] and GO–silica composite coating hollow fibre solid-phase micro-extraction online coupled with ICP-MS [42]. These studies demonstrated the great potential of GO as an excellent sorbent in the preconcentration field of analytical chemistry.

The main purpose of the present research is to develop a new analytical method for simultaneous preconcentration and determination of trace amounts of Pb (II) and Ni (II) ions in water samples. The method is based on the combination of GO-packed micro-column SPE and flame atomic absorption spectrometry (FAAS) detection method. All main factors for the quantitative recoveries of Pb (II) and Ni (II) ions were investigated and optimised. The established procedure was also applied to preconcentration of analytes in some real water samples.

2. Experimental

2.1. Apparatus

Heavy metals analysis was carried out using atomic absorption spectrophotometer (GBC, Plus 932, Australia) under the conditions given by the manufacturer with air-acetylene flame. A Pb and Ni hollow cathode lamps as the radiation sources were used for metal ions determination at the wavelengths of 283.3 and 232.0 nm, respectively. A BEL pH-meter (model PHS-3BW, Italy) with a combined glass-calomel electrode was used throughout this study. The sample separation was achieved using a Demerd centrifuge (model LC8-12). A Brandson Digital Sonifer (S450D, 35% amplitude) was used for ultrasonic treatments. A peristaltic pump (Lambda, Switzerland) was used in the SPE process. A stainless steel 304 hypodermic thin wall tubing (11 gauge) with outer diameter of 0.12 inch, inner diameter of 0.1 inch, length of 50 mm, and the wall thickness of 0.01 inch (ASIN: B001DD0LWA) was used as a preconcentration micro-column. The morphology of GO was examined by transmission electron microscopy (TEM, CM30, Philips, Netherlands). X-ray diffraction pattern was carried out by X-ray diffractometer (XRD, PW 1840, Phillips, Netherland) with Cu-K radiation source. Functional groups of GO were analysed by Fourier Transform Infrared (IFS 88, Bruker Optik GmbH, Germany) spectrophotometer using KBr pelleting method in the 4000–400 cm^{-1} . The Brunauer–Emmett–Teller (BET) surface area of GO was determined using a Micrometrics ASAP 2010 system (Micrometric Instruments Co, Cleveland, OH, USA).

2.2. Chemical reagents and materials

Graphite powder (particle size $<20\ \mu\text{m}$) was purchased from Sigma-Aldrich. Sodium nitrate, potassium permanganate, sulphuric acid, standard stock solutions ($1000\ \text{mg L}^{-1}$) of Pb (II) and Ni (II), and all of the other reagents used for experiments and analysis were of analytical grade and purchased from Merck, Darmstadt, Germany. Deionised water produced using a Milli-Q plus water purification system (Millipore, Bedford, MA, USA) was used throughout this study.

The experimental solutions of SPE method were prepared daily by diluting the stock solutions with deionised water. The working standard solutions were prepared daily by diluting the stock solutions of lead and nickel ions with deionised water prior to analysis with SPE method. The calibration curves were established using the standard solutions. The pH adjustments were made using appropriate buffer solutions including sodium phosphate ($\text{H}_3\text{PO}_4/\text{NaH}_2\text{PO}_4$, $0.1\ \text{mol L}^{-1}$) for pH 2–3, ammonium acetate ($\text{CH}_3\text{COOH}/\text{CHCOONH}_4$, $0.1\ \text{mol L}^{-1}$) for pH 4–6, sodium borate (NaBO_2/HCl , $0.1\ \text{mol L}^{-1}$) for pH 7, and ammonium chloride ($\text{NH}_3/\text{NH}_4\text{Cl}$, $0.1\ \text{mol L}^{-1}$) for pH 8–10. All the laboratory glassware and plastics were cleaned by soaking in 10% (v/v) nitric acid for at least 24 h and then rinsed with deionised water prior to use.

2.3. Preparation of graphene oxide

The GO was obtained via exfoliation of graphite oxide [44]. Graphite oxide was prepared using modified Hummers method through the oxidation of natural graphite powder [39,45]. Details about experimental procedure for GO preparation are presented in Supplemental data.

2.4. Test procedure

In SPE procedure, a total of 20 mg of GO was placed into the stainless steel micro-column. Two small pieces of 0.22- μm filter membrane cut to the size of the inner diameter of micro-column were placed at the lower end of GO, and then small amount of glass wool was also placed at both ends of this sorbent to avoid any loss of the solid phase during sample loading. An aliquot of the sample solution (200 mL) containing 50 $\mu\text{g L}^{-1}$ of Ni (II) and Pb (II) ions (from each one) was adjusted to pH = 6 with acetate buffer solution. The resulting sample solution was pumped through the GO-packed micro-column at a flow rate of 0.8 mL min^{-1} . The micro-column was then rinsed with 5 mL deionised water. Afterwards, the retained metal ions were completely eluted from the solid phase with 2 mL of 1 mol L^{-1} nitric acid at a flow rate of 1 mL min^{-1} . The metal ions content of the eluent was then determined by FAAS. A blank solution was also run under the same analytical conditions without adding any analytes. The GO adsorbent was used freshly for blank experimental run. The recovery was calculated by using Equation (1), where C_i is the initial concentrations of analytes in solution phase, and C_f is the concentration of analytes determined by FAAS after the SPE process. All the experimental data were the averages of triplicate determinations.

