

ORIGINAL ARTICLE

Separation of Trace Amount Cu (II) Using Octadecyl Silica Membrane Disks - Nano Graphene Modified N, N'-disalicylideneethylenediamine

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ABSTRACT: A simple, highly sensitive, accurate and selective method was presented for determination of trace amounts of Cu (II) in water samples. The stability of an N, N' - disalicylideneethylenediamine modified Nano Graphene especially in concentrated hydrochloric acid was studied which used as a recycling and pre-concentration reagent for further uses of N, N'-disalicylideneethylenediamine modified Nano Graphene. The method was based on N, N'-disalicylideneethylenediamine modified Nano Graphene of Cu (II) on surfactant coated C₁₈, modified with a N, N' -disalicylideneethylenediamine modified Nano Graphene. The retained ions were then eluted with 4 ml of 4 M nitric acid and determined by flame atomic absorption spectrometry (FAAS) at 283.3 nm for Cu. The influence of flow rates of sample and eluent solutions, pH, breakthrough volume, effect of foreign ions were investigated on chelation and recovery. (1.5 g of surfactant coated C₁₈ adsorbs 40 mg of the Schiff's base which in turn can retain 15.2±0.8mg of ion) The limit of detection (3σ) for Cu (II) was found to be 3.20 ng l⁻¹. The enrichment factor for both ions was 100. The mentioned method was successfully applied on determination of Cu in different water samples. The ions were also speciated by means of three- column system.

INTRODUCTION

Cu at trace concentrations acts as both a micronutrient and a toxicant in marine and fresh water systems [1, 8]. This element is needed by plants at only very low levels and is toxic at higher levels. At these levels, Cu can bind to the cell membrane and

hinder the transport process through the cell wall. Cu at nearly 40ng mL⁻¹ is required for normal metabolism of many living organisms [9, 10]. On the other hand, Cu is an important element in many industries. Thus, the development of new methods for selective separation, concentration and

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determination of it in sub-micro levels in different industrial, medicinal and environmental samples is of continuing interest. The determination of Cu is usually carried out by flame and graphite furnace atomic absorption spectrometry (AAS) [11, 12] as well as spectrometric methods [13, 14].

Solid phase extraction (SPE) methods are the best alternatives for traditional classic methods due to selective removal of trace amounts of metal ions from their matrices. SPE determinations can be carried out on different efficient ways. One of the most appropriate performance features of SPE is achieved by using octadecyl silica membrane disks. SPE reduces the use of toxic solvent, disposal costs, and extraction time [15, 16]. The octadecyl silica membrane disks involves shorter sample processing time and decreased plugging due to the large cross-sectional area of the disk and small pressure drop which allows higher flow-rates; reduced channeling resulting from the use of sorbent with smaller particle size and a greater mechanical stability of the sorbent bed [17].

In our previous attempts, we modified SPE membrane disks with suitable compounds for selective determination of chromium [18, 19] and lead [22]. Meanwhile, other investigators have successfully utilized these sorbents for quantitative extraction and monitoring trace amounts of lead [21, 23], copper [24, 26], silver [27, 28], mercury [29], cadmium [31], palladium [32], Ce [33] and UO_2^{30} .

Ionic liquids (ILs) seem well positioned to address this challenge. Due to their wide solubility, and by introducing a surface charge, modification with ILs should enable the preparation of long-term stable and N, N'-disalicylideneethylenediamine modified Nano Geraphene that can be dispersed in various matrices. To date, investigations into the covalent attachment of an ionic material to nanoGeraphene surface have not been carried out. In this communication, we

report a convenient method to obtain polydisperse N, N'-disalicylideneethylenediamine modified Nano Geraphene that are functionalized with 1-(3-aminopropyl) - 3-methylimidazolium bromide (IL-NH₂) [20]. The main goal of the present work was development of a fast, sensitive and efficient way for enrichment and extraction of trace amounts of Cu(II) from aqueous media by means of a surfactant coated C₁₈ modified with , N, N'-disalicylideneethylenediamine modified Nano Geraphene [20].

