Enrichment of copper and nickel with solid phase extraction using multiwalled carbon nanotubes modified with Schiff bases

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The behaviour of some Schiff bases in the presence of metal ions is very selective in complex formation. In this study, new, selective and easily prepared adsorbent materials have been developed. Multiwalled carbon nanotubes (MWCNTs) are quite suitable as supporting material for preparation of new solid phase adsorbents modified with Schiff bases due to their selective nature. Different Schiff bases were designed and synthesised as adsorbent agents for Ni(II) and Cu(II) ions, according to the literature, and MWCNTs were modified with these Schiff bases. The modification of CNTs was performed by adsorption from the alcoholic solution of Schiff base. The measurements of Ni(II) and Cu(II) ions were carried out using ICP-MS. Different parameters such as pH, model and eluent solution flow rates, eluent type, amount of ligand, sample volume and effect of foreign ions, which have an effect upon recovery of analytes, were investigated. The obtained results indicated that enrichment can be done with six modified adsorbent materials for Cu(II) at pH 9 and two modified adsorbent materials for Ni(II) at pH 8. It was concluded that four adsorbent materials were selective only for the enrichment of Cu(II). Merely one modified adsorbent material was noneligible for the enrichment of Cu(II) and Ni(II). The solid phase adsorbents prepared by modification with two of the Schiff bases used in this study showed an enrichment factor of 80 for both metal ions, whereas the solid phase adsorbents prepared by modification with four of the Schiff bases showed an enrichment factor of 40 for Cu(II) ions. The confirmation of the developed method was tested with certified reference materials with satisfactory results.

Keywords: multiwalled carbon nanotubes; Schiff base; solid phase extraction; copper; nickel; enrichment

1. Introduction

In the growing world, heavy metal contamination is a huge risk for human health and the environment, and their effects are increasing day by day. Even a very little dose of these elements is risky for human health and the environment [1]. That is why it is very important to determine trace amounts of heavy metals in the biological, clinical and environmental samples. Therefore, this area is still interesting for analytical chemistry. One of the other related areas of analytical chemistry that investigates chemical systems and components is advanced materials and their applications [2]. Carbon nanotubes (CNTs) are considered as nanomaterials due to their unique structural, electronic, mechanical, chemical and physical properties. Therefore, CNTs are of interest to many different disciplines [3]. CNTs were characterised by Iijima in 1991 [4] with high-resolution electron microscopy during the arc discharge synthesis and they were called as ‘helical microtubules’. CNTs can be described as an atomic sheet
sp²-hybridised carbon atoms arranged in a honeycomb encircled on a cylinder perfectly and continuously. If this encirclement is composed of a single cylindrical structure it is called singlewalled CNT (SWCNT), if it is a structure where more than one graphene layers interlace concentrically it is called multiwalled CNT (MWCNT) [5]. CNTs have many various analytical applications, such as sensor design [6], hydrogen storage [7] and chromatography techniques [8]. Especially in recent years, CNTs have drawn attention as solid phase adsorbent materials [9]. CNTs have strong Van der Waals, π–π interactions [10], and they also possess large surface area. In this regard, the usage of CNTs in solid phase extraction (SPE) method for the purpose of enrichment became attractive [9,11–13]. SPE is preferred, compared with the other enrichment methods, because this method consumes less organic solution, has high enrichment factor, can work with huge volumes and enables to work with different adsorbent materials [14,15]. As solid phase adsorbent materials, as-grown CNTs are insoluble in most of the solvents and water because of their non-polar bonds and this situation limits their application as SPE sorbents [16]. On the other hand, CNT surfaces can be modified purposefully using various oxidation [17] and/or complexing agents [18]. This makes the usage of new adsorbent materials possible in the enrichment of inorganic and organic types with SPE [19]. In modification, ethylenediamine [20], iminodiacetic acid [21], 4-aminoazobenzene [22], 2-((3-silylpropylimino) methyl) phenol [23] and quinalizarin [24] were used in recent studies. However, the studies where Schiff bases, known as being one of the best ligands for metal ions since 1930, are used as an enrichment material with CNTs for analytical purpose are limited in the literature [9,25,26].