$$\text{Recovery \%} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

2.5. Preparation of real water samples

The developed method was applied to four water samples including oil refinery wastewater (Ray, Tehran, Iran), petrochemical factory wastewater (Tehran, Iran), agricultural water, and well water (both from Ray, Tehran, Iran). For sampling, all the laboratory glassware and plastics were cleaned by soaking in 0.5 mol L^{-1} nitric acid for at least 24 h and then rinsed six times with deionised water before to use. In order to reduce interferences, organic matrix of the samples should be destroyed by digestion as well as metal-containing compounds are decomposed to obtain free metal ions that can be determined by FAAS. For this, all of the water samples were acidified with concentrated HNO_3 to pH ~ 2 just after collecting, filtered through a cellulose acetate membrane filter (Millipore, 0.45 μm pore size) in order to eliminate any particulate and/or insoluble materials and then stored in precleaned polyethylene bottles. Before the analysis, 1000 mL of each sample was prepared according to the American Society for Testing and Materials (ASTM) standards including ASTM D-3559 and ASTM D-1886 for total recoverable lead and nickel. Then, 200 mL of the as-prepared samples were preconcentrated according to the general SPE procedure and determined with FAAS.

3. Results and discussion

Based on the preliminary experiments, the retention of Pb (II) and Ni (II) ions on a GO-packed micro-column was chosen for preconcentration of the metal ions and their subsequent determination by FAAS. Hence, in order to obtain quantitative recoveries of Pb (II) and Ni (II) ions with good sensitivity and precision, the presented SPE system was optimised for various analytical parameters.

3.1. Characterisation of graphene oxide

The TEM image (Figure 1a) shows that few-layered GO is formed with flake-like structure, smooth surface, and some wrinkles. Moreover, the transparent sheets comprise very thin layers that are noticeable from the image. The wrinkles regions are due to the formation of oxygen functional groups on the surface of GO. The XRD pattern of GO is displayed in Figure 1b. An intense and sharp diffraction peak at $2\theta = 12.26$ ($d = 0.72$ nm) corresponds to the typical diffraction peak of GO nanosheets. The d -spacing increases from 0.33 to 0.72 nm after the graphite is converted into GO nanosheets, which may be due to the creation of the abundant oxygen functional groups on the surface of GO [33]. The oxygen-containing groups on the surfaces of GO nanosheets were characterised by FT-IR analysis (Figure S1). The C=O and -COOH/-OH groups were indicated by the peaks at 1725 and 3417 cm^{-1} , respectively. The presence of C-O was indicated by the peak at 1100–1220 cm^{-1} . Moreover, the peak at 1620 cm^{-1} was assigned to C=C stretching vibration. Similar results have also been reported by the investigators [45–47]. The BET surface areas of GO was 200 $\text{m}^2 \text{g}^{-1}$. This is in agreement with the results reported by other researchers who found that the BET surface area values of the graphene sheets are between 50 and 1300 $\text{m}^2 \text{g}^{-1}$ [48–50].

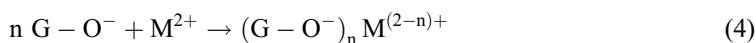
3.2. Effect of pH

In the SPE studies, the pH of the sample solution is an important parameter to obtain quantitative recoveries of metal ions, because it affects the surface charge of the adsorbent, the degree of ionisation, and speciation of the adsorbate [51]. Due to this important point, the influence of sample pH on the recovery efficiency of metal ions was investigated in the pH ranges of 2–10 by using buffered sample solutions containing 50 $\mu\text{g L}^{-1}$ of Pb (II) and Ni (II) ions. As illustrated in Figure 2, recovery percentages of Pb (II) and Ni (II) ions increased from pH 2 to 6. Both of the metal ions were quantitatively recovered (>97%) at pH = 6–7. After pH 7, further increase in pH value decreased the recovery percentages of both the metal ions.

The analyte ions can be adsorbed onto GO surface by reacting with -COOH and -OH groups. Depending on the solution pH, the surfaces of the GO nanosheets can undergo protonation or deprotonation reaction. As previously reported by Zhao *et al.* [47] at low pH values (pH < 4), the surface charge of GO nanosheets is positive due to the protonation reaction (Equation (2)):



where G and OH represent the surface of GO nanosheets and oxygen-containing functional groups, respectively. Therefore, low recovery efficiencies of metal ions at low pH range are due to the electrostatic repulsion between the metal ions and positively charged GO surface. However, as the pH increases, the surface charge of GO is more negative because of the deprotonation mechanism (Equation (3)), and the G-O^- becomes the dominating species. So, the electrostatic attraction (Equation (4)) between negatively charged adsorbent surface and positively charged metal ions increases, which plays an important role in the adsorption process.