Such a determination has not been reported in the literature. The chelated ions were desorbed and determined by FAAS. The modified solid phase could be used at least 50 times with acceptable reproducibility without any change in the composition of the sorbent, N, N'-disalicylideneethylenediamine modified Nano Geraphene or SDS. On the other hand, in terms of economy it is much cheaper than those in the market, like C₁₈ SPE mini-column.

MATERIALS AND METHODS

Reagents and Apparatus

Nano Geraphene oxide was prepared from purified natural graphite (SP-1, Bay Carbon, Michigan, average particle size 30 nm) by the Hummers [2]. Dried for a week over phosphorus pentoxide in vacuum desiccators before using. 4-Isocyanatobenzenesulfonyl azide was prepared from 4-carboxybenzenesulfonyl azide via a published procedure [17]. All solutions were prepared with doubly distilled deionized water from Merck (Darmstadt, Germany). C₁₈ powder for chromatography with diameter of about 50 μm obtained from Katayama Chemicals from supelco. It was conditioned before using by suspending in 4 M nitric acid for 20 min, and then washed two times with water. Sodium dodecyl sulfate (SDS) was

obtained from Merck (Darmstadt, Germany) and used without any further purification.

Synthesis of SALEN

SALEN [N, N'-bis (salicylidene) ethylenediamine] was prepared according the literature Methods [23] by using Schiff base reaction. The condensation ethylenediamine (0.1mol) with (0.2mol) Salicylaldehyde in ethanol the ratios 1:2 of ligand, the mixture was refluxed for 2hr after cooling, A yellow colour solid was precipitated ligand and was filtered and recrystallized from hot ethanol and dried [24]. Melting point was 122-125°C. The percentage yield 78%. The reaction procedure is shown schematically in scheme 1.



Schematic 1. Synthesis and Molecular structure of N, N' -disalicylideneethylenediamine.

Column preparation

N, N' -disalicylideneethylenediamine modified Nano Graphene (40mg) was packed into an SPE mini-column (6.0 cm × 9 mm i.d., polypropylene). A polypropylene frit was placed at each end of the column to prevent loss of the adsorbent. Before using, 0.5 mol L⁻¹ HNO₃ and DDW were passed through the column to clean it.

Apparatus

The pH measurements were conducted by an ATC pH meter (EDT instruments, GP 353) calibrated against two standard buffer solutions of pH 4.0 and 9.2. Infrared spectra of N,N' -disalicylideneethylenediamine modified Nano Graphene were carried out from KBr pellet by a Perkin-Elmer 1430 ratio recording spectrophotometer. Atomic absorption analysis of all the metal ions except Zn (II) was performed with a Perkin-Elmer 2380 flame atomic absorption

spectrometer. Zn (II) determinations were performed by a Varian Spect AA-10. Raman spectrophotometer analysis was performed with a Perkin-Elmer.

Preparation of admicell column:

To 40 ml of water containing 1.5 g of C₁₈, 150 mg of the above Schiff base-chitosan grafted multi walled carbon nanotubes was loaded after washing acetone, 1 mol l⁻¹ HNO₃ solution and water, respectively, solution was added. The pH of the suspension was adjusted to 2.0 by addition of 4 M HNO₃ and stirred by mechanical stirrer for 20 min. Then the top liquid was decanted (and discarded) and the remained C₁₈ was washed three times with water, then with 5 ml of 4 M HNO₃ and again three times with water. The prepared sorbent was transferred to a polypropylene tube (i.d 5 mm, length 10mm).

Determination of Cu²⁺ contents in working samples was carried out by a Varian spectra A.200 model atomic absorption spectrometer equipped with a high intensity hollow cathode lamp (HI-HCL) according to the recommendations of the manufacturers. These characteristics are tabulated in Table 1.

Table 1. The operational conditions of flame for determination of Cu

Slit width	0.7 nm
Operation current of HI-HCL	15 mA
Resonance fine	324.8nm
Type of background correction	Deuterium lamp
Type of flame	Air/acetylene
Air flow	7.0 mL.min ⁻¹
Acetylene flow	1.7 mL.min ⁻¹

A metrohm 691 pH meter equipped with a combined glass calomel electrode was used for pH measurements.