In this study, six symmetric Schiff bases specific to Cu(II) and Ni(II) ions were synthesised, and some were used in the preparation of new solid phase adsorbents with modification of the MWCNT surfaces. The study’s originality is closely connected with the selected Schiff bases’ selectiveness to Cu(II) and Ni(II). The Schiff bases that were used in the study were obtained as a result of condensation reaction between symmetric diamines \( (n = 3,4,6,7,8,9,12) \) and salicylaldehyde. These were called as L1, L2, L3, L4, L5, L6 and L7, respectively. When the coordination chemistry literature [27–32] was surveyed, it was seen that L1 and L2 ligands complexed with both Cu(II) and Ni(II); but L4, L5, L6, L7 ligands complexed with only Cu(II). Complexes of the concerned metals with L3 were not formed. Ligands were selected as they were specific to the metals in question. The hypothesis of the study was created on the bases of this coordination chemistry information and the data we obtained from our study is parallel to this information. In the study, the design of new enrichment materials was based upon the idea that CNTs are used as SPE adsorbent materials because they are strong adsorbents; hydrophobic side of the Schiff base can be adsorbed onto the MWCNT surface; hydrophilic groups are found on Schiff bases can be complexed with metal ions and accordingly Schiff bases’ creation of an interface between CNTs surface and aqueous solution. Optimisation studies were carried out in order to determine the optimum conditions for the enrichment of Cu(II) and Ni(II) with these new adsorbent materials. Then the developed method was tested with NIST-1640a Natural water – Trace elements, NIST-2670a Toxic elements in freeze-dried urine and BCR-277R Estuarine sediment – Trace elements certified reference materials; the obtained results agreed with certified values.

2. Experimental

2.1. Reagents and chemicals

In experimental studies, analytical grade chemicals and reagents were used. 18.2 mΩ deionised water needed throughout the study was obtained from pure water equipment Millipore, Milli-Q A-10 (Darmstadt, Germany). Throughout the study, copper and nickel solutions were prepared daily.
by diluting stock standard solutions, 1000 mg/L (Merck, Darmstadt, Germany). Hydrochloric (37%, Merck) acid and nitric acid solutions (≥69%, Fluka), which were used as eluents, were prepared by diluting concentrated solutions. Buffer solutions used in the study were prepared using pH 2–3 \( \text{H}_3\text{PO}_4/\text{NaH}_2\text{PO}_4/\text{H}_2\text{O} \), pH 4–6 \( \text{CH}_3\text{COONH}_4/\text{CH}_3\text{COOH} \), pH 7 \( \text{NaH}_2\text{PO}_4/\text{H}_2\text{O}/\text{Na}_2\text{HPO}_4 \), pH 8–10 \( \text{NH}_3/\text{NH}_4\text{Cl} \). MWCNT (D × L = 110–170 nm × 5–9 μm), which was used as an adsorbent, was obtained from Sigma Aldrich (Milwaukee, WI, USA). Triton X-100 (Fluka) was used in the modification of adsorbent material. All glass and plastic materials used for experiments were kept in 10% (v/v) nitric acid for at least 48 h and subsequently washed three times with distilled water and deionised water before use. In the study, three certified standard materials, BCR-277R Estuarine sediment – Trace elements (European Commission DG Joint Research Centre Institute for Reference Materials and Measurements, IRMM), NIST-2670a Toxic elements in freeze-dried urine (National Institute of Standards and Technology) and NIST-1640a Natural water – Trace elements (National Institute of Standards and Technology), were used in order to test the confirmation of the method.

2.2. Instrumentation

Copper and nickel measurement was carried out by Agilent 7500ce (Tokyo, Japan) Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) equipped with a collision/reaction cell in the form of octopole reaction system (ORS). The instrumental parameters were set as recommended by the manufacturer. Surface images of modified CNTs used as an adsorbent material were taken by Zeiss/Supra 55 Field Emission Scanning Electron Microscope (FESEM; Oberkochen, Germany). An Energy Dispersive X-ray (EDX) mapping system was used to demonstrate the elemental composition of the carbon nanotubes surface (Oberkochen, Germany). IR spectrums of Schiff bases which were used in the modification of adsorbent materials were taken by Perkin Elmer Fourier Transform Infrared Spectrometer (FT-IR/FIR/NIR Spectrometer Frontier, ATR; Norfolk, VA, USA). NMR spectrums were taken by Bruker Ultrashield Plus Biospin GmbH Nuclear Magnetic Resonance Spectroscopy (Avance III 400 MHz NaNoBay FT-NMR; Rheinstetten, Germany) and their characterisations were carried out. Throughout the study, all pH measurements were carried out with İnoLab pH 720 pH meter (Apeldoorn, the Netherlands). The control of model solution and eluent flow rate during the enrichment studies was achieved with KNF, N026.1.2 AN.18 vacuum pump (Freiburg, Germany). In the process of adsorbent material preparation, Bandelin, RK 100H ultrasonic bath (Berlin, Germany) and Velp Scientifica (Usmate Velate MB, Italy) were used as magnetic stirrers. Mars 240/50 model microwave digestion system (CEM Matthews, NC, USA) was used in sample solubilisation.

