Synthesis, characterisation and application of mercapto- and polyaminophenol-bifunctionalised MCM-41 for dispersive micro solid phase extraction of Ni(II) prior to inductively coupled plasma-optical emission spectrometry (DMSPE-ICP-OES)

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Highly ordered adsorbent mesoporous silica (MCM-41) was synthesised using a rapid method and its subsequent chemical modification with 3-mercaptopropyltrimethoxysilane (MPTMS) in toluene medium at 60°C was performed. The electro-reduction product of 4-nitrophenol (EP4NP), as a new kind of polyaminophenol-type chelating agent with a high affinity to Ni(II), was then incorporated into MPTMS-MCM-41. The resulting materials (MCM-41, MPTMS-MCM-41 and EP4NP-MPTMS-MCM-41) were characterised by scanning electron microscopy, powder X-ray diffraction, nitrogen gas sorption and Fourier transform-infrared spectrometry. The new modified adsorbent EP4NP-MPTMS-MCM-41 was then employed for preconcentration of ultra-trace amounts of Ni(II) by dispersive micro solid phase extraction prior to inductively coupled plasma-optical emission spectrometry. The effects of variables such as pH, mass of the chelating agent, the amount of EP4NP-MPTMS-MCM-41, stirring time of extraction step, HCl concentration and stirring time during elution were optimised and the calibration curve was plotted. The limits of detection and quantitation were 0.006 and 0.019 μg L\textsuperscript{−1}, respectively. The mean, standard error and relative standard deviation for five replicates of 0.5 μg L\textsuperscript{−1} Ni(II) were calculated to be 0.48 μg L\textsuperscript{−1}, 4.0% and 3.2%, respectively. The proposed method was successfully applied for determination of Ni(II) in wastewater samples.

**Keywords:** 4-nitrophenol; electropolymerisation; nickel(II); mesoporous MCM-41; dispersive micro solid phase extraction

1. Introduction

Global, environmental and social problems such as water pollution have in recent decades received great attention. Toxic metals such as mercury, nickel and cadmium have been the major environmental pollutants threatening the health of human. The toxic effect of nickel on human health has been investigated intensively [1,2]. Many workers are continuously exposed to airborne nickel and some of them are afflicted with lung and nasal cancers [3]. However, many environmental analytical chemists have been focused on the monitoring and measuring of this element polluting the ecosystems. Various techniques such as flame atomic absorption spectrometry [4], micellar electrokinetic capillary chromatography [5], inductively coupled plasma optical emission spectrometry (ICP-OES) [6], electrochemical analysis [7] and inductively coupled plasma mass spectrometry (ICP-MS) [8] are available for the determination of nickel for most applications. Nevertheless, it is clear that all of the mentioned methods (with the exception of ICP-MS) cannot...
determine ultra-trace amounts of Ni(II), directly. Thus, a quantitative preconcentration step is necessary. Different sample preparation methods, such as liquid–liquid extraction [9], membrane filtration [10], cloud point extraction [11], ion exchange [12] and solid phase extraction (SPE), are employed [13]. Among them, SPE offers advantages including high preconcentration factor, easy operation (batch or column) and employing various kinds of adsorbents such as polymers, bonded silica, modified alumina and microorganisms [14–18]. In addition, SPE is used in micro scale as solid phase micro extraction (SPME) and dispersive micro solid phase extraction (DMSPE). Therefore, SPME and DMSPE are promising techniques that not only provide clean extraction with less solvent, but also notably improve analytical figures of merit. Consequently, significant efforts have been made for developing simpler and cheaper adsorbents to improve the SPME and DMSPE selectivity and efficiency [19–23].