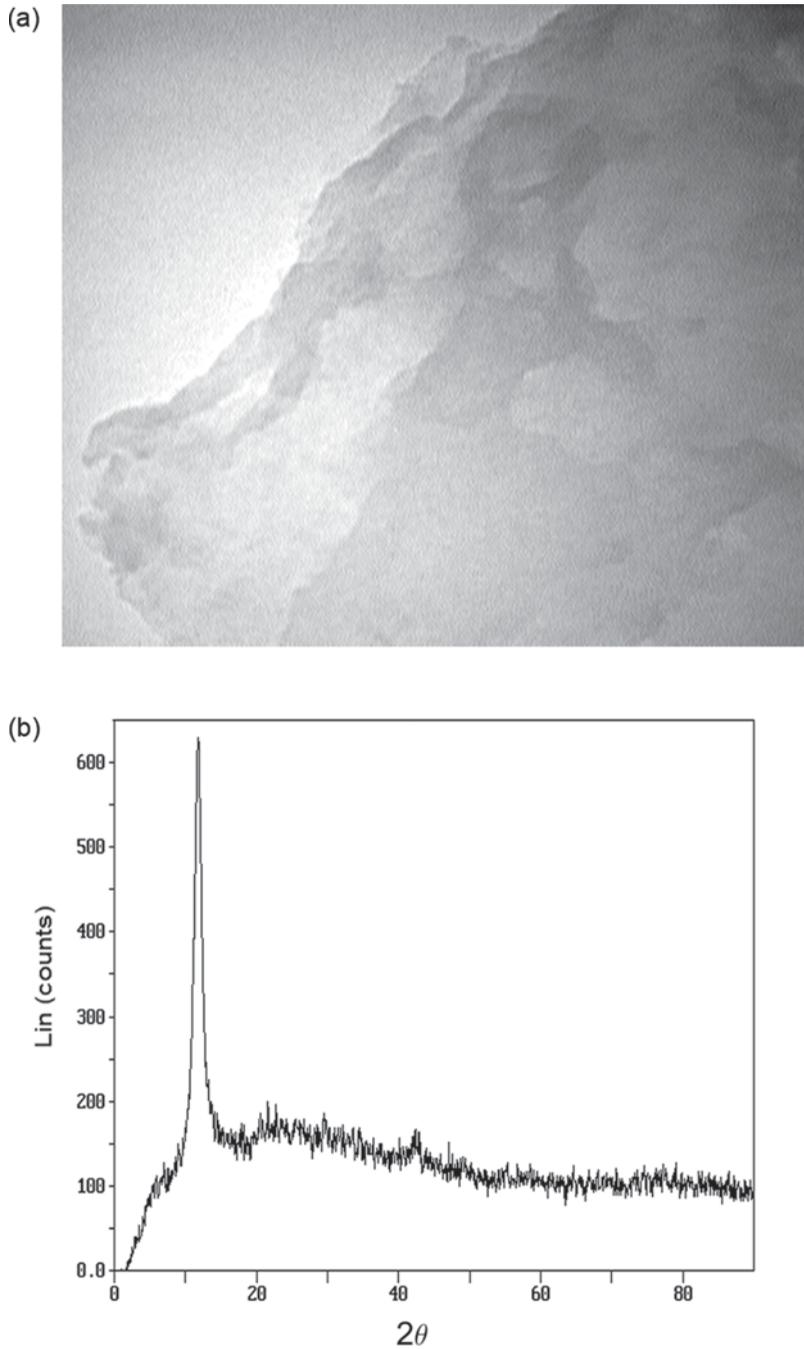


Figure 1. (a) TEM image of graphene oxide, (b) XRD pattern of graphene oxide.

On the other hand, the decrease in the recovery efficiencies of metal ions at higher pH values ($\text{pH} > 7$) may be due to increase in precipitation of metal ions in the form of hydroxyl complexes. Thus, for all further studies, pH of 6 was considered as optimum pH value.

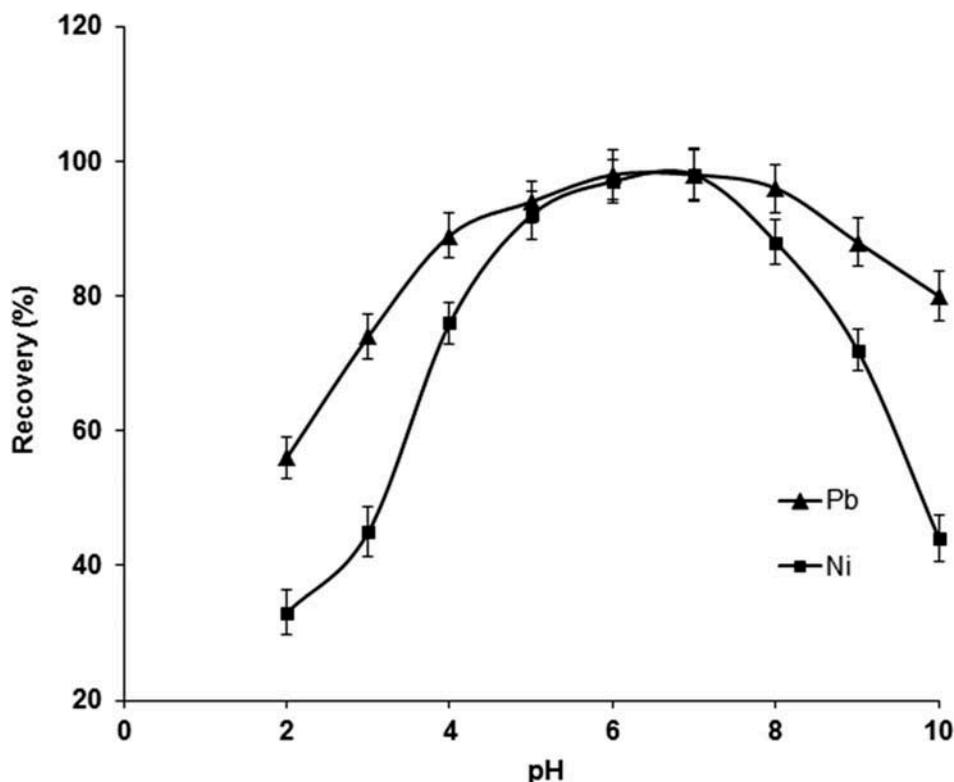


Figure 2. Effect of solution pH on the recovery of metal ions (200 mL of sample containing $50 \mu\text{g L}^{-1}$ metal ions; adsorbent amount 20 mg; eluent 2 mL of $1 \text{ mol L}^{-1} \text{ HNO}_3$; flow rates of sample and eluent 0.8 and 1.0 mL min^{-1}).

Previous studies also reported that the maximum recovery efficiency for SPE of both Pb (II) and Ni (II) ions was observed at pH 6 [28,29].