2.3. Preparation of the Schiff bases

Seven ligands, used in the modification of adsorbent material, were chosen from symmetric diamines’ salicylaldehyde and Schiff bases, which were synthesised as a result of condensation reactions in ethanol [33]. Schiff bases were respectively called \( \text{N,N’-bis(salicylidene)-1,3 dianminopropene, L1; \text{N,N’-bis(salicylidene)-1,4 dianminobutane, L2; \text{N,N’-bis(salicylidene)-1,6-diaminohexane, L3; \text{N,N’-bis(salicylidene)-1,7-diaminoheptane, L4; \text{N,N’-bis(salicylidene)-1,8-diaminoctane, L5; \text{N,N’-bis(salicylidene)-1,9-diaminononane, L6; and \text{N,N’-bis(salicylidene)-1,12-diaminododecane, L7 (Figure 1).} } \)
2.4. *Preparation and modification of adsorption materials*

For the modification of MWCNTs, used as adsorbent materials for the enrichment of Cu(II) and Ni (II) with SPE, the MWCNTs were first treated with nitric acid to generate oxygen-containing groups. This treatment was achieved by the dispersion of 500 mg MWCNTs in 30 mL concentrated HNO₃, after which the solution was refluxed at 120°C for 1 h [34]. Oxidised MWCNTs (O-MWCNTs) were washed with ultrapure water until neutral pH was reached, and then evaporated at 100°C in an oven. Afterwards, MWCNTs were modified using Triton X-100 and seven Schiff bases prepared as described in Section 2.3. At this stage, Triton X-100 was used because it decreased the surface tension, increased CNT’s dispersion ability, and changed adsorption property positively [35,36]. Schiff bases were used as chelating agent for metal ions. Modification was made according to the following procedure. For each adsorbent, 50 mL of 0.2% (w/v) Schiff base solution in methanol and 0.4 g Triton X-100 were added to 200 mg O-MWCNT, the mixture was sonicated in ultrasonic bath for 4 h and then refluxed in the magnetic stirrer for 12 h. The seven different modified MWCNTs (MMWCNTs) obtained were filtered and dried at room temperature and made ready for their use in the enrichment of heavy metal in SPE. Consequently, seven different adsorbent materials were prepared with Schiff bases which connected to CNT surfaces, whose disperse ability increases with the help of Triton X-100 as a result of physical adsorption. The adsorbent materials, which were prepared for the enrichment of Cu(II) and Ni(II), were as follows: O-MWCNT & N,N’-bis(salicylidene)-1,3-diaminopropane & Triton X-100: MMWCNT L1, O-MWCNT & N,N’-bis(salicylidene)-1,4-diaminobutane & Triton X-100: MMWCNT L2, O-MWCNT & N,N’-bis(salicylidene)-1,6-diaminohexane & Triton X-100: MMWCNT L3, O-MWCNT & N,N’-bis(salicylidene)-1,7-diaminooctane & Triton X-100: MMWCNT L4, O-MWCNT & N,N’-bis(salicylidene)-1,8-diaminononane & Triton X-100: MMWCNT L5, O-MWCNT & N,N’-bis(salicylidene)-1,9-diaminodecane & Triton X-100: MMWCNT L6, O-MWCNT & N,N’-bis(salicylidene)-1,12-diaminododecane & Triton X-100: MMWCNT L7.

2.5. *Column preparation*

Glass columns (10 mm i.d. and 300 mm length) were used for SPE. A piece of polyethylene glass wool was placed at the bottom of the column to avoid loss of the adsorbent. Afterwards, 200 mg modified MWCNTs that were used as column filling material were placed onto it. A small amount of polyethylene glass wool was put onto the adsorbent in order to fix the columns, and bed height was determined to be approximately 1.5 cm. Columns were washed with deionised water before each use and the column’s conditioning was carried out with buffer solutions according to the model solution’s pH value.

2.6. *General enrichment procedure*

The enrichment studies performed with adsorbent materials which were modified with Schiff bases are described in Section 2.4, and prepared columns are described in Section 2.5. After
that, 100 mL model solutions containing 1 μg Ni(II) and 1 μg Cu(II) were adjusted at pH 8 and 9, respectively, using the related buffer solutions. The related model solutions were passed through the columns at a flow rate of 5 mL min\(^{-1}\) for MMWCNT L2; similarly, model solutions which were filled with MMWCNT L1, MMWCNT L3, MMWCNT L4, MMWCNT L5, MMWCNT L6 and MMWCNT L7 were passed through the columns at a flow rate of 6 mL min\(^{-1}\), after which they were taken back from the column using nitric acid and determined by ICP-MS. All the enrichment studies were carried out by declaring and following this procedure.

