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Application of multiwall carbon nanotubes impregnated with 5-dodecylsalicylaldoxime for on-line copper preconcentration and determination in water samples by flame atomic absorption spectrometry

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ABSTRACT

The paper presents application of multiwall carbon nanotubes (MWCNTs) modified with 5-dodecylsalicylaldoxime to copper(II) flow-injection on-line preconcentration and flame atomic absorption spectrometric (FAAS) determination. Two new sorbents were obtained by impregnation of MWCNTs with Cu(II)-LIX 622® complex, however in the first case modification was preceded by carbon wall activation via oxidization (Cu-LIX-CNT-A sorbent), and in the second one no surface activation was performed (Cu-LIX-CNT sorbent). It was found that effective leaching of initially introduced copper and Cu(II) retained in preconcentration process could be realized with the use 7% and 5% (v/v) nitric acid, for particular sorbents. Testing the influence of loading solution pH and rate of loading on sorption it was found out that optimal range of loading solution pH was about 4.5–6.3 for activated and 6.15–6.25 for non-activated CNT. Investigation of sorption kinetics showed that the process can be described by pseudo-second order reaction model. Sorption equilibrium conditions (90% sorption) for LIX-CNT-A and LIX-CNT were obtained after 8–15 min, respectively and maximum sorption capacity for the new sorbents amounted to 18.1 mg g^{-1} and 31.6 mg g^{-1}, respectively. For the examined sorbents enrichment factors increased with extension of loading time up to 180 s: linearly for activated and non-linearly for non-activated MWCNTs. Influence of potential interferents such as Cd(II), Zn(II), Fe(III), Mg(II) and Ca(II) ions on copper(II) sorption on the new CNT materials was examined individually and with the use of 2^{5-2} factorial design. The study revealed significant interference from iron, magnesium and calcium ions at relatively high concentrations. Applicability of the proposed sorbents was tested for Cu(II) determination in various kinds of water samples and the results were compared with those obtained with the use of ICP MS as a reference technique. Copper(II) determination in two certified reference materials: waste water (EU-H-3) and ground (ES-H-2) water was performed in order to assess trueness of the evaluated preconcentration procedures. Satisfactory values of relative errors were obtained for both procedures.

1. Introduction

Copper and its compounds play significant role in a contemporary world. Excellent conductivity, or ductility make copper popular electric, construction or plumbing material. Especially the last application takes significant part in introducing copper into drinking water. This problem is especially significant for first-draw portion of water collected after a few hour static period. Water conditions as pH above 7 or high concentration of carbonates can increase copper concentration in drinking water. Other important sources of copper ions in water are related to widespread chemicals: algaecides and fungicides (e.g. substances used for cleaning water in swimming pools), wood preservation substances or fertilizers. Copper ions released to environment accumulate in living organisms. Health symptoms of deficiency or excessive exposition to copper observed for plants, water organism and humans are widely reported, e.g. in WHO report [1].

Atomic spectrometry techniques are the most popular for copper(II) determination at the moment. Both advanced methods like inductively coupled plasma mass spectrometry and simple ones like flame atomic absorption spectrometry (FAAS) have to be often preceded with a preconcentration step improving detection limit and/or reducing potential interference effects due to isolation of the analyte from the sample and its transfer to a new simple matrix.

Preconcentration step is often realized via solid phase extraction and synthetic resins, modified silica gel, cellulose or carbon sorbents are most frequently used for metal ion sorption. In the last group, activated carbon has been mainly used so far, however last years opened new possibilities for carbon as sorption material

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through growing interest in analytical application of new carbon forms: fullerenes and carbon nanotubes (CNTs).

Carbon nanotubes consist of graphite sheets rolled up into nanoscale tube and represent unique sorption and electrical properties. In relation to the number of graphite sheets typically two carbon tubes structures are used: single wall CNTs and multiwall CNTs. Application of CNTs in analytical field has been recently reviewed [2–4].

El-Sheikh et al. [5] investigated effect of dimensions of CNTs on enrichment efficiency of Pb(II), Cd(II) and Zn(II) ions. Metals uptake was efficient at pH 9, probably due to precipitation of the metal hydroxides. Tubes in length of 5–15 μm and 10–30 nm external diameters were found to give the highest enrichment effectiveness.

Carbon nanotubes are chemically inert, therefore adsorb molecules mainly via non-covalent forces like hydrogen bonding, electrostatic forces or van der Waals forces. Duran et al. [6] applied CNTs for Cu(II), Co(II), Ni(II) and Pb(II) preconcentration from water samples by loading onto the sorbent previously formed metal-*o*-cresolphthalein complexes. Other frequently used chelating compounds are ammonium pyrrolidine dithiocarbamate [7,8] or *N*,*N*′-bis(2-hydroxybenzylidene)-2,2′-(aminophenylthio)ethane [9].