3.3. Effect of the amount of adsorbent

The effect of the adsorbent dosage on the recoveries of Pb (II) and Ni (II) ions was investigated using various amounts of GO in the range of 2–30 mg (Figure S2). The maximum recoveries of both the metal ions ($R > 97\%$) were obtained using 20–30 mg of GO. So, 20 mg of GO was considered as the optimum adsorbent amount. More details are presented in Supplemental data.

3.4. Effect of eluent type, concentration, and volume

In order to select the best eluent solution for desorption of the metal ions from GO-packed micro-column, various eluents such as HNO_3 , HCl , H_2SO_4 , and CH_3COOH with different concentrations of 0.2 – 2.0 mol L^{-1} were examined. As seen in Figure 3a and b, desorption of metal ions increased with increase of the eluent concentration from 0.2 to 2.0 mol L^{-1} . Among the acidic studied solutions, especially the HNO_3 provided higher recovery efficiency compared to the other acids. The highest recoveries for both metal ions were obtained with 1 – $2 \text{ mol L}^{-1} \text{ HNO}_3$ solutions, while $1 \text{ mol L}^{-1} \text{ HNO}_3$ was specified as the best eluent for further studies.

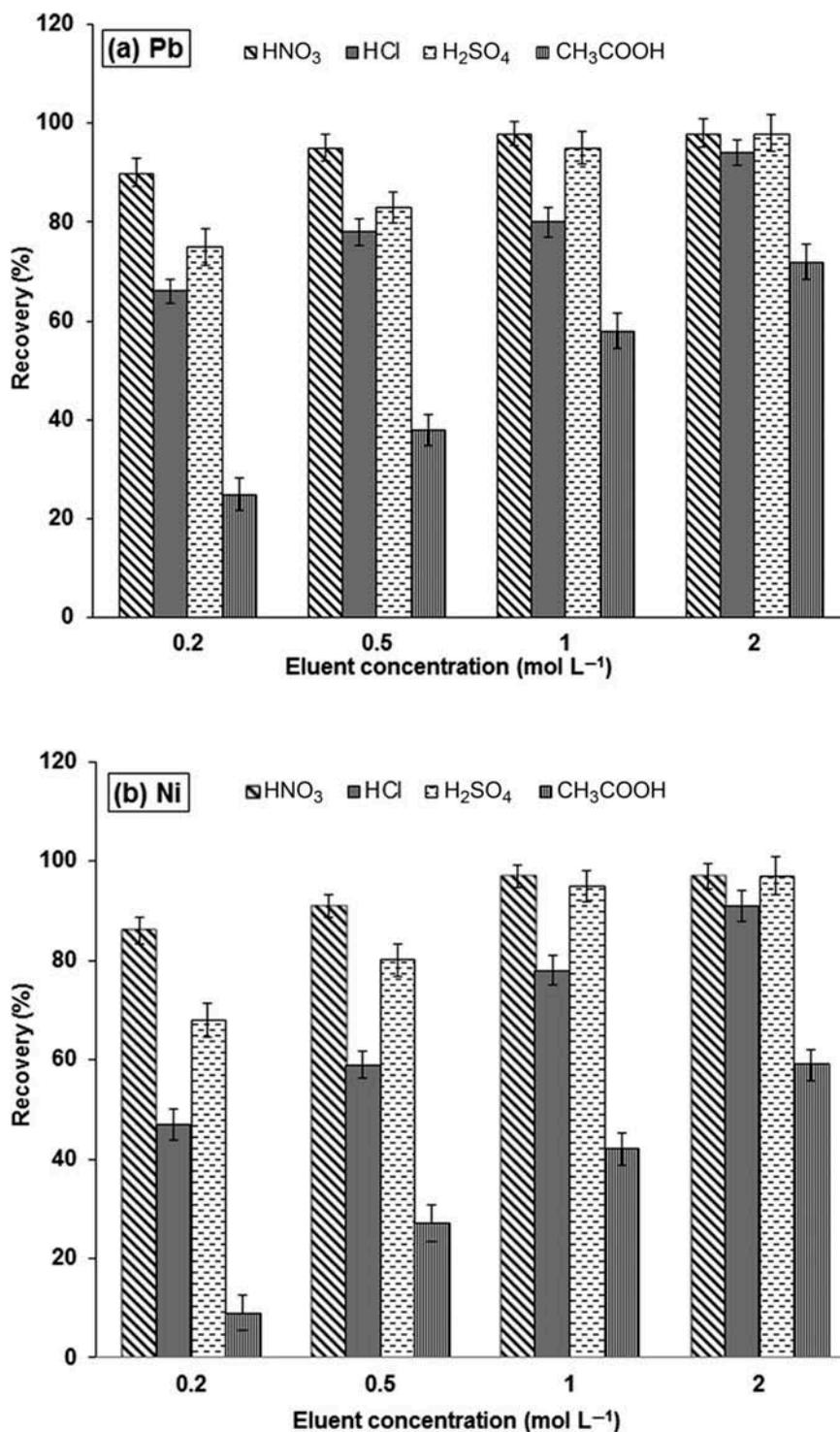


Figure 3. Effect of eluent type and concentration on the recovery of (a) lead and (b) nickel ions (200 mL of sample containing 50 $\mu\text{g L}^{-1}$ metal ions; pH = 6; adsorbent amount 20 mg; eluent 2 mL with different concentrations; flow rates of sample and eluent 0.8 and 1.0 mL min⁻¹).