### 2.7. Certified samples preparation

In this study, three certified reference materials, BCR-277R Estuarine sediment–Trace elements, NIST-2670a Toxic elements in freeze-dried urine and NIST-1640a Natural water – Trace elements, were used for the confirmation of the method. BCR-277R Estuarine sediment – Trace elements certified standard reference material was prepared for the solubilisation according to the certificate. The solubilisation was carried out using the appropriate burning programme of the microwave digestion system. The necessary dilution and pH adjustment were carried out before the analysis. In the same way, the NIST-2670a Toxic elements in freeze-dried urine and NIST-1640a Natural water – Trace elements certified standard reference materials were prepared as reported in certificate. After that, pH adjustment was completed and dilution was made before analysis.

### 3. Results and discussion

The influence of the analytical parameters, including pH, model and eluent solution flow rate, eluent type, amount of ligand, sample volume and effect of foreign ions, was investigated. This was done in order to achieve the best optimum conditions for the enrichment of Cu(II) and Ni (II) with the newly designed adsorbent materials. In all experiments, the recovery values (\(R\%\)) were calculated on the basis of the ratio of the amount of the element in the solution after adsorption/elution to that in the initial sample solution [37].

#### 3.1. FESEM images of modified MWCNTs

FESEM images of all modified adsorbent materials showed that the surface of MWCNTs became different after the modification. The relative abundance of nitrogen and oxygen attached to the surface of modified MWCNTs was shown with EDX mapping. We observed considerable increase in the relative abundance of nitrogen and oxygen and considerable thickening in CNT diameter. The as-grown MWCNTs FESEM image and the obtained modified adsorbent materials’ EDX mapping images are shown as supplementary material (Figures S1 and S2, respectively).

#### 3.2. Effect of pH on adsorption

The control of pH in the enrichment of metals with SPE is a crucial parameter. For this purpose the pH of sample solutions was adjusted to a range of 2–9 and the general procedure, stated in Section 2.6, was applied to all the prepared adsorbent materials and the two metals. According to the results, we obtained quantitative recovery values (\(R > 97\%\)) for the enrichment of Cu(II) with MMWCNT L1, MMWCNT L2, MMWCNT L4, MMWCNT L5, MMWCNT L6 and MMWCNT L7 when the pH was 9 (Figure 2). However, in the enrichment of Ni(II), we could
get quantitative recovery values ($R > 98\%$) with only MMWCNT L1 and MMWCNT L2 adsorbent materials at pH 8 (Figure 3). In the event that MMWCNT L3 adsorbent material was used, satisfactory recovery values ($R < 60\%$) could not be acquired for both of the metals (Figures 2 and 3), and this adsorbent material was not used in this study afterwards.

3.3. **Effect of the ligand concentration**

In order to investigate the effect of Schiff base concentration upon the recovery, 50 mL of 0.1%, 0.2% and, 0.3% (w/v) ligand solutions were used during the preparation of adsorption materials, and the general procedure, stated in Section 2.6, was applied to all the adsorbent materials and two metals. According to the results (Figure 4), quantitative recovery (94.30%–104.60%) values were obtained with 0.2% ligand solution.

3.4. **Effect of sample flow rate**

Another parameter that affects the recovery because of its interaction with analyte adsorbent material in the enrichment process with SPE is the model solutions’ flow rate. Therefore, the
effect of sample flow rate was examined by passing 100 mL of model solution containing 1 μg metal ions with flow rate in the range of 2–10 mL min\(^{-1}\) through the column. For the enrichment of Cu(II) and Ni(II), sample flow rate was chosen as 6 mL min\(^{-1}\) for MMWCNT L1\( (R > 94\%)\) and 5 mL min\(^{-1}\) for MMWCNT L2\( (R > 99\%)\), respectively. For the enrichment of Cu(II), the sample flow rate was chosen as 6 mL min\(^{-1}\) for MMWCNT L4, MMWCNT L5, MMWCNT L6 and MMWCNT L7\( (R > 90\%)\).