For direct metal ions preconcentration onto carbon nanotubes often preliminary surface oxidation which generates carboxyl and carbonyl groups is realized. Concentrated nitric acid [10,11], potassium permanganate [12] or hydrogen peroxide [13] belongs to the most frequently used oxidizing agents. Stafiej and Pyrzyńska [10] applied oxidized CNTs for preconcentration of some divalent ions: Cu(II), Co(II), Ni(II), Zn(II), Pb(II), Mn(II) and Cd(II). Cationic species preferably adsorbed on CNTs under pH 8–9 due to increase in negative charge of the oxidized surface. The highest sorption capacity at pH 9 occured as follows: Cu(II) > Pb(II) > Co(II). Probably preconcentration in basic region is possible thanks to simultaneous adsorption and precipitation.

Ghaseminejad et al. [14] showed that oxidized CNTs have a low retention tendency of Rh(III) and they are not selective for its separation from other ions. Therefore, Rh(III)-1-(2-pyridylazo)-2-naphthol (PAN) complex was loaded onto the oxidized CNTs for this aim. The proposed method was successfully applied to determination of rhodium in water samples and platinum-iridium alloy.

Current research involves a new approach to carbon nanotubes modification where oxidized CNTs serve as a precursor for their further modification by covalent binding of a chelating reagent. Zang et al. [15] proposed a method of covalent binding of ethylenediamine to oxidized surface of carbon nanotubes leading to improvement of selectivity towards Cr(III), Fe(III) and Pb(II). The maximum sorption capacity of the adsorbent at optimum conditions was found to be 39.58, 28.69 and 54.48 mg g^{-1} for Cr(III), Fe(III) and Pb(II), respectively. The detection limits of ICP OES method were below 0.35 ng mL^{-1} and the relative standard deviations were lower than 3.5%.

Also biomolecules as cysteine were used for improvement of CNTs selectivity [16]. Effective preconcentration of Cd(II) on CNTs-cysteine sorbent was achieved at pH range of 5.5–8.0. The modified sorbent exhibited up to 1600-fold improvement of the tolerable concentrations of co-existing metal ions compared to non-modified one and good tolerance of ionic strength.

The aim of the presented research was to overcome the problem of insufficient FAAS detection limit for copper determination in water samples by application of solid phase extraction technique and a new sorbent: carbon nanotubes modified with LIX 622 – commercial liquid ion exchanger widely applied in hydrometallurgy. This reagent belongs to the family of solvent extractants based on 5-dodecylsalicylaldoxime as a chelating agent dissolved in kerosene. Copper(II) solvent extraction with LIX 622® has been reported to be fast and effective. Furthermore, in proper conditions LIX 622® has been proved to extract copper selectively from complicated matrices [17]. Herein, LIX 622®-modified carbon nanotubes were applied to copper preconcentration in on-line FAAS determination procedure.

2. Experimental

2.1. Apparatus

Experiments were carried out using flame atomic absorption spectrometer AAnalyst 300 coupled with FIAS 400 flow injection system (both Perkin Elmer, USA) with the use a 15-cm long capillary. An air/acetylene flame was applied in measurements and analytical signal was registered in a form of peak height measured at 324.8 nm wavelength with deuterium background correction. The flow-injection set comprised two peristaltic pumps, a two-positional valve and a homemade cylindrical column filled with the examined sorbent. Each pump was equipped with two Tygon R3607 red-red tubes (ID 1.14 mm). WinLab software provided by the spectrometer manufacturer was exploited to control the FI-FAAS setup and to register analytical signals.

Additional (control copper determinations at ultra-trace concentrations) were executed with inductively coupled plasma mass spectrometer ELAN DRC-e (Perkin Elmer, USA).

Microcomputer pH/Ion meter CPI-551 (Elmetron, Poland) was utilized for pH measurements of all standard solutions and samples.

2.2. Reagent and solution

Deionized water after reversed osmosis was used throughout the work. All glassware used for preparation of samples and standards was cleaned by overnight soaking in 1% (v/v) HNO_3 and then rinsed with deionized water. Standard stock solutions of heavy metal ions were prepared by dilution of corresponding Titrisol® standards supplied by Merck (Darmstadt, Germany). Eluent solutions were prepared by appropriate dilution of a concentrated acid (pro analysis, Merck, Germany).

Acetate buffer prepared by mixing appropriate volumes of equimolar (0.2 mol L^{-1}) solutions of CH_3COOH and CH_3COONa was used to maintain the adequate pH. Both reagents used to prepare buffer solutions were of pro analysis grade (POCh, Poland).

The studied sorbents were obtained by impregnation of multiwall carbon nanotubes (MWCNTs, external diameter 110–170 nm, length 5–9 μm, 90% purity, Aldrich, USA) with LIX 622® solution in kerosene (Henkel Corporation, Germany). Copper(II) sulphate ($CuSO_4{\cdot}5H_2O$, pro analysis), was supplied by Merck, Germany.

Certified reference materials: EnviroMAT waste water EU-H-3 and ground water ES-H-2, both obtained in SCP Science (Canada), were applied to evaluate the method trueness.

2.3. Preparation of modified carbon nanotubes

Modification of carbon nanotubes was performed in two steps, namely via surface activation and with the use of a procedure similar to imprinting process. Presence of metal complex during synthesis of such sorbents is responsible not only for creating selective binding sites but also for providing spatial recognition. In our case, Cu-LIX complex was employed to achieve the abovementioned effects.