Eluent volume is another important factor of SPE experiments. Volume of the eluent should reach an amount that is able to desorb analyte ions. Therefore, the recoveries were carried out using different volumes (1–5 mL) of 1 mol L⁻¹ HNO₃ solution. According to the results, the recovery values of Pb (II) and Ni (II) ions were quantitative (>97%) with 2–5 mL HNO₃ (Figure S3). Thus, 2 mL of eluent was recommended for subsequent works. This is in agreement with the results obtained by Wang *et al.* for preconcentration of Pb (II) [28] and Ni (II) [29] by graphene-based SPE. They used 2 mL of 2 mol L⁻¹ HNO₃ as eluent solution.

3.5. Effect of sample and eluent flow rates

In the SPE method, flow rates of the sample and eluent solutions are important parameters affecting both the recoveries of the analyte ions and the extracting time. The sample flow rate through the column should be low enough to enable an efficient retention of the analytes, and also be high enough to avoid excessive duration. In addition, the eluent flow rate should be correctly adjusted so as to ensure quantitative elution [52]. The influences of the sample and eluent flow rates on the recoveries of analyte ions from the GO-packed micro-column were investigated in the flow rate ranges of 0.2–3.0 mL min⁻¹ under the optimum conditions. The results were depicted in Figures 4 and 5 for sample flow rates and eluent flow rates, respectively. The analyte ions were quantitatively retained and recovered in the sample flow rates of 0.2–1.0 mL min⁻¹ and eluent flow rates of 0.2–1.25 mL min⁻¹. However, for both the sample

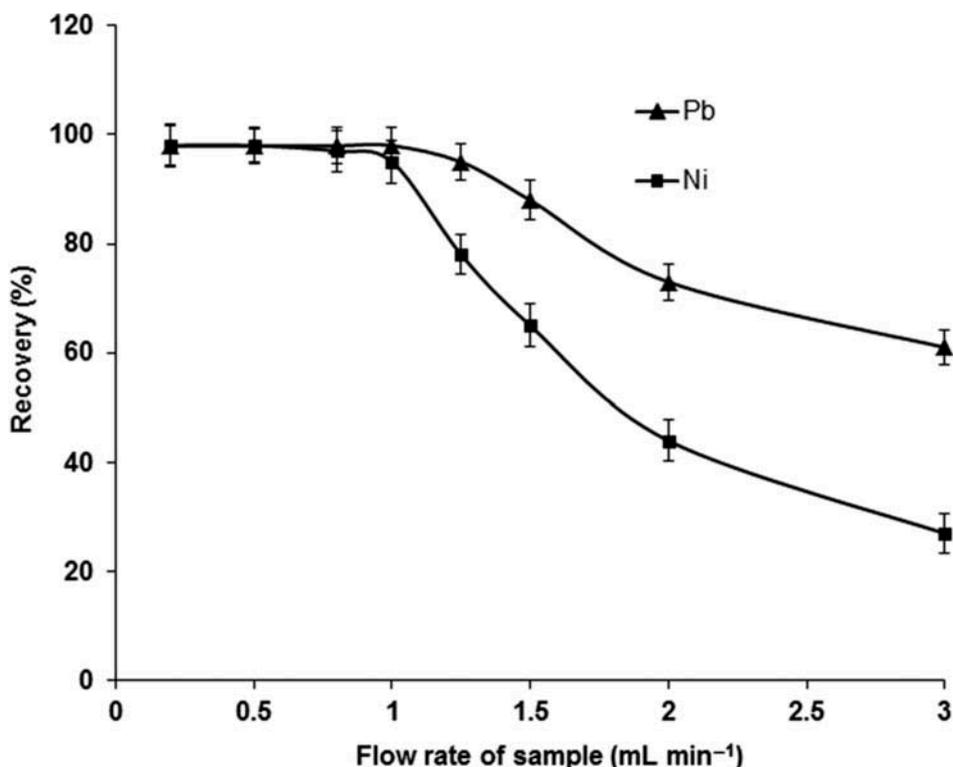


Figure 4. Effect of sample flow rates on the recovery of metal ions (200 mL of sample containing 50 µg L⁻¹ metal ions; pH = 6; adsorbent amount 20 mg; eluent 2 mL of 1 mol L⁻¹ HNO₃).