3.5. Effect of eluent type, volume and flow rate
The selection of the eluent type, volume and which flow rate is suitable for the recovery of metals in the column are essential factors affecting the studies’ performance and thus they must be optimised. As a result of the optimisation study, where 1 M and 2 M of nitric acid and hydrochloric acid solutions were used, 2 M HNO\(_3\) was selected as the best eluent for enrichment of Cu(II) and Ni(II) with MMWCNT L1 and MMWCNT L2 (Table 1). The effect of the eluent volume was also studied using various volumes (2–10 mL) of 2 M HNO\(_3\). It was found that quantitative recoveries were obtained using 5 mL of 2 M HNO\(_3\), and this was selected for further experiments. In order to select the best eluent flow rate for the recoveries of the analytes, different flow rates were studied (1–5 mL min\(^{-1}\)). The flow rate of 2 mL min\(^{-1}\) was determined to be the best eluent flow rate \( (R > 94\%)\) for the related adsorbent material and metal combination. In order to select the best eluent concentration for enrichment of Cu(II) with MMWCNT L4, MMWCNT L5, MMWCNT L6 and MMWCNT L7, various concentrations of HNO\(_3\) were studied. As a result of these experiments, it was found that 4 M HNO\(_3\) was sufficient for quantitative elution (Table 1). To investigate the effect of the eluent volume on the recoveries, various volumes (2–10 mL) of 4 M HNO\(_3\) were used. It was found that maximum recoveries were obtained using 5 mL 4 M HNO\(_3\), and this was selected for the following experiments. The effect of the eluent flow rate on the recoveries of the analytes was assessed by adjusting the flow rates in a range of 1–5 mL min\(^{-1}\). 2 mL min\(^{-1}\) was determined to be the best eluent flow rate \( (R > 90\%)\) for the related adsorbent material and metal combination.

The proper conditions for the selection of adsorbent material and metal combination that would be used for the enrichment of Cu(II) and Ni(II) with the developed method are described in Table 2.
|       | MMWCNT L1 recovery<sup>a</sup> (%) | MMWCNT L2 recovery<sup>a</sup> (%) | MMWCNT L4 recovery<sup>a</sup> (%) | MMWCNT L5 recovery<sup>a</sup> (%) | MMWCNT L6 recovery<sup>a</sup> (%) | MMWCNT L7 recovery<sup>a</sup> (%) |
|-------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| Cu(II) | Ni(II)                            | Cu(II)                            | Ni(II)                            | Cu(II)                            | Cu(II)                            | Cu(II)                            |
| 1 M HNO<sub>3</sub> | 86.84 ± 1.75                      | 88.12 ± 4.20                      | 81.31 ± 2.50                      | 86.10 ± 3.87                      | -                                 | -                                 |
| 2 M HNO<sub>3</sub> | 98.06 ± 1.73                      | 96.32 ± 3.88                      | 96.83 ± 1.09                      | 97.64 ± 1.83                      | -                                 | -                                 |
| 1 M HCl  | 70.22 ± 3.94                      | 74.60 ± 3.60                      | 73.30 ± 2.83                      | 84.60 ± 3.70                      | -                                 | -                                 |
| 2 M HCl  | 81.42 ± 3.98                      | 79.02 ± 1.73                      | 81.14 ± 3.86                      | 88.12 ± 3.71                      | -                                 | -                                 |
| 2 M HNO<sub>3</sub> | -                                 | -                                 | -                                 | -                                 | 55.20 ± 2.20                      | 76.55 ± 2.50                      |
| 4 M HNO<sub>3</sub> | -                                 | -                                 | -                                 | -                                 | 96.83 ± 3.24                      | 95.20 ± 1.20                      |

Note: <sup>a</sup>Results are given with 95% confidence level, mean ± ts<√N, (N = 3).
3.6. Effect of sample volume and enrichment factor

In order to investigate the effect of sample volume on the recovery of analyte with adsorbent materials, 100, 200, 400, 500 and 600 mL model solutions used containing 1 μg Cu(II) and 1 μg Ni(II) and the general procedure, stated in Section 2.6, was applied to all the prepared adsorbent materials and the two metals. The recovery values of Cu(II) and Ni(II) with MMWCNT L1 and MMWCNT L2 were quantitative up to 400 mL. When sample volume was higher than 400 mL, the recoveries decreased gradually (Figure 5). Consequently, the highest enrichment factor was 80, using 5 mL eluent solution, with recovery >94%. The recovery results for Cu(II) with MMWCNT L4, MMWCNT L5, MMWCNT L6 and MMWCNT L7 are presented in Figure 5. As shown in the figure, quantitative recoveries of Cu(II) were obtained when sample volume was less than 200 mL. So the enrichment factor was found to be 40, using 5 mL eluent solution, with recovery >91%.

3.7. Effect of interfering ions

In the application of the developed method, a certain amount of zinc, cobalt, manganese and cadmium salts was added to model solutions and the developed method was applied under the conditions stated in Table 2. It was concluded that the existence of the mentioned types does not have a remarkable negative effect on the recovery of Cu(II) and Ni(II) (Table 3).