Modifying agent was obtained via shaking 5 mL of saturated copper(II) sulphate solution and previously prepared mixture of 2.5 mL of LIX 622® in 2.5 mL 1,2-dichlorethane. The organic dark blue phase was applied to CNTs modification. Two carbon sorbents modified in different way were obtained and evaluated in further study.

The first procedure was initiated with carbon nanotubes activation followed by impregnation with Cu-LIX 622®. For this purpose 0.76 g of MWCNT was stirred mechanically with 25 mL of 8 mol L^{-1} HNO_3 for 72 h, then washed with deionized water until pH 7 was reached and finally dried in 60 °C. Next 0.2 g of oxidized carbon nanotubes was mixed with 1.0 mL Cu-LIX dissolved in 6 mL of 1,2-dichloroethane and the solvent was subsequently evaporated at room temperature. The obtained sorbent was called Cu-LIX-CNT-A.

The second sorbent was prepared according to the following procedure: 0.5 mL of Cu-LIX 622 complex was mixed with 6 mL of 1,2-dichloroethane and finally added to 0.2050 g non-activated CNTs. The mixture was allowed to dry at room temperature. This material was called Cu-LIX-CNT.

2.4. Column preparation

Homemade Plexiglass® column (5 mm × 3 mm) was filled with ca. 18 mg of a sorbent. SPE frits (Supelco, Bellefonte, USA) were used to hold the sorbent in the column. The packed material was washed in flow mode with: 7% or 5% (v/v) HNO_3 for Cu-LIX-CNT-A and Cu-LIX-CNT, respectively, to release binding sites. The washing was continued until the signal obtained for copper reached background level. Obtained sorbents were named LIX-CNT-A and LIX-CNT properly.

2.5. On-line preconcentration of Cu(II)

Preconcentration procedure was realized as follows (for detailed program see [18]): after initialization of the system (1 s), pump 1 tubes were filled with sample (10 s) and afterwards pump 2 tubes were filled with eluent (20 s) then the sorbent was washed with eluent for conditioning. Next, 30 s sample loading step was initiated. Ten seconds before valve position was changed into *inject*, pump 2 started propelling eluent into the nebulizer allowing to stabilize flame conditions. Then pump 1 was stopped and 30 s elution step was initiated. Absorbance was registered for first 12 s of elution time (read time) and peak height was the analytical signal.

2.6. Sample preparation

Tap water, artesian well water and commercial mineral water were utilized as samples. After sampling or purchasing water was refrigerated until used. Tap water was analyzed without additional preparation. Mineral water was sonicated for 5 min before analysis. All kinds of water were filtered through 0.45 μm cellulose acetate membrane filters (Sartorius, Goettingen, Germany) and sample pH were adjusted to value 4.5–5.0 for LIX-CNT-A and 6.15–6.25 for LIX-CNT with the use of acetate buffer: 2 mL per 50 mL of water sample.

3. Results and discussion

3.1. Elution conditions

In the hydrometallurgical processes the extraction of Cu(II) by aldoxime type of liquide-ion exchanger, as LIX 622® is realized out in sulphuric acid medium. In fact, a concentrated H_2SO_4 solution is used to strip out Cu(II) from the extractant organic phase [19]. However, Walas et al. [20] tested HNO_3 and H_2SO_4 solutions of in the concentration range of 1–5% (v/v) for elution of Cu(II) ions from silica gel modified with LIX 622®, and 5% (v/v) HNO_3 occurred to be the most effective eluent.

Bearing it in mind, nitric acid was selected as potential eluent in this research. Optimization of elution conditions was based on a study of elution effectiveness of copper(II) retained on the sorbent from 0.3 mg L^{-1} standard solution. For LIX-CNT-A sorbent experiments were performed for the eluent concentration range of 1 to 15% (v/v). The obtained results were presented in Fig. 1. Nitric acid solutions in concentration above 7% (v/v) were found the most effective for copper(II) elution, therefore 7% (v/v) HNO_3 was selected as eluent for further studies (Fig. 1).

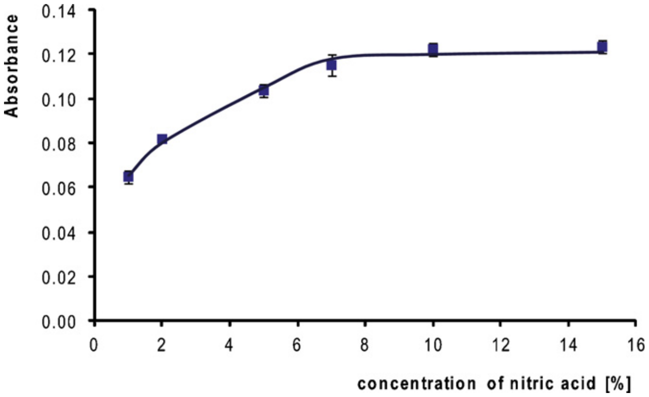

Fig. 1. Influence of nitric acid concentration on analytical signal obtained for the use of LIX-CNT-A sorbent.