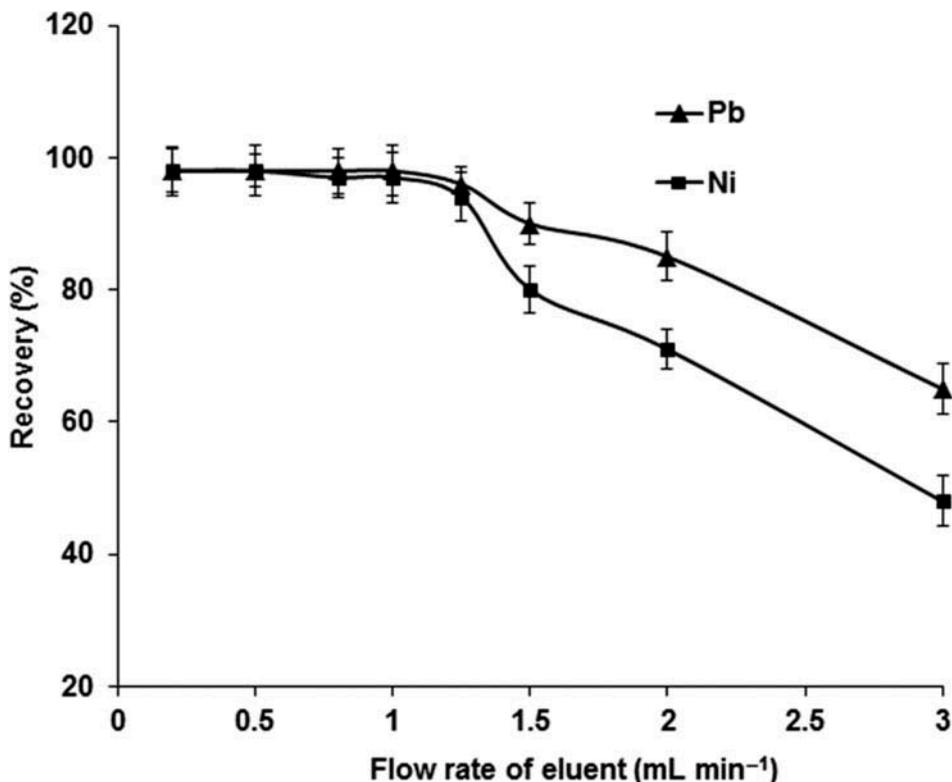


Figure 5. Effect of eluent flow rates on the recovery of metal ions (200 mL of sample containing $50 \mu\text{g L}^{-1}$ metal ions; pH = 6; adsorbent amount 20 mg; eluent 2 mL of $1 \text{ mol L}^{-1} \text{ HNO}_3$).

and eluent solutions, higher flow rates reduce the efficiency of the extraction, suggesting a less effective metal reagent interaction. Similar observations have also been reported by other researchers [53,54]. So, to obtain the maximum quantitative recoveries of metal ions (>97%), the sample and eluent flow rates were maintained at 0.8 and 1.0 mL min^{-1} , respectively.

3.6. Effect of sample volume

To deal with real samples, especially water samples, containing very low concentrations of the metal ions, the maximum applicable sample volume should be determined. Under the optimised conditions, the effect of aqueous sample volume on the recoveries of analyte ions was examined by passing different volumes (20–250 mL) of sample solution containing $10 \mu\text{g}$ of Ni (II) and Pb (II) ions from the micro-column. Elution of the SPE micro-column was performed with 2 mL of $1 \text{ mol L}^{-1} \text{ HNO}_3$. The results were illustrated in Figure S4. The analyte ions could be recovered quantitatively when up to 200 mL of the sample solution was used. At higher sample volumes, the recoveries were decreased, suggesting an incomplete retention of metal ions by the sorbent. This is probably because the sample itself acts as eluent or less contact of analyte ions on sorbent. Similar observations have also been reported by researchers [28,29,53,54]. Hence, 200 mL was chosen as the optimum sample volume.

3.7. Column reuse

To evaluate the stability and reusability of the GO-packed micro-column, several extraction and elution operation cycles were carried out under the optimised conditions. It was found that the micro-column could be reused after being regenerated with 2 mL of nitric acid (5%) and then rinsed by 10 mL deionised water. The GO adsorbent was stable for over 36 adsorption–elution cycles without significant decrease of extraction recoveries of Pb (II) and Ni (II) ions (Figure S5).

3.8. Adsorption capacity

Adsorption capacity is a key parameter to evaluate the adsorbent. For investigation of adsorption capacity of Pb (II) and Ni (II) ions, 200 mL of aqueous sample solution containing 1000 mg L⁻¹ Pb (II) and Ni (II) ions (from each one) at pH 6 was added to 0.25 g GO, in the batch mode. Desired pH value in the solution was adjusted by using 10 mL of CH₃COONH₄/CH₃COOH buffer solution. After agitating for 12 min, the mixture was filtered through a 0.22- μ m filter membrane (GSWP 47, Millipore, Billerica, MA, USA). The residual concentrations of metal ions in the filtrate were determined using FAAS. The adsorption capacities of GO for Pb (II) and Ni (II) ions were found to be 195 and 178 mg g⁻¹, respectively.

A comparison of the adsorption capacities of the current study with other adsorbents for the removal of Pb (II) and Ni (II) ions from aqueous phase was also reported in Table 1. In view of favourable characteristics of GO, it is obvious that the adsorption capacity of GO used in the present study is significant. Therefore, GO is considered to be excellent and potential adsorbent for simultaneous removal of Pb (II) and Ni (II) ions from effluents. Higher q_{\max} values of some other works may be related with the higher density of surface functional groups of the GO used in these studies, depending not only on the particular oxidants used but also on the graphite source, preparation route, and reaction conditions [37].

Table 1. Comparison of the adsorption capacities of various nanoadsorbents for Pb (II) and Ni (II) removal by batch method.

Adsorbent	Adsorption capacity (mg g ⁻¹)		References
	Pb (II)	Ni (II)	
GO	367	–	[49]
GO	1119	–	[55]
GO	36.00	–	[50]
TiO ₂ /GO	65.60	–	[50]
MCGO ^a	76.94	–	[56]
SiO ₂ -graphene	113.60	–	[57]
Amino modified MWCNT ^b	58.26	–	[58]
GO/CMC ^c	76.90	72.04	[59]
CNT-GAC ^d	86.26	0.07	[60]
Nanostructured Al ₂ O ₃	125.00	83.33	[61]
Nano-HAp ^e	–	2.28	[62]
Graphene	–	10.80	[5]
Graphene/MnO ₂	–	46.55	[5]
GO	195	178	Present study

Notes: ^aMagnetic chitosan/graphene oxide composite, ^bmultiple-walled carbon nanotube, ^cgraphene oxide/carboxy methyl cellulose, ^dcarbon nanotube-granular-activated carbon, ^enanocrystalline hydroxyapatite.