| Modified adsorbent material | Analyte | pH  | Type and concentration of eluent | Flow rate of model solution (mL min\(^{-1}\)) | Flow rate of eluent (mL min\(^{-1}\)) |
|----------------------------|---------|-----|-----------------------------------|---------------------------------------------|-------------------------------------|
| MMWCNT L1 Cu(I)           | 9       | 2 M HNO\(_3\)          | 6                                 | 2                                           |
| MMWCNT L1 Ni(II)          | 8       | 2 M HNO\(_3\)           | 6                                 | 2                                           |
| MMWCNT L2 Cu(II)          | 9       | 2 M HNO\(_3\)           | 5                                 | 2                                           |
| MMWCNT L2 Ni(II)          | 8       | 2 M HNO\(_3\)           | 5                                 | 2                                           |
| MMWCNT L4 Cu(II)          | 9       | 4 M HNO\(_3\)           | 6                                 | 2                                           |
| MMWCNT L5 Cu(II)          | 9       | 4 M HNO\(_3\)           | 6                                 | 2                                           |
| MMWCNT L6 Cu(II)          | 9       | 4 M HNO\(_3\)           | 6                                 | 2                                           |
| MMWCNT L7 Cu(II)          | 9       | 4 M HNO\(_3\)           | 6                                 | 2                                           |

Table 2. Optimised conditions of enrichment for Cu(II) and Ni(II) with modified adsorbent materials.

Figure 5. Effect of sample volume on the recovery of metal ions and related adsorbent. Model solution: 1μg Cu(II) and 1μg Ni(II), MMWCNTs: 200 mg, eluent: nitric acid, pH: 8 for Ni(II), pH: 9 for Cu(II).
Table 3. Recoveries of Cu(II) and Ni(II) with modified adsorbent materials in the presence of interfering ions.

| Interfering ion | Interfering ion/analyte | MMWCNT L1 recovery<sup>a</sup> (%) | MMWCNT L2 recovery<sup>a</sup> (%) | MMWCNT L1 recovery<sup>a</sup> (%) | MMWCNT L2 recovery<sup>a</sup> (%) | MMWCNT L4 recovery<sup>a</sup> (%) | MMWCNT L5 recovery<sup>a</sup> (%) | MMWCNT L6 recovery<sup>a</sup> (%) | MMWCNT L7 recovery<sup>a</sup> (%) |
|----------------|------------------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| Zn            | 10                     | 95.74 ± 2.24                        | 94.40 ± 2.43                        | 93.83 ± 2.72                        | 91.06 ± 1.20                        | 91.98 ± 2.80                        | 91.00 ± 1.97                        | 90.23 ± 2.15                        | 90.70 ± 2.73                        |
| Co            | 10                     | 97.44 ± 2.71                        | 95.60 ± 2.60                        | 93.10 ± 2.40                        | 92.43 ± 2.83                        | 91.80 ± 2.86                        | 94.21 ± 2.94                        | 90.30 ± 2.60                        | 90.15 ± 2.50                        |
| Mn            | 10                     | 94.70 ± 2.60                        | 95.52 ± 1.25                        | 95.90 ± 2.30                        | 93.90 ± 1.14                        | 92.50 ± 2.37                        | 91.77 ± 2.40                        | 90.45 ± 2.73                        | 90.34 ± 1.44                        |
| Cd            | 10                     | 96.16 ± 2.09                        | 95.56 ± 1.41                        | 93.17 ± 1.64                        | 94.73 ± 2.71                        | 92.05 ± 2.38                        | 91.41 ± 2.43                        | 90.91 ± 2.46                        | 90.42 ± 1.70                        |

Note: <sup>a</sup>Results are given with 95% confidence level, mean ± t/s/√N, (N = 3).
3.8. Analytical performances

In order to identify the developed method’s limit of detection (LOD) and limit of quantitation (LOQ), 10 blank solutions were prepared for each modified adsorbent material and metal according to the literature [38–40]. Under the conditions stated in Table 2, the developed method was applied to the blank solutions. LOD and LOQ values were calculated as follows:

The limit of detection was calculated using the formula \( \text{LOD}_{\text{signal}} = x_m + 3\sigma \) (\( x_m \) = mean value of noise for blank solution, \( \sigma \) = standard deviation of this noise); limit of quantification was calculated using the formula \( \text{LOQ} = 3 \times \text{LOD} \). The LOD–LOQ values obtained for MMWCNT L1 and Cu(II) were calculated as 0.0455 \( \mu \text{g L}^{-1} \) and 0.1365 \( \mu \text{g L}^{-1} \), for Ni(II) 0.0477 \( \mu \text{g L}^{-1} \) and 0.1431 \( \mu \text{g L}^{-1} \), respectively. LOD–LOQ values in the enrichment of MMWCNT L2 and Cu(II) were found as 0.0389 \( \mu \text{g L}^{-1} \) and 0.1167 \( \mu \text{g L}^{-1} \), for Ni(II) 0.0193 \( \mu \text{g L}^{-1} \) and 0.0579 \( \mu \text{g L}^{-1} \) respectively. In Cu(II) enrichment studies carried out with MMWCNT L4, MMWCNT L5, MMWCNT L6 and MMWCNT L7, LOD values were calculated as 0.0405 \( \mu \text{g L}^{-1} \), 0.0931 \( \mu \text{g L}^{-1} \), 0.1238 \( \mu \text{g L}^{-1} \) and 0.0576 \( \mu \text{g L}^{-1} \), respectively. LOQ values were calculated as 0.1215 \( \mu \text{g L}^{-1} \), 0.2793 \( \mu \text{g L}^{-1} \), 0.3714 \( \mu \text{g L}^{-1} \) and 0.1728 \( \mu \text{g L}^{-1} \), respectively.