The recently discovered mesoporous silica (MCM-41) has received great interest as a solid support because of its unique large surface area, well-defined pore size, shape and its modifiable surface [19–24]. This major discovery came when Mobil reported the successful synthesis of mesoporous M41S materials in 1992 [25]. Among the members of the M41S family, the synthesis and different applications of MCM-41-type mesoporous materials have been investigated extensively. MCM-41, the most used member of the M41S, possesses a high surface area and a large pore volume due to highly ordered hexagonally packed cylindrical pores [25]. Surface modification of these materials by functionalisation with organic groups permits their utilisation for different applications, such as ion exchange, encapsulation of transition-metal complexes, chemical sensors, catalysts, environmental purification, drug delivery, adsorption and nanomaterial fabrication [26,27].

Nowadays a large number of investigations have focused on the application of ligand-functionalised amorphous silica in heavy metals adsorption. Therefore, various types of functional groups and molecules can be incorporated into the MCM-41 host, to meet a given requirement [17,28–31]. For example, thiol functionalised silicas exhibit selective binding ability for Hg(II) in coexistence with other metal ions [32]. Thiol and amino functionalised SBA-15 silicas were used by Liu et al. for removal of Hg(II), Cu(II), Zn(II), Cr(III) and Ni(II) [33]. For the preparation of MCM-41, the most commonly used methods are hydrothermal and room temperature synthesis, as described in the literature [34,35].

According to the above-mentioned features of MCM-41 (high-surface area, mesoporosity and modification), a new adsorbent was prepared by modification of calcinated MCM-41 with 3-mercaptopropyltrimethoxysilane (MPTMS) and electro-reduction product of 4-nitrophenol (EP4NP). The EP4NP is a new Ni(II) selective chelating agent (polymer) which was synthesised by EP4NP in acetate medium [36]. The prepared polymer was characterized and a suitable chemical structure for that was proposed [36]. This polymer, which is a new kind of polyaminophenol, has a high tendency to form complex with Ni(II) [36]. The colour of this complex is blue and no other cations make complex with this ligand [36]. This adsorbent was characterised by X-ray diffraction (XRD), gas sorption and Fourier transform-infrared spectrometry (FT-IR). The major aim of this work was to investigate the capacity of this new hybrid material for preconcentration and determination of ultra-trace Ni(II) measured by the DMSPE-ICP-OES technique. The effect of the major parameters was investigated and optimised. Eventually, under optimum conditions, the new adsorbent was tested for its efficiency in extraction of ultra-trace amount of Ni(II) from real samples.

2. Experimental
2.1. Chemicals and reagents
4-Nitrophenol, cetyltrimethylammonium bromide (CTAB), tetraethylorthosilicate (TEOS), aqueous ammonia (25% w−1), ethanol (96%), methanol, sodium acetate trihydrate and common
chemicals such as hydrochloric acid, phosphoric acid and sodium hydroxide were all purchased from Merck (Darmstadt, Germany). MPTMS (99%) was purchased from Sigma Aldrich. Nickel standard stock solution was purchased from Carl Roth GmbH (Karlsruhe, Germany). Working standard solutions were made daily by stepwise dilution of standard stock solution with ultrapure water (<0.054 µs cm$^{-1}$, Milli-Q water system). The buffer solutions (0.5 mol L$^{-1}$, pH = 7) were prepared from phosphoric acid and sodium hydroxide solutions. Standard reference material analysed for method validation was trace elements in water (SRM 1640a) from the National Institute of Standard and Technology (NIST, Gaithersburg, MD, USA).

2.2. Instruments

An Expert MPD diffractometer (Philips Analytical) using Cu K$_\alpha$ radiation of wavelength 0.15405 nm was used to record XRD patterns. A Belsorp-mini volumetric analyser (Japan) was used to measure the surface area of MCM-41 samples using nitrogen physisorption isotherms. The morphology, size and size distribution of the MCM-41 particles were determined by scanning electron microscopy (SEM) (Hitachi su8040). Infrared spectra were recorded by RX1 FT-IR spectrophotometer (Perkin Elmer, Norfolk, VA, USA) in the region 4000–400 cm$^{-1}$. The pH of buffered samples was controlled by a pH-metre Model 780 (Metrohm, Switzerland). A centrifuge model 3–16k (Sigma) was used to separate the Ni(II)-containing adsorbent from aqueous phase. All quantitative measurements were carried out by the ICP-OES model ultima2 (HORIBAJOBIN YVON). A FAAS Model AA-6800 (Shimadzu, Japan) equipped with a graphite furnace was also used for quantitative analysis of nickel in real samples.