Procedure

The pH of a solution containing 100 ng of each Cu (II) was adjusted to 2.0. This solution was passed through the admicell column with a flow rate of 5 ml

min^{-1} . The column was washed with 10 ml of water and the retained ions were desorbed with 1ml of 4M HNO_3 with a flow rate of 2 ml min^{-1} . The desorption procedure was repeated 3 more times. All the acid solutions (4 ml all together) were collected in a 10 ml volumetric flask and diluted to the mark with water. The concentrations of Cu in the solution were determined by FAAS at 283.3.

Determination of Cu in water Samples

Polyethylene bottles, soaked in 1M HNO_3 overnight, and washed two times with water were used for sampling. The water sample was filtered through a $0.45 \mu\text{m}$ pores filter. The pH of a 1000 ml portion of each sample was adjusted to 2.0 (4M HNO_3) and passed through the column under a flow rate of 5 ml min^{-1} . The column was washed with water and the ions were desorbed and determined as the above mentioned procedure.

RESULTS AND DISCUSSION

Stability studies

The stability of the newly N,N'-disalicylideneethylenediamine modified Nano Geraphene phases was performed in different buffer solutions (pH 1, 2, 3, 4, 5, 6 and 0.1M sodium acetate) in order to assess the possible leaching or hydrolysis processes. Because the metal capacity values determined in Section 3.2 revealed that the highest one corresponds to Cu (II)s, this ion was used to evaluate the stability measurements for the N,N'-disalicylideneethylenediamine modified Nano Geraphene phase. The results of this study proved that the N, N' -disalicylideneethylenediamine modified Nano Geraphene is more resistant than the chemically adsorbed analog especially in 1.0, 5.0 and 10.0 M hydrochloric acid with hydrolysis percentage of 2.25, 6.10 and 10.50 for phase, respectively.

Thus, these stability studies indicated the suitability of phase for application in various acid solutions

especially concentrated hydrochloric acid and extension of the experimental range to very strong acidic media which is not suitable for other normal and selective chelating ion exchangers based on a nano polymeric matrix [9]. Finally, the N, N' -disalicylideneethylenediamine modified Nano Geraphene phases was also found to be stable over a range of 1 year during the course of this work.

Primary investigations revealed that surfactant coated C_{18} could not retain Cu (II) cations, but when modified with the N, N' -disalicylideneethylenediamine modified Nano Geraphene retains these cations selectively. It was then decided to investigate the capability of the N, N' -disalicylideneethylenediamine modified Nano Geraphene as a lig and for simultaneous preconcentration and determination of Cu on admicell.

The C_{18} surface in acidic media ($1 < \text{pH} < 6$) attracts protons and becomes positively charged. The hydrophyll part of SDS ($-\text{SO}_3^-$) is attached strongly to these protons. On the other hand, the N, N' -disalicylideneethylenediamine modified Nano Geraphene are attached to hydrophobe part of SDS and retain small quantities of metallic cations [22].

Effect of pH

The effect of pH of the aqueous solution on the extraction of 100 ng of each of the cations Cu (II) was studied in the pH rang of 1-10. The pH of the solution was adjusted by means of either 0.01 M HNO_3 or 0.01M NaOH. The results indicate that complete chelation and recovery of Cu (II) occur in pH range of 2-4 and that of in 2-8 and is shown in Figure 1. It is probable that at higher pH values, the cations might be hydrolysed and complete desorption occurs. Hence, in order to prevent hydrolysis of the cations and also keeping SDS on the C_{18} , pH=2.0 was chosen for further studies.