3.9. Application of the method

The confirmation of the developed method was tested with NIST-1640a Natural water – Trace elements, NIST-2670a Toxic elements in freeze-dried urine and BCR-277R Estuarine sediment – Trace elements certified reference materials. For this purpose, the samples were prepared as described in Section 2.7 and the method was adopted for each adsorbent material under the conditions stated in Table 2, and results are shown in Tables 4–6. Furthermore, the results are in good agreement with certified values.

4. Conclusions

In this study, novel adsorbent materials that would be used in the enrichment of Cu(II) and Ni(II) with SPE were developed. It was concluded that MMWCNT L1 and MMWCNT L2 were the most appropriate and new adsorbent materials for both Cu(II) and Ni(II). Conversely, in the studies carried out with MMWCNT L3, successful results could not be

| Modified adsorbent material | Analyte | Certified value \((\mu \text{g L}^{-1})\) | Found \(^a\) \((\mu \text{g L}^{-1})\) | Recovery (%) |
|-----------------------------|---------|---------------------------------|-------------------------------|-------------|
| NIST-1640a                  | MMWCNT L1 Cu(II) | 85.75 ± 0.51 | 86.60 ± 1.46 | 100.97 |
|                             | MMWCNT L1 Ni(II) | 25.32 ± 0.14 | 24.46 ± 2.81 | 96.60 |
|                             | MMWCNT L2 Cu(II) | 85.75 ± 0.51 | 86.95 ± 1.75 | 101.43 |
|                             | MMWCNT L2 Ni(II) | 25.32 ± 0.14 | 24.30 ± 2.42 | 95.89 |
|                             | MMWCNT L4 Cu(II) | 85.75 ± 0.51 | 83.02 ± 1.32 | 96.82 |
|                             | MMWCNT L5 Cu(II) | 85.75 ± 0.51 | 81.50 ± 1.88 | 95.04 |
|                             | MMWCNT L6 Cu(II) | 85.75 ± 0.51 | 81.40 ± 2.75 | 94.89 |
|                             | MMWCNT L7 Cu(II) | 85.75 ± 0.51 | 81.33 ± 2.75 | 94.85 |

Note: \(^a\)Results are given with 95% confidence level, mean ± ts/\(\sqrt{N}\), (\(N = 3\)).
accomplished for both of the metals. MMWCNT L4, MMWCNT L5, MMWCNT L6 and MMWCNT L7 were selective adsorbent materials only for the enrichment of Cu(II). The highest enrichment factor was 80 with MMWCNT L1 and MMWCNT L2 for both Cu(II) and Ni(II). On the other hand, the highest enrichment factor for MMWCNT L4, MMWCNT L5, MMWCNT L6 and MMWCNT L7, which are only selective for Cu(II), was determined as 40. The comparison of the results found in the present study and reported studies using CNTs for enrichment of trace elements with SPE is given in Table 7. Furthermore, the modification procedure is simple and can be easily repeated. Therefore, this was the most important advantage of the system. In addition to this, we are of the opinion that this enrichment study that was carried out with new and selective adsorbent materials would be useful for other studies on with Schiff bases and with CNTs of other ligands that can easily set up a complex with metals.

### Table 5. Analytical results for determination of Cu(II) and Ni(II) in NIST-2670a.

| Modified adsorbent material | Analyte | Certified value (mg kg\(^{-1}\)) | Found \(^a\) (mg kg\(^{-1}\)) | Recovery (%) |
|-----------------------------|---------|----------------------------------|-------------------------------|--------------|
| NIST-2670a                  | MMWCNT L1 Cu(II) | 110 ± 4 | 109.82 ± 1.98 | 99.84        |
|                             | MMWCNT L1 Ni(II) | 100     | 100.82 ± 1.70 | 100.82       |
|                             | MMWCNT L2 Cu(II) | 110 ± 4 | 108.09 ± 2.62 | 99.08        |
|                             | MMWCNT L2 Ni(II) | 100     | 102.48 ± 1.94 | 102.48       |
|                             | MMWCNT L4 Cu(II) | 110 ± 4 | 106.09 ± 2.20 | 96.45        |
|                             | MMWCNT L5 Cu(II) | 110 ± 4 | 107.10 ± 1.90 | 97.36        |
|                             | MMWCNT L6 Cu(II) | 110 ± 4 | 104.03 ± 1.30 | 94.57        |
|                             | MMWCNT L7 Cu(II) | 110 ± 4 | 103.74 ± 1.42 | 94.31        |

Note: \(^a\)Results are given with 95% confidence level, mean ± ts/√N, (N = 3).