2.3. Preparation of Ni(II) selective ligand by electro-reduction of 4-nitrophenol

The Ni(II) selective chelating agent was prepared by electro-reduction of 4-nitrophenol in acetate medium on lead cathode (2 cm × 8 mm × 2 mm) based on electrolysis procedure reported in our previous work [36]. The concentrations of 4-nitrophenol, sodium acetate and sodium chloride were 2, 20 and 15 mg mL$^{-1}$, respectively; and the volume of catholyte was 100 mL. Anolyte was HCl (5%) and graphite rod (5 cm × 2 mm) was used as the anode. Two half cells were separated by glass frits (Schot No. 4, 10–16 µm) and electro-reduction was conducted under constant current of 15 mA. After 10 h of electrochemical synthesis, a dark brown powder was precipitated. The insoluble electrode product was separated and washed five times with double-distilled water to remove sodium acetate, sodium chloride, unreacted 4-nitrophenol and soluble electrode products. The electrode product was then dried at 60°C for 6 h. The electrode product was insoluble in water, but soluble in methanol, N,N-dimethylformamide and tetrahydrofuran.

2.4. Synthesis and calcination of MCM-41 mesoporous

A rapid method was applied for the synthesis of highly ordered MCM-41 [27]. For this purpose, the surfactant CTAB was dissolved in a mixture of water (155 mL)/ethanol and then the ammonia solution and sodium acetate were added. After about 10 min stirring at 200 rpm, a clear solution was obtained. After that the TEOS was added immediately to this solution. The final molar ratio of the resulting gel composition was TEOS: 1; CTAB: 0.22; sodium acetate: 0.034; NH$_3$: 11; ethanol: 1; water: 155. After 2.5 h stirring at room temperature, the obtained gel was transferred to a Teflon-lined stainless steel vessel and aged at 70°C for 5 h. Finally, the white precipitate was filtered and washed with copious amounts of water. The resulting
surfactant containing MCM-41 was dried at 70°C for 3 h and then calcinated in air atmosphere at a heating rate of 5°C min⁻¹ up to 550°C (held at this temperature for 5 h).

2.5. Modification of calcinated-MCM-41

In this work, the post-synthesis route was chosen for chemical modification of calcinated MCM-41 by MPTMS [37]. The calcinated MCM-41 (0.5 g) was dispersed in 100 mL of dry toluene at 60°C. After 30 min stirring at 350 rpm, 2 mL of MPTMS was added. The mixture was stirred at 60°C for 6 h and then filtered and the resulting modified material washed with 100 mL of toluene. The MPTMS-MCM-41 was dried at 70°C for 3 h and then left for characterisation. After characterisation of MPTMS-MCM-41, incorporation of Ni(II) selective chelating agent was carried out in water/methanol (1:1) mixture. In this procedure, the electrode product or Ni(II) selective chelating agent (20 mg as an optimum amount) was dissolved in 15 mL methanol (as sol. 1). Then 0.5 g MPTMS-MCM-41 was dispersed in 15 mL water (as sol. 2). Lastly, two solutions were mixed and agitated at ambient temperature for 6 h. The resulting EP4NP-MPTMS-MCM-41 was filtered, washed with ultrapure water and then dried at 70°C for 3 h. The EP4NP-MPTMS-MCM-41 was applied for DMSPE-ICP-OES determination of ultra-trace amount of Ni(II).