Similar experiment was carried for LIX-CNT sorbent and 5% (v/v) nitric acid was chosen for later experiments.

3.2. Effect of loading solution pH on preconcentration efficiency

Loading solution pH plays an important role in sorption process of metal ions. According to the equilibrium isotherm reported for copper(II) extraction with LIX 622®, recoveries of 100% were obtained in pH range 3–10 [21]. Nevertheless, in the reported study optimum pH range was verified due to immobilization of the complexing agent onto the surface of CNTs and application of the sorbent in non-equilibrium flow conditions.

Hence 0.3 mol L^{-1} copper(II) solution buffered to proper pH (range 3–9) was loaded onto the examined sorbent. For LIX-CNT-A the most efficient sorption was observed for sample pH 4.5–6.3, while for LIX-CNT material preconcentration from samples of narrower pH range: 6.15–6.25 was preferred.

At pH below 7 Cu retention is low (signal of low intensity is observed) suggesting that the main mechanisms of binding might be ion-exchange and adsorption. With pH increase, the amount of Cu(II) sorbed on the modified CNTs also increases, since the functional groups of the chelating agent present in LIX 622® are deprotonated and can readily trap Cu(II) ions. Therefore, both complex formation and adsorption mechanisms are responsible for the total sorption phenomenon.

3.3. Sorption parameters

In on-line procedures loading flow rate is one of the most important factors influencing sorption effectiveness. Here, on the basis of our previous experiences [18,20], this parameter was optimized at 8 mL min^{-1} warranting high sample throughput and efficient sorption. Another crucial factor is the loading time which is limited from one side by obtainable signal of sufficient intensity and from the other side by sample throughput. Therefore, generally this parameter can be adjusted as required in wide range. In our investigations we focused on application of loading time values in the range of 30 up to 150 s. Elongation of sample loading time resulted in signal increase both for LIX-CNT-A and LIX-CNT sorbent.

Effectiveness of preconcentration step can be described by several indexes, generally related to each other. Enrichment factor (EF) can be expressed as a ratio of FI-FAAS calibration slope to FAAS slope, therefore direct measurements of copper(II) standard solutions, without preconcentration step, were also performed.

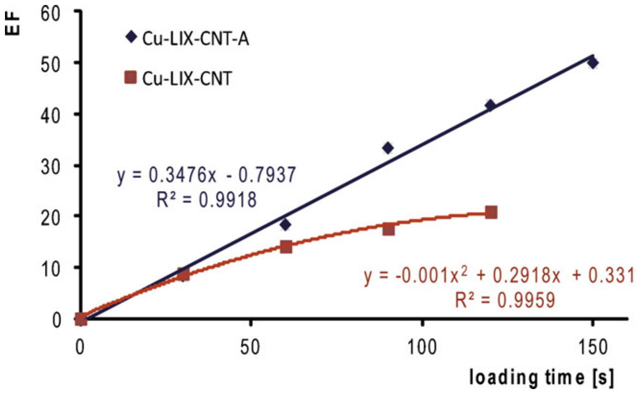

Fig. 2. Influence of loading time on enrichment factor for the examined modified carbon sorbents.

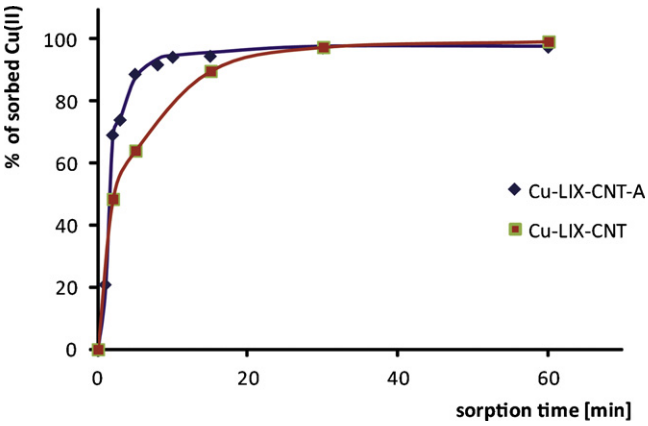

Fig. 3. Influence of sorption time on Cu(II) sorption effectiveness.

Influence of the applied loading time on the obtained EF value is presented in Fig. 2.

It was observed that for LIX-CNT-A sorbent the obtained EF values plotted versus loading time formed linear dependence in all tested time intervals and 30 s loading time resulted in EF = 8. However, for LIX-CNT:

- Loading Cu(II) solution for 30 s resulted in EF 10.
- Up to 60 s almost linear relationship existed between EF value and loading time.
- Increase in EF became less significant above 60 s loading time and the dependence between the variables changed into non-linear.

Consumptive index (CI) was calculated from the following equation:

$$\mathrm{CI} = \frac{V_s}{\mathrm{EF}}\,[\mathrm{mL}] \qquad (1)$$

where V_s is sample volume required to achieve one unit of EF and the obtained values were 0.5 and 0.4 mL for LIX-CNT-A and LIX-CNT, respectively. Concentration efficiency factor CE was found according to formula:

$$\mathrm{CE} = \mathrm{EF} \cdot f\ [\mathrm{min}^{-1}] \qquad (2)$$

where f is sampling frequency [h^{-1}].