3.9. Effect of foreign ions

In this section, the interfering effect of various matrix ions, most probably present in the environmental samples, as well as interfering effect of the considered cations extracted simultaneously on the recoveries of metal ions from the GO-packed micro-column was examined. The procedure was performed using 200 mL sample solution containing $50 \mu\text{g L}^{-1}$ of analyte ions and different concentration of matrix ions. The tolerance limit is defined as the ion concentration causing a relative error smaller than $\pm 5\%$ in the sorption of the analyte ions. As shown in Table 2, Pb (II) and Ni (II) ions have high affinity towards the solid phase and can be preconcentrated on GO with very good recovery ($>96\%$) under optimised conditions. Generally, Pb (II) and Ni (II) ions were quantitatively recovered in the presence of optimum amount of alkaline, earth alkaline, transition and heavy metal ions, as well as some anions. Moreover, simultaneous extraction of Pb (II) and Ni (II) ions has not any interfering effect on the recovery efficiency under the selected conditions. On the other word, although GO can be utilised by competing metal ions, the sorption capabilities of GO towards the determined elements expressed as recovery can remain high, e.g. better than 96%. This is in agreement with the results reported by Zawisza *et al.* for preconcentration and determination of Co(II), Ni(II), Cu(II), Zn(II), and Pb(II) ions using GO-based dispersive micro-SPE combined with energy-dispersive XRF spectrometry [40]. Moreover, similar results have been reported by Wang *et al.* for preconcentration and determination of Pb (II) and Ni (II) by graphene-based SPE combined with FAAS [28,29]. They demonstrated that the presence of major cations and anions in natural water has no significant influence on the adsorption of studied metal ions under the selected conditions.

3.10. Analytical performance

Under the previously optimised conditions, the analytical figures of merit of the developed method for preconcentration and determination of Pb (II) and Ni (II) ions were determined. The results are summarised in Table 3. First of all, the calibration curves of metal ions were constructed by preconcentrating the standard solutions of Pb (II) and Ni (II) with different

Table 2. Effect of foreign ions on the recovery of $50 \mu\text{g L}^{-1}$ of Pb (II) and Ni (II) ions in water samples using developed method.

Foreign ions	Concentration ratio (interferent ion/ Pb^{2+} or Ni^{2+})		Recovery (%)	
	Pb^{2+}	Ni^{2+}	Pb^{2+}	Ni^{2+}
Cu^{2+}	1000	800	95	97
Cd^{2+}	2000	500	98	96
Zn^{2+}	1000	500	96	99
Ni^{2+}	600	–	96	–
Pb^{2+}	–	600	–	96
Ag^+ , Ca^{2+} , Na^+ , Mn^{2+} , Cr^{3+} , Cl^- , Li^+ , NO_3^- , Fe^{3+} , K^+ , Br^- , CH_3COO^-	1600	1000	97	98
F^-	2000	600	98	95
Co^{2+}	1000	700	96	97
Mg^{2+}	700	500	95	99
Al^{3+}	1200	900	98	97
I^-	800	1000	96	97

Table 3. Analytical characteristics of the developed method at the optimum conditions.

Metal ions	Linear range ($\mu\text{g L}^{-1}$)	Slope	Regression coefficient (R^2)	LOD ^a ($n = 10$) ($\mu\text{g L}^{-1}$)	RSD ^b ($n = 10$) (%)	PF ^c
Pb (II)	7–260	4.1×10^{-3}	0.9994	2.1	4.1	102.5
Ni (II)	5–85	1.9×10^{-3}	0.9997	1.4	3.8	95.0

Notes: ^aDetection limit, ^brelative standard deviation, ^cpreconcentration factor.

concentrations, according to the general SPE procedure. The data were analysed by least squares method, then, the linear working ranges; regression equations and correlation coefficients were obtained (Figures S6 and S7). The regression equations for the calibration curves of Pb and Ni were $A = 4.1 \times 10^{-3} C + 0.026$ with regression coefficient (R^2) of 0.9995, and $A = 1.9 \times 10^{-3} C + 0.0039$ with R^2 of 0.9997, respectively. In these equations, A is the absorbance and C is the concentration of analytes ($\mu\text{g L}^{-1}$) in the aqueous phase (200 mL). The sensitivity of the developed method is reflected by the limit of detection (LOD), which defined as $3S_b/m$ (where m is the slope of the calibration curve and S_b is the standard deviation of 10 replicate readings of the reagent blank). In order to determine the LOD values, the proposed method was applied to 10 blank solutions (200 mL). The precision, expressed as a relative standard deviation for 10 replicate measurements (RSD, $n = 10$), was evaluated with model solutions (200 mL) containing $50 \mu\text{g L}^{-1}$ of metal ions under the optimum conditions. PF, calculated as the ratio of the slopes of calibration curves obtained with and without preconcentration, using FAAS. The slopes without preconcentration were 4×10^{-5} and 2×10^{-5} for Pb (II) and Ni (II), respectively. So, the PF values were obtained 102.5 and 95 for lead and nickel ions, respectively. According to Table 3, the results show good linear ranges, low LODs and RSD (%) as well as high PF values for both metal ions. These results demonstrate high sensitivity and precision of the method.

A comparison of the current method with the other reported methods is given in Table 4. It can be seen that the PF and LOD values of the present method, for determination of trace lead and nickel ions, are better than or comparable to that reported in the literature. Lower LOD values of some other works are related with higher sensitivity of the instrument used in these studies and higher preconcentration factor than the presented work.

3.11. Analysis of real samples

The developed method was successfully employed for the determination of Pb (II) and Ni (II) ions in four water samples. The results are presented in Table 5. The accuracy of the results was verified by analysing the spiked water samples with known lead (II) and nickel (II) concentrations. As it can be seen from Table 5, a good agreement was obtained between the added and measured analytes amount, which confirms the accuracy of the procedure and its independence from the matrix effects. The recovery values of spiked samples were higher than 96% for both metal ions.