2.6. DMSPE-ICP-OES procedure of Ni(II)

In total, 50 mL of the Ni(II) solutions (in the concentration range 0.05–1.0 μg L⁻¹) containing 0.5 mol L⁻¹ phosphate buffer (pH = 7) was prepared. The EP4NP-MPTMS-MCM-41 was (0.2 g) dispersed in Ni(II) solutions as a new Ni(II) selective adsorbent. After 20 min extraction (as optimum time), the dispersed solid phase was centrifuged (3000 rpm and 5 min) and the liquid phase was removed by inverting. The Ni(II)-containing EP4NP-MPTMS-MCM-41 was washed with 10 mL ultrapure water and then centrifuged. In the end, 2 mol L⁻¹ HCl of 1 mL was used for elution of Ni(II) before ICP-OES determination. The instrumental parameters in all experiments of this work were generator power 1.2 kW, plasma gas flow rate 15 L min⁻¹, auxiliary gas flow rate 1.3 L min⁻¹, sheath gas flow rate 0.2 L min⁻¹, rinsing time 5 s, nebulisation flow rate 0.02 L min⁻¹, nebulisation pressure 1 bar (parallel type), normal speed of pump 20 rates min⁻¹ and stability time 15 s. The extraction recovery percentage (ER%) was calculated by ER% = 100 × (1.0 × Cₓ)/(Cᵢ × 50), where the Cₓ is final concentration, Cᵢ is initial concentration, 50 is the initial volume of Ni(II)-containing solution and 1.0 is the final volume of extractant.

3. Results and discussion

3.1. Characterisation of EP4NP and chelation investigation

Based on characterisation results in our previous work [36], the electro-reduction of 4-nitrophenol in sodium acetate aqueous medium produces a kind of polyaminophenol (Figure 1). This product could be act as Ni(II) selective chelating agent to form a blue complex with pH in the range of 6–10 [36]. The study of IR spectrum of Ni(II) complex with electrode product (EP4NP) showed some peaks around 490–520 and 600–680 cm⁻¹ (Figure 1S). Some authors have reported for different ligands the Ni–N and Ni–O stretching vibration around 450–500 and 550–600 cm⁻¹, respectively [38].
3.2. Adsorbent characterisation and stability

The SEM images of the calcinated MCM-41 are shown in Figure 2. The particle morphology of the MCM-41 is variable. The particle size ranges from approximately 40 to 100 nm. Nevertheless, some particles larger than 100 nm can be seen in SEM images.

The XRD patterns for MCM-41 are shown in Figure 3. Unmodified MCM-41 samples appeared with a well-known pattern at low 2θ values with very sharp (100) diffraction peaks at 2.15° (surfactant-containing MCM-41) and 2.37° (calcinated MCM-41). These materials showed two additional peaks (110 and 200) at higher 2θ values. These reflection patterns can be attributed to the hexagonal lattice of mesoporous materials. A unit cell parameter (a₀) for calcinated MCM-41 was calculated to be 42.89 Å using the equation a₀ = 2d₁₀₀/√3 [39]. However, after functionalisation, the XRD patterns showed significant decreases in intensities with peak broadening for (100) reflections. The intensity decrease also appeared for higher-order reflections. The intensity decrease in 2θ = 2.24° (100) of MPTMS-MCM-41 provides further evidence that grafting of MPTMS mainly occurred inside the mesoporous nanochannels. It is clear that the attachment of organic functional groups to MCM-41 walls tends to reduce the scattering power of the structure. Additionally, comparison of XRD patterns of unmodified MCM-41 samples (Figure 3(a) and 3(b)) and functionalised MCM-41 materials (Figure 3(c) and 3(d)) revealed that the dominant (100) reflection that appeared at 2.37° for calcinated MCM-41 was found to be shifted to 2.24° and 2.21° for MPTMS-MCM-41 and EP4NP-MPTMS-MCM-41, respectively. Comparatively, modified MCM-41 samples changed into a slightly disordered structure after functionalisation in comparison with unmodified MCM-41. The alterations in the XRD pattern between modified and unmodified MCM-41 are attributed to several factors [37] such as the decrease in x-ray contrast of air-silica to organic-silica that causes peak intensity reduction and loss of the periodicity or long range order. However, the XRD pattern of the functionalised MCM-41 also suggests that the structural order of the prepared material is partially maintained after functionalisation.