The calculated CE values were 5.2 and 6.5 for LIX-CNT-A and LIX-CNT, respectively.

3.4. Kinetic models and sorption capacity

The first step for estimation of the maximum sorption capacity of the studied sorbents was to determine the time necessary to reach sorption equilibrium. For this purpose aliquots of 7 mL of copper(II) standard solutions (0.1 and 0.5 mg L^{-1} for LIX-CNT-A and LIX-CNT, respectively) were loaded onto a column in a closed circuit within the time range of 2–60 min and at flow rate of 8 mL min^{-1}. Concentration of copper in the initial and final solutions were determined by ICP MS (^{65}Cu). The experiments revealed that 8 and 15 min were the minimum times required to reach the equilibrium conditions (90% sorption) for LIX-CNT-A and LIX-CNT sorbent, respectively. The detailed data are shown in Fig. 3.

Two models of kinetic reaction were fitted to the data:

- pseudo-first order $\log(Q_e - Q_t) = \log(Q_e) - \frac{k_t}{2.303}$ (3)
- pseudo-second order $\frac{t}{Q_t} = \frac{1}{k_2 \cdot Q_e^2} + \frac{1}{Q_e} t$ (4)

where Q_t is the amount of analyte adsorbed on sorbent after time t [mg g^{-1}], Q_e stands for amount of analyte adsorbed on sorbent at equilibrium time [mg g^{-1}], k and k_2 are constants for pseudo-first order [min^{-1}] and pseudo-second order [g min^{-1} mg^{-1}], respectively and t is sorption time [min].

The obtained results presented in Fig. 4 demonstrate that pseudo-second order kinetic model was preferred in case of both sorbents which is reflected by higher correlation coefficient (R) ca. 0.999 – when compared to pseudo-first order model. Therefore, the most probable limiting step for the sorption process is interaction between the analyte and the sorbent.

In the second part of the research, sorption capacity for both sorbents was evaluated in the established equilibrium sorption time.

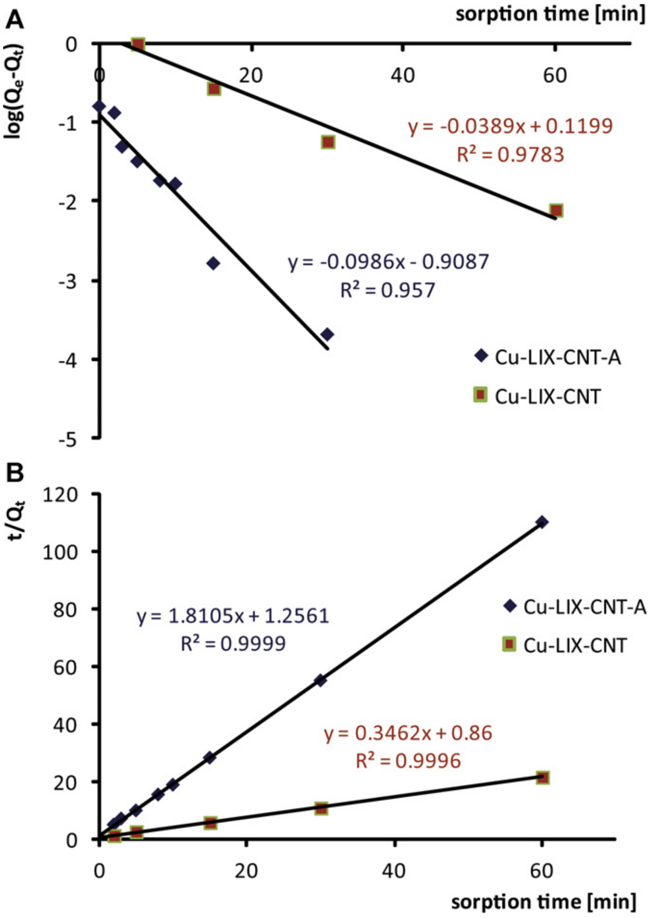

Fig. 4. Kinetic evaluation of the new sorbents. (A) pseudo-first order kinetic model and (B) pseudo-second order kinetic model.

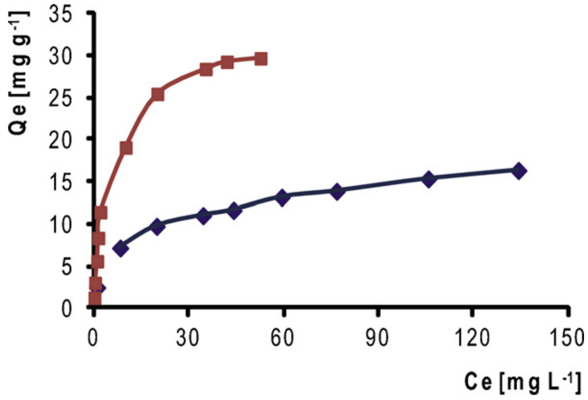

Fig. 5. Adsorption isotherms of copper(II) on modified CNT sorbents. C_e: Cu(II) equilibrium concentration; Q_e: amount of sorbed Cu(II) at equilibrium conditions.