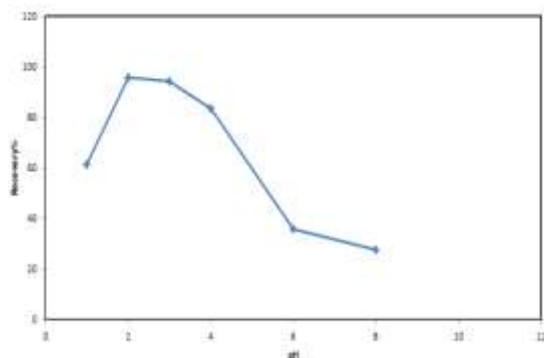


Figure 1. Extraction percentage of Cu (II) against pH.

Effect of flow rates of the solutions

Effect of flow rate of the solutions of the cations was also studied on chelation of them on the substrate. It was indicated that flow rates of $1\text{--}5\text{ ml min}^{-1}$ would not affect the retention efficiency of the substrate. Higher flow rates cause incomplete chelation of the cations on the sorbent. The similar range of flow rate for chelation of cations on modified C_{18} with SDS and a N, N' -disalicylideneethylenediamine modified Nano Geraphene has been reported in literature [21, 22]. Flow rate of $1\text{--}2\text{ ml min}^{-1}$ for desorption of the cations with 4 ml of 4 M HNO_3 has been found suitable. Higher flow rates need larger volume of acid. Hence, flow rates of 5 ml min^{-1} and 2 ml min^{-1} were used for sample solution and eluting solvent throughout respectively.

Effect of the N, N' -disalicylideneethylenediamine modified Nano Geraphene quantity

To study optimum quantity of the N, N' -disalicylideneethylenediamine modified Nano Geraphene on quantitative extraction of Cu, 50 ml portions of solutions containing 100 ng of each cation were passed through different columns the sorbent of which were modified with various amounts, between 10–50 mg of the N, N' -disalicylideneethylenediamine modified Nano Geraphene. The best result was obtained on the sorbent that was modified with 40 mg of the N, N' -

disalicylideneethylenediamine modified Nano Geraphene.

Figures of merit

The break through volume is of prime importance for solid phase extractions. Hence, the effect of sample volume was studied on the recovery of the cations. 100 ng of each cation was dissolved in 50, 100, 500 and 1000 ml of water. It was indicated that in all the cases, chelation and desorption of the cations were quantitative. It was then concluded that the breakthrough volume could be even more than 1000 ml. Because the sample volume was 1000 ml and the cations were eluted into 10 ml solution, the enrichment factor for both cations is 100, which is easily achievable. The maximum capacity of 1.5 g of the substrate was determined as follow; 500 ml of a solution containing 50 mg of each cation was passed through the column. The chelated ions were eluted and determined by FAAS. The maximum capacity of the sorbent for three individual replicates was found to be $15.2 \pm 0.8\text{ }\mu\text{g}$ of each cation. The limit of detection (3σ) for the cations [30] was found to be 3.20 ng l^{-1} for Cu ions. Reproducibility of the method for extraction and determination of 100 ng of each cation in a 50 ml solution was examined. As the results of seven individual replicate measurements indicated, they were 2.85% and 2.98% for Cu (II).

Effect of foreign ions

Effect of foreign ions was also investigated on the measurements of Cu. Here a certain amount of foreign ion was added to 50 ml of sample solution containing 100 ng of each Cu (II) with a pH of 2.5. The amounts of the foreign ions and the percentages of the recovery of Cu are listed in Table 2. As it is seen, it is possible to determine Cu without being affected by the mentioned ions.

Analysis of the water samples

The prepared sorbent was used for analysis of real samples. To do this, the amounts of Cu were

determined in different water samples namely: distilled water, tap water of Tehran (Tehran, taken after 10 min operation of the tap), rain water (Tehran, 2^o January, 2013), Snow water (Tehran, 7 February, 2013), and two synthetic samples containing different cations. The results are tabulated in Table 3. As it is seen, the amounts of Cu added to the water samples are extracted and determined quantitatively which indicates accuracy and precision of the present method.

Separation and speciation of cations by three column system. It is possible to preconcentrate and at the same time separate the neutral metal complexes of N, N'-disalicylideneethylenediamine modified Nano Graphene, anionic complexes and free ions from each other by this method [27]. Water samples were passed through the three connected columns: anion exchanger, C