The nitrogen adsorption–desorption isotherms for MCM-41 are shown in Figure 2S. They all displayed type IV isotherms. The volume of nitrogen adsorbed decreased with functionalisation, which is indicative of a reduction in pore size. The Brunauer–Emmett–Teller (BET) specific surface area, pore volume and average pore diameters of MCM-41 were calculated using the Barrett–Joyner–Halenda model of the adsorption branch (Table 1). As can be seen, the BET surface area and total pore volume decreased after chemical modification and...
incorporation. Because the mercaptopropyle chains were grafted to the surface of hexagonal channels and then facilitated the strong incorporation of the EP4NP via SH-NH interactions.

The FT-IR spectra of surfactant-containing MCM-41, calcinated-MCM-41, MPTMS-MCM-41 and EP4NP-MPTMS-MCM-41 are shown in Figure 3S. The characteristic peaks related to O–H stretching of surface silanol groups, Si–O–Si groups, Si–O stretching, C–H stretching of CTAB (Figure 3Sa) can be observed [40]. MPTMS-MCM-41 and EP4NP-MPTMS hybrid materials showed bands for C–H stretching vibration around 3000–2800 cm\(^{-1}\). These
confirmed grafting and incorporation of MPTMS and EP4NP into calcinated MCM41 and caused the colour change from white to brown (Figure 3, inset).

### 3.3. Preliminary experiments

In the initial measure, three solutions with initial volumes of 50 mL (pH 7.0) containing 1.0 μg L⁻¹ Ni(II) were prepared. Then 0.2 g of calcinated MCM-41, 0.2 g of MPTMS-MCM-41 and 0.2 g of EP4NP-MPTMS-MCM-41 (20 mg EP4NP loaded on 0.5 g MPTMS-MCM-41 as EP4NP-MPTMS-MCM-41 (4.0% w w⁻¹)) was added to each solution. After 20 min extraction and 5 min re-extraction (with 1 mL HCl 2 mol L⁻¹), the emission line of nickel at 221.647 nm was evaluated. The time of centrifugation (3000 rpm) was 5 min and ultrapure water was used for washing. The intensities of signals were 22,321, 48,356 and 85,832 for calcinated MCM-41, MPTMS-MCM-41 and EP4NP-MPTMS-MCM-41, respectively. These results cleared the effective role of the EP4NP in DMSPE of Ni(II). Therefore, EP4NP-MPTMS-MCM-41 was chosen as the adsorbent in this study.
3.4. Optimisation of the effect of parameters

All following experiments were carried out under conditions of Ni(II) concentration 1 μg L$^{-1}$, mass of adsorbent (4.0% w w$^{-1}$) was 0.2 g, pH of solutions were 7 (adjusted by phosphate buffer 0.5 mol L$^{-1}$), centrifugation at 3000 rpm for 5 min, initial volumes of samples were 50 mL and elution volume was 1 mL (HCl 2 mol L$^{-1}$); except when that parameter was under investigation.

3.4.1. Effect of pH

The effect of pH on the DMSPE of Ni(II) was investigated in the range of 2–10. Figure 4(a) shows the obtained results. The low complex formation at pH < 6.5 and nickel hydroxide formation at pH > 8 will decrease the efficiency of Ni(II) extraction. As mentioned in Section 3.1, the FT-IR of Ni(II) complex with EP4NP showed some peaks which are related to formation Ni–N and Ni–O vibration bands [38]. In acidic media (pH < 4), the N atoms of EP4NP (Figure 1) will be protonated and cannot act as donor. Therefore, the efficiency of complex formation decreases [36]. However, pH 7.5 was selected as the best condition.