Aliquots (7 mL) of Cu(II) standard solutions within the concentration range of 2–180 mg L^{-1} were loaded on LIX-CNT-A and LIX-CNT in a closed circuit for 8 and 15 min, respectively. Initial and equilibrium copper(II) concentrations were found by ICP-MS (^{65}Cu). The obtained data was used to construct sorption isotherms presented in Fig. 5. These isotherms reflect the relationship between the amount of copper(II) ions sorbed per gram of a sorbent (Q) and the concentration of Cu(II) in solution at equilibrium (C_e). According to Langmuir equations:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{max}} + \frac{1}{K_L \cdot Q_{max}} \quad (5)$$

where K_L is the Langmuir constant [L mg^{-1}], which is associated to the energy of sorption and Q_{max} [mg g^{-1}] is the maximum sorption capacity defined as the maximum amount of metal ions sorbed per unit mass of a sorbent.

For LIX-CNT-A sorbent the Langmuir constant, K_L was found to be 0.045 L mg^{-1} and Q_{max} was equal to 18.1 mg g^{-1}, whereas for the second sorbent – LIX-CNT, the obtained K_L and Q_{max} values were 0.254 L mg^{-1} and 31.6 mg g^{-1}, respectively. Experimental maximum sorption capacities (16.4 and 29.7 mg g^{-1} for LIX-CNT-A and LIX-CNT properly) seems to be in good correlation with theoretical ones obtained from isotherm.

3.5. Sorbent long-term stability test

The sorbents reusability was examined in multiple consecutive preconcentration cycles of copper(II) solution (0.1 mg L^{-1}). The tested materials exhibited good repeatability of signal for at least 100 sorption–desorption cycles. Regression equation obtained for absorbance versus number of cycle was expressed by slope 0.00001 and RSD 10^{-6} which indicates no systematic signal change and good stability of sorbent.

3.6. The effect of possible matrix components on copper sorption

Selectivity of the LIX-CNT-A sorbent was examined in several steps. First of all, enrichment factors for potentially interfering metal ions such as: Cd(II), Fe(III), Zn(II), Pb(II), Cr(III), Ni(II), Ag(I), Co(II), Mn(II), Ca(II) and Mg(II) were found. Preconcentration effectiveness of the above-mentioned ions was examined for two concentration levels: 0.05 and 0.2 mg L^{-1}, pH equal to 4.5 (i.e. optimal for copper(II) preconcentration) and 30 s loading time. In these conditions significant EF values (i.e. within the range of 1.14–1.78) were obtained only for Mg(II), Zn(II), Cd(II), Ca(II) and Fe(III) ions. Consequently, influence of loading solution pH on the measured analytical signal (in the form of EF) was determined for the designated ions. Preconcentration study was performed for a set of 0.1 mg L^{-1} metal ions solutions adjusted to pH in the range of 3 to 10. It was found that narrowing the optimal pH for Cu(II) sorption to about 4.5–5.0 allows to reduce potential interferences. Fig. 6 depicts detailed influence of loading solution pH on the obtained enrichment factors of the designated ions.

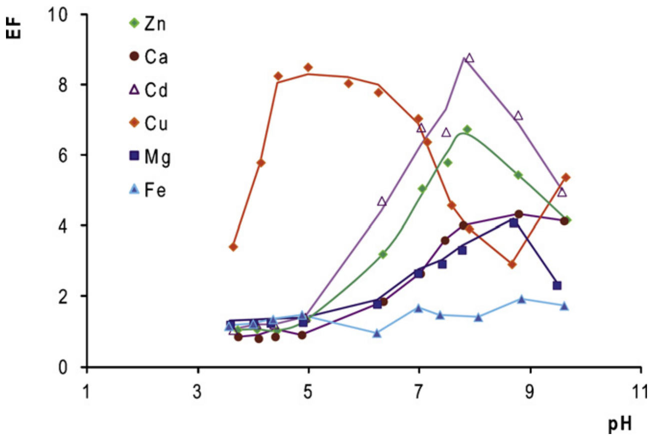

Fig. 6. Influence of loading solution pH on the ability of LIX-CNT-A sorbent to retain various metal ions.

Detailed evaluation of influence of the particular ions on the Cu(II) sorption was realized in one-factor experiments. Copper(II) was retained on the sorbent from two element solution containing 0.05 mg L^{-1} of Cu(II) and one interferents in concentration range from 0 to 5 mg L^{-1}. It was found that ions like Zn(II), Fe(III), Cd(II) did not influence copper(II) sorption in the whole investigated interferent concentration range (signal decrease was smaller than 5%), however presence of Ca(II) and Mg(II) ions had significant influence the copper(II) retention. Therefore influence of these ions was tested for their concentrations up to 500 mg L^{-1}, according to their natural concentration level in water samples (Fig. 7).