### Table 6. Analytical results for determination of Cu(II) and Ni(II) in BCR-277R.

| Modified adsorbent material | Analyte | Certified value (μgL\(^{-1}\)) | Found \(^a\) (μgL\(^{-1}\)) | Recovery (%) |
|-----------------------------|---------|--------------------------------|----------------------------|--------------|
| BCR-277R                    | MMWCNT L1 Cu(II) | 63 ± 7 | 62.75 ± 2.34 | 99.60        |
|                             | MMWCNT L1 Ni(II) | 100   | 100.82 ± 1.70 | 100.82       |
|                             | MMWCNT L2 Cu(II) | 130 ± 8 | 127.40 ± 2.04 | 98.00        |
|                             | MMWCNT L2 Ni(II) | 63 ± 7 | 61.15 ± 1.51 | 97.06        |
|                             | MMWCNT L4 Cu(II) | 130 ± 8 | 126.80 ± 1.54 | 97.54        |
|                             | MMWCNT L5 Cu(II) | 63 ± 7 | 60.97 ± 2.35 | 96.45        |
|                             | MMWCNT L6 Cu(II) | 63 ± 7 | 60.20 ± 1.71 | 95.56        |
|                             | MMWCNT L7 Cu(II) | 63 ± 7 | 60.30 ± 2.24 | 95.71        |

Note: \(^a\)Results are given with 95% confidence level, mean ± ts/√N, (N = 3).
Table 7. Comparative studies using CNTs for enrichment of trace elements with SPE.

| Analytes                     | Adsorbent/detection                                                                 | Medium pH | Eluent                 | EF | LOD (μg L\(^{-1}\)) | Ref  |
|------------------------------|-------------------------------------------------------------------------------------|-----------|------------------------|----|----------------------|------|
| \(\text{Cu}^{2+} , \text{Co}^{2+} , \text{Ni}^{2+}, \text{Pb}^{2+}\) | Multiwalled carbon nanotubes/o-cresolphthalein complexone/AAS                      | pH 7      | 2 mol L\(^{-1}\) HNO\(_3\) | 40 | 1.64–5.68            | [41] |
| \(\text{Cu}^{2+}\)           | Activated carbon impregnated by Schiff base (HPPS)/AAS                             | pH 6      | 4 mol L\(^{-1}\) HNO\(_3\) | 25 | 2.62                 | [42] |
| \(\text{Fe}^{3+}, \text{Cu}^{2+}, \text{Mn}^{2+}, \text{Pb}^{2+}\) | MWCNTs/AAS                                                                          | pH 9      | 1 M HNO\(_3\) in acetone | 20 | 3.5–8                | [43] |
| \(\text{V}^{5+}, \text{Cr}^{6+}, \text{Pb}^{2+}, \text{Cd}^{2+}, \text{Co}^{2+}, \text{Cu}^{2+}, \text{As}^{3+}\) | IDA functionalised MWCNTs/ICP-MS                                                   | pH 8      | 0.5 mol L\(^{-1}\) HNO\(_3\) | 66–101 | 0.00040–0.0034 | [21] |
| \(\text{Cu}^{2+}, \text{Co}^{2+}, \text{Pb}^{2+}\) | Oxidised SWNTs/ICP-MS                                                              | pH 8      | 0.5 mol L\(^{-1}\) HNO\(_3\) | 50 | 0.0012–0.039         | [44] |
| \(\text{Ni}^{2+}, \text{Pb}^{2+}\)       | Oxidised CNTs/ETAAS                                                                 | Ni\(^{2+}\): pH 7, Pb\(^{2+}\): pH 3 | 5% HNO\(_3\). | 38–40 | 10–30                | [45] |
| \(\text{Cu}^{2+}, \text{Ni}^{2+}\)       | Oxidised MWCNTs/ Schi f f Base/Triton X-100/ICP-MS                                 | Cu\(^{2+}\): pH 9, Ni\(^{2+}\): pH 8 | 2, 4 mol L\(^{-1}\) HNO\(_3\) | 40, 80 | 0.0193–0.1238       | Present method |

Notes: HPPS: 5-[(4-heptyloxyphenyl)azo]-N-(4-proploxyphenyl)-salicylaldimineIDA: Iminodiacetic acid; EF: Enrichment factor.
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Supplemental data
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