3.4.2. Effect of mass of EP4NP

The amount of EP4NP loaded on 0.5 g MPTMS-MCM-41 varied from 5 to 30 mg. After desorption, the intensities of nickel emission line (221.647 nm) were determined. The results

Figure 4. The effect of pH (a), extraction time (b), mass of chelating agent (c) and EP4NP-MPTMS-MCM-41(4.0%) (d) on the DMSPE-ICP-OES of Ni(II).
revealed that the extraction efficiency increased by increasing the mass of ligand up to 20 mg (4.0% w w\(^{-1}\)) and remained nearly constant at higher amounts. Hence, subsequent DMSPE experiments were carried out in this condition (Figure 4(c)).

3.4.3. Effect of adsorbent mass
The amount of the new modified adsorbent EP4NP-MPTMS-MCM-41 varied in the range of 0.05–0.25 g. Figure 4(d) shows the obtained results. The maximum extraction recovery was achieved in the range of 0.15–0.25 g. Therefore, the optimal amount of adsorbent was chosen as 0.2 g.

3.4.4. Effects of eluent concentration
The extraction recovery of Ni(II) was studied at different HCl concentrations (as eluent) in the range of 0.1–3 mol L\(^{-1}\) (because of the oxidation property of HNO\(_3\), HCl was preferred as eluent). Due to the low stability constant of Ni(II)-EP4NP complex at pHs < 4 \[^{36}\], it seems that the Ni(II) ions are almost completely desorbed by acidic elution. The best quantitative results were obtained for the HCl concentrations greater than 1 mol L\(^{-1}\). Hence, the HCl 2 mol L\(^{-1}\) was preferred as eluent in this work. On the other hand, structural and chemical stability of the MCM-41 decreases at higher acidic strength of the medium.

3.4.5. Effect of contact time
The contact time varied from 5 to 60 min, and the results are presented in Figure 4(b). The results indicate that the adsorption kinetic is approximately rapid and the equilibrium state is achieved after 20 min. There is a linear relationship between log ([Ni]/mol L\(^{-1}\)) and contact time (min) as follows:

\[
\log([\text{Ni}]/\text{mol L}^{-1}) = -0.40t - 7.97 \quad r^2 = 0.986
\]

It means that the preconcentration process obeyed the pseudo first-order kinetic because the amount of adsorbent was constant. Therefore, 20 min was selected for subsequent experiments.

3.4.6. Effect of elution time
The Ni(II) extraction efficiency was investigated by varying the elution or re-extraction time. The elution times of 2, 5, 8, 10 and 15 min were tested. The obtained results revealed that the best extraction efficiency could be accomplished after 5 min elution with HCl 2 mol L\(^{-1}\). The elution time is dependent on the kinetic of the desorption process. It seems this concentration level of H\(^+\) ions not only provides a proper thermodynamic condition to dissociate the Ni(II) complex but also accelerates the desorption process. Therefore, 5 min elution was chosen for subsequent experiments.

3.4.7. Effect of ionic strength
The influence of ionic strength on the extraction efficiency of Ni(II) was investigated by adding different concentrations of NaCl in the range of 0–150 g L\(^{-1}\). The obtained results demonstrated that there is no significant effect on the DMSPE of Ni(II) with increasing ionic strength. This is
because of the high tendency of the ligand to Ni(II) ions [36]. Therefore, the results obtained in this study were expected. Hence, the proposed DMSPE can be used easily in high salt media.

3.4.8. Effect of foreign ions

A set of experiments was carried out to investigate the interferences of heavy metal ions and major ions present in seawater. The obtained results are presented in Table 2. It can be concluded that foreign ions have no significant interferences in selective DMSPE-ICP-OES determination of ultra-trace Ni(II). These results suggest that the new modified adsorbent has a high selectivity towards Ni(II) and has significant potential for application to real samples.