Owing to its strong ability to form complexes with copper ions in water samples humic acid was also investigated as a potential interferent in a manner similar to that for metal ions. The conducted research confirmed strong influence of humic acid on copper(II) preconcentration starting from its concentration of 0.04 mg L^{-1}. For humic acid concentration of 20 mg L^{-1} about 30% decrease of signal was observed.

Study of LIX-CNT sorbent selectivity was based on some general evaluations obtained for LIX-CNT-A material.

In order to investigate interferences in complex solution a fractional design 2^{5-2} was employed for Cd(II), Zn(II), Fe(III), Mg(II) and Ca(II) and fixed concentration of Cu(II). Mathematical model

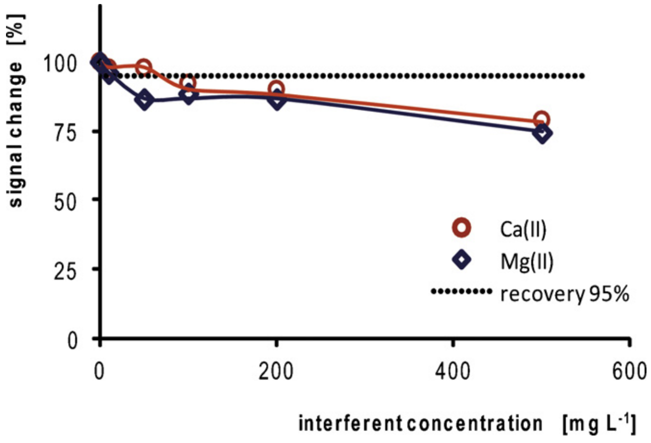

Fig. 7. Effect of calcium and magnesium on copper sorption onto LIX-CNT-A.

Table 1
Coefficients of the regression model fitted to the signals measured for copper in presence of iterferents according to the 2^{5-2} factorial design.

Metal ion	Factor	Concentration level (mg L^{-1})		Regression coefficient	Student's factor	Significance
		Low (−)	High (+)	b	t_j	
	x_0[a]			0.0466	67.30	Yes
Cd(II)	x_1	0.0	5.0	0.0011	1.57	No
Zn(II)	x_2	0.0	5.0	0.0003	0.48	No
Fe(III)	x_3	0.0	2.0	0.0067	9.63	Yes
Mg(II)	x_4	0.0	10.0	−0.0019	2.77	Yes
Ca(II)	x_5	0.0	50.0	−0.0016	2.29	Yes

[a] x_0: corresponds to average influence of mean concentration value of each interferent (central point of design) on copper signal.

Table 2
Analytical results of determination of trace copper in different water samples obtained for preconcentration with the use of the presented sorbents.

Sample	ICP MS	FI-FAAS	
	C_{Cu} (μg L^{-1})	C_{Cu} (μg L^{-1})	RE (%)
Cu-LIX-CNT-A			
Artesian well water	14.5 ± 0.2	13.9 ± 0.6	−4.1
Vistula river water	17.6 ± 0.1	16.6 ± 0.6	−5.9
Well water	64.2 ± 1.0	60.0 ± 2.8	−6.5
ES-H-2	–	791 ± 29	1.3
EU-H-3	–	698 ± 26	6.1
Cu-LIX-CNT			
ES-H-2	–	774 ± 20	0.9
EU-H-3	–	678 ± 9	3.0

C_{Cu}: concentration of copper(II), concentration of copper in CRMs materials ES-H-2 and EU-H-3 was 781 (tolerance interval 0.658–0.903) and 658 μg L^{-1} (tolerance interval 0.580–0.735) respectively.

of dependence of signal vs. concentration of interferents was constructed according to the following equation:

$$\hat{y}_i = b_0X_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_5X_5$$

where $\hat{y}_i$ is the mean predicted absorbance for the i-th solution, b_{0-5} are regression coefficients and x_{0-5} are concentrations of particular interferents in coded units (−1 for lower level, +1 for upper level). Statistical significance of each coefficient was verified with the use of the Student's t-test. Whenever the calculated t_j values were lower than the tabular ones ($t = 2.12$; $p = 0.05$ and $f = 16$ degrees of freedom), hypothesis H_0 assuming that the true regression coefficient was equal to zero was accepted. The detailed data is collected in Table 1.

The test proved that factors like Fe(III), Mg(II) and Ca(II) interfere sorption of Cu(II) ions significantly. Adequacy of this model was confirmed by Fisher's criterion.

3.7. Application of the proposed sorbents to copper determination in natural water samples

Both new sorbents were applied to preconcentration and determination of copper(II) ions in the following water samples: Cisowianka® mineral water with high mineral components content, tap water and two water certified reference materials. Set of standards method (SSM) and standard addition method (SAM) were used for calibration of copper determination in Cisowianka® mineral water (declared by manufactures Ca(II) and Mg(II) content were 131.26 and 22.48 mg L^{-1}, properly). Calibration curves obtained with LIX-CNT-A sorbent indicated multiplicative interference effect occurring in the examined system, however application of LIX-CNT sorbent did not exhibit such a problem. The detailed data are presented in Fig. 8. An attempt was made to eliminate interference effect from calcium and magnesium ions via increase of LIX-CNT-A sorbent mass. This procedure could not be fully exploited however, due to high back pressure which occurred whenever amounts of the sorbent higher than 18 mg were packed in a column.