The validity of the developed method was established by analysis of the standard reference material, NIST SRM 1640a (trace elements in 250 mL natural water), from the National Institute of Standard and Technology (NIST, Gaithersburg, MD, USA). According to the results, the developed method was in good agreement with the certified values (Table 6). These results prove the applicability of the present SPE system for determination of trace lead and nickel ions in natural water samples.

Table 4. Comparison of the developed method with other procedures for Pb (II) and Ni (II) determination.

Metal ion	Method/instrumental detection	PF ^a	DL ^b ($\mu\text{g L}^{-1}$)	Reference
Pb (II)	SPE on graphene/FAAS	50	0.61	[28]
Pb (II)	SPE on MWCNT ^c /FAAS	20	8.0	[53]
Pb (II)	SPE on TAA ^d grafted MWCNT/ICP-OES ^e	60	0.32	[63]
Ni (II)	SPE on modified C18 disks/ICP-OES ^e	100	0.60	[64]
Ni (II)	SPE on SiAT ^f /FAAS	10	1.73	[65]
Ni (II)	SPE on graphene/FAAS	200	0.51	[29]
Ni (II)	SPE on IIP ^g /FAAS	–	1.60	[66]
Ni (II) & Pb (II)	SPE on MWCNT/FAAS	80	0.57–0.60	[67]
Ni (II) & Pb (II)	SPE on SDS ^h -coated alumina/FAAS	63	2.1–2.8	[68]
Ni (II) & Pb (II)	GO-silica coating HF-SPME/ICP-MS ⁱ	10	0.02–0.03	[42]
Ni (II) & Pb (II)	DMSPE ^j on GO/EDXRF ^k	–	0.7–1.4	[40]
Ni (II) & Pb (II)	SPE on GO packed micro-column/FAAS	95–102.5	1.4–2.1	This work

Notes: ^aPreconcentration factor, ^bdetection limit, ^cmultiple-walled carbon nanotube, ^dTris(2-aminoethyl)amine, ^einductively coupled plasma optical emission spectrometry, ^f2-aminotiazole modified silica gel, ^gion-imprinted polymer, ^hsodium dodecyl sulphate, ⁱgraphene oxide–silica composite coating hollow fibre solid-phase microextraction coupled with inductively coupled plasma mass spectrometry, ^jdispersive micro-solid-phase extraction, ^kenergy-dispersive X-ray fluorescence spectrometry.

Table 5. Analytical results for determination of metal ions in natural water samples.

	Added ($\mu\text{g L}^{-1}$)	Found ^a ($\mu\text{g L}^{-1}$)	RSD (%)	Recovery (%)
Ni (II)				
Wastewater (1) ^b	0	38.2 ± 1.2	3.1	–
	10	47.9 ± 1.9	3.9	97
	20	58.8 ± 1.5	3.4	103
Wastewater (2) ^b	0	43.2 ± 1.4	2.9	–
	10	52.9 ± 2.3	4.1	97
	20	62.4 ± 2.5	4.5	96
Well water	0	12.5 ± 0.7	2.8	–
	10	22.7 ± 2.4	4.3	102
	20	31.7 ± 1.0	3.2	96
Agricultural water	0	26.4 ± 1.2	3.5	–
	10	35.9 ± 0.9	2.1	95
	20	45.8 ± 1.6	3.9	97
Pb (II)				
Wastewater (1) ^b	0	108.2 ± 2.7	4.5	–
	10	118.3 ± 1.8	3.7	101
	20	127.8 ± 0.7	3.1	98
Wastewater (2) ^b	0	121.3 ± 1.5	3.3	–
	10	131.6 ± 2.3	3.9	103
	20	140.7 ± 0.9	2.1	97
Well water	0	23.2 ± 2.5	4.8	–
	10	32.9 ± 1.9	4.2	97
	20	42.8 ± 0.8	3.6	98
Agricultural water	0	43.6 ± 1.4	3.8	–
	10	53.8 ± 2.6	4.3	102
	20	63.4 ± 1.7	4.0	99

Note: ^aMean value ± ts/ \sqrt{N} , ^bfrom (1) oil refinery, (2) petrochemical factory.

Table 6. Validation of developed method by Standard Reference Material, NIST SRM 1640a, ($N = 7$).

Recovery (%)	Found ^a ($\mu\text{g L}^{-1}$)	Certified ($\mu\text{g L}^{-1}$)	Sample
101.2	12.24 ± 0.11	12.10 ± 0.05	Pb (II)
96.3	24.38 ± 0.14	25.32 ± 0.14	Ni (II)

Note: ^aMean value \pm ts/ \sqrt{N} .

4. Conclusion

The simple, fast, reliable, and economical technique for simultaneous determination of trace levels of Pb (II) and Ni (II) ions in real water samples was developed by combining the GO-packed micro-column SPE technique with FAAS. The method provided high PFs and good recoveries (>97%) at the optimal conditions. The system showed reproducibility and reliability in analytical data with low RSD (%) values in 10 experiments. In addition, the method was free of interference. The batch adsorption capacities of lead and nickel ions on GO were found to be 195 and 178 mg g⁻¹, respectively. The developed procedure has some advantages over other preconcentration–separation methods in literature, such as low consumption of only 20 mg GO as adsorbent and also 2 mL of eluent per extraction, high sorption capacities, low detection limits, and good reusability (up to 36 cycles). It is expected that the developed method could successfully be utilised to separation, preconcentration, and determination of lead and nickel ions in different real samples.

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Supplemental data

Supplemental data for this article can be accessed at

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