3.5. Calibration and merit figures

Under optimum conditions described in the optimisation section, the calibration curve was drawn. The curve was found to be linear for a working range of 0.05–2.0 μg L⁻¹. The linear equation along with correlation coefficient or regression (r²) is as follows:

\[ I = 67.62 \times 10^3 C_0 + 1.87 \times 10^3 \quad r^2 = 0.995 \]

where \( I \) is the intensity of the nickel emission line (after background correction) and \( C_0 \) is the amount of nickel in μg L⁻¹ of initial solution. The limit of detection given by LOD = (3 × SD)/\( m \), where SD is the standard deviation of 5 blanks (50 mL of ultrapure water subjected to the DMSPE-ICP-OES procedure), and \( m \) is the slope of the calibration curve, was calculated to be 0.006 μg L⁻¹. The limit of quantification (LOQ) is the lowest level of the analyte that can be accurately and precisely measured. The LOQ is given by the equation LOQ = (10 × SD)/\( m \) and was calculated to be 0.019 μg L⁻¹ for the proposed method. Under the optimum conditions, the mean, standard error and relative standard deviation (RSD) for five replicate determinations of

| Foreign ion | mgL⁻¹ a | \( (w_{\text{ion}}/w_{\text{Ni}}) \times 10^2 \) | ER% |
|-------------|---------|-----------------------------------------------|-----|
| Na⁺        | >1000   | >10,000                                      | 98.3|
| K⁺         | 1000    | 10,000                                       | 98.4|
| Mg²⁺       | 1000    | 10,000                                       | 98.1|
| Ca²⁺       | 1000    | 10,000                                       | 98.0|
| Ba²⁺       | 500     | 5000                                         | 98.4|
| Mn²⁺       | 50      | 500                                          | 98.1|
| Pb²⁺       | 50      | 500                                          | 98.5|
| Zn²⁺       | 50      | 500                                          | 98.2|
| Hg²⁺       | 10      | 100                                          | 98.5|
| Cd²⁺       | 10      | 100                                          | 98.3|
| Co²⁺       | 10      | 100                                          | 98.3|
| Cu²⁺       | 10      | 100                                          | 97.8|
| Cr³⁺       | 10      | 100                                          | 97.9|
| Cl⁻        | >1500   | >15,000                                      | 98.5|
| SO₄²⁻      | 100     | 1000                                         | 98.3|
| NO₃⁻       | 100     | 1000                                         | 98.3|
| CO₃²⁻      | 100     | 1000                                         | 97.7|

Note: *Ni(II) = 1 μg L⁻¹.
0.5 μg L\(^{-1}\) of Ni(II) were calculated to be 0.48 μg L\(^{-1}\) (preconcentration factor = 48), 4.0% and 3.2%, respectively. However, such merit figures are sufficient enough to determine precisely and accurately trace nickel in unpolluted seawater samples (approximately 0.6 μg L\(^{-1}\)) \[^{41}\].

### 3.5.1. Reliability of the method using standard reference material

The reliability of this method was tested by analysing the diluted standard reference material (NIST). The two solutions of Ni(II) with concentrations of 1 and 0.5 μg L\(^{-1}\) were prepared by dilution of SRM 1640a (25.32 ± 0.14 μg L\(^{-1}\)). Also, 50 mL of these solutions was utilised under optimised conditions of the proposed method and the concentrations were found. The calculated recovery percentages were 103 and 96, respectively. These results reveal that there is a good agreement between the results with the certified values.

### 3.5.2. Stability of EP4NP-MPTMS-MCM-41

Twenty samples with the same volume (50 mL distilled water) and the same concentration of nickel (1 ng mL\(^{-1}\)) were prepared. The samples were analysed during 20 days. After each analysis, the adsorbent was washed by ultrapure water and dried at 70°C and used again the next day. The average recovery percentage was 98.2 ± 1.2%. This result showed that the prepared adsorbent was stable and reproducible.