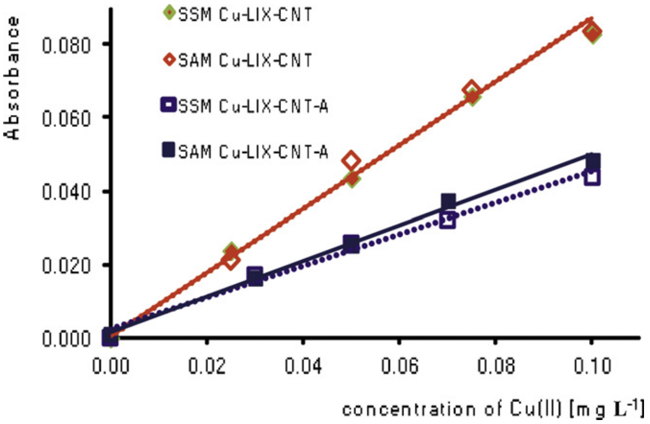

Fig. 8. Influence of composition of Cisowianka® water matrix on copper(II) preconcentration.

Consequently, two procedures were applied to copper preconcentration and FAAS determination: one with the use of LIX-CNT-A sorbent (loading time 60 s, sorbent mass 18 mg) and the standard addition calibration method and the other one with the use of LIX-CNT (loading time 110 s, sorbent mass 18 mg) and set of standards method. The proposed procedures were employed for copper determination in water samples (Artesian well water, Vistula river water, well water). ICP MS was applied as a reference method. Finally, accuracy of the proposed FI-FAAS copper determination procedures was evaluated with the use of waste (EU-H-3) and ground (ES-H-2) water certified reference materials (SCP Science, Canada). Copper content found in CRMs was in good agreement

Table 3
Carbon nanotubes as solid sorbents for on-line copper(II) preconcentration and determination.

Sorbent (modifying agent)	m_s (mg)	C_e (mol L^{-1})	pH	EF	t_s (s)	Sample flow rate (mL min^{-1})	LOD (μg L^{-1})	RSD (%)	Q_{max} (mg g^{-1})	Ref
CNTs (iminodiacetic acid)	20	0.5 HNO_3	8.0	101	180	5	2.5	3.4	6.64	[22]
Oxidized CNTs[a]	20	2.0 HCl	6.0	20.3	90	1	0.59	3.43	–	[23]
LIX-CNT-A	18	7.0 HNO_3	4.5	18.3	60	8	4.1	<4	16.4	This work
LIX-CNT	18	5.0 HNO_3	6.2	16.5	110	8	4.8	<4	29.7	This work

m_s: sorbent mass; C_e: eluent concentration; EF: enrichment factor; t_s: sorption time; Q_{max}: sorption capacity.

[a] Oxidized with HNO_3.

with the CRMs confidence intervals. This confirms that the proposed sorbents and copper determination method is of practical value. The detailed results are listed in Table 2.

4. Conclusion

The presented two new sorbents prepared on the basis of multiwall carbon nanotubes fulfill all requirements imposed for sorbents dedicated to on-line flow injection preconcentration. 5-dodecylsalicylaldoxime appeared to be a very selective modifying agent towards Cu(II) ions. Generally, it is recommended to activate (oxidize) surface of a CNTs support before impregnation. This results in increase of the number of active groups capable to bind modifying chelating agents. Nevertheless, as we observed, introduction of groups of low selectivity leads to loss of the main aim of modification i.e. the expected sorbent selectivity. In case of FI-FAAS preconcentration and determination of copper(II), when inactivated CNT was used as a sorbent the set of standard method was sufficient for calibration purposes, however in case of activated CNT, standard addition method had to be applied due to occurring interferences. On the other hand, as expected, the sorbent based on activated CNT showed higher EF for comparable loading time and reached sorption equilibrium faster. Humic acid appeared to be the most significant interferent, therefore when it is expected in a sample (lake or pond water) the fact has to be taken into account e.g. proper calibration method (SAM) or digestion procedure has to be performed prior determination.

Analytical characteristics of the evaluated preconcentration methods were compared with the ones reported for other carbon nanotubes-based materials applied to copper on-line preconcentration and FAAS determination, and are presented in Table 3.

It should be noted that the proposed CNTs sorbents modified with copper(II)-LIX 622 complex presented high sorption capacity, higher than those reported for other sorbents (e.g. [22]) and the demonstrated procedures allowed to obtain results of high precision.

The proposed preconcentration procedure provides all the benefits associated to miniaturized FIA systems: the use of small volumes of both sample and eluent, high sample throughput and simple operation. Moreover, the preconcentration step in our method can be performed with the use of small amounts of a sorbent; this is an advantage when the analysis cost is taken into account. The durability and stability of the material should also highlighted here, since the microcolumn filling can be reused at least 100 measuring cycles without any lost of the sorbent activity.

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