### 3.5.3. Comparison with other methods

Table 3 compares analytical characteristics (LOD and RSD) of the proposed method with those reported previously for the determination of nickel by ICP-OES associated with solid phase extraction. It is evident from Table 4 that the proposed DMSPE-ICP-OES procedure utilising bifunctionalised MCM-41 has a lower detection limit compared to the other methods reported in literature \[^{42–44}\]. This signifies that the proposed method is quantitatively more reliable than the previous reported methods for nickel determination using DMSPE-ICP-OES.

### 4. Analysis of real samples

In order to evaluate the analytical applicability, the proposed method was used for the determination of nickel ions in mineral water, demineralised water (reverse osmosis plant, pet zone, Mahshahr, Iran) and inlet brine to membrane chlor-alkali electrolyzers (chlor-alkali plant, Arvand petrochemical complex, pet zone, Mahshahr, Iran). Monitoring and determination of ultra-trace amounts of heavy metal ions in the inlet brine are more important due to the deposition of these ions on the surface of the membrane and current efficiency loss.

| Method               | Chelating reagent                | LOD (μg L\(^{-1}\)) | RSD (%)  | Reference |
|----------------------|----------------------------------|---------------------|----------|-----------|
| Proposed method      | Synthesised chelating agent      | 0.006               | 3.2 (n = 5) | –         |
| SPE-ICP-OES          | C\(_{18}\) cartridges            | 0.030               | 0.2 (n = 3) | \[^{42}\] |
| SPE-ICP-OES          | Surface-imprinted silica gel     | 0.16                | 1.48 (n = 8) | \[^{43}\] |
| FI-ICP-OES           | ACSchiffs base                   | 0.07                | 2.2 (n = 10) | \[^{44}\] |

Note: FI, flow injection; AC, activated carbon.
Moreover, the proposed method was applied to the determination of nickel ions in some internationally registered lagoons south of the Caspian Sea (Amirkelayeh, Ravansar and Gomishan). These samples were also analysed by graphite furnace atomic absorption spectrometry (GFAAS). The results are shown in Table 4. It is evident that the proposed method could be successfully utilised to ultra-trace level determination of nickel ions in salty and soft water samples.

| Sample            | Spiked (μg L$^{-1}$) | DMSPE-ICP-OES (μg L$^{-1}$)$^a$ | GFAAS$^a$ |
|-------------------|----------------------|---------------------------------|-----------|
| Mineral water     | 0.1                  | 0.109 ± 0.005                   | Not detected |
| DM water          | 0.1                  | 0.104 ± 0.007                   | Not detected |
| Inlet brine$^b$   | –                    | 0.470 ± 0.04                    | Not detected |
| Amirkelayeh       | –                    | 1.35 ± 0.08                     | 1.5 ± 0.10 |
| Ravansar          | –                    | 1.62 ± 0.10                     | 1.77 ± 0.13 |
| Gomishan          | –                    | 1.53 ± 0.09                     | 1.66 ± 0.11 |

Notes: $^a$Mean value of three replicates ± standard deviation; $^b$twofold diluted.

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5. Conclusion
A new Ni(II) selective adsorbent was developed by modification of calcinated MCM-41 with MPTMS and EP4NP. Characterisation of the mesoporous materials by various techniques, including SEM, XRD, nitrogen adsorption–desorption and FT-IR, demonstrated the grafting and stable incorporation of MPTMS and EP4NP, respectively. After characterisation, the new adsorbent was successfully applied for selective dispersive micro solid phase extraction of Ni (II) ions from water samples prior to the ICP-OES determination. The adsorption and desorption of nickel were optimised to result in a limit of detection of 0.006 μg L$^{-1}$, which is approximately 50-fold lower than that of direct ICP-OES. Finally, the proposed method was successfully employed for the determination of trace nickel ions in salty and soft water samples.

Disclosure statement
No potential conflict of interest was reported by the authors.

Supplementary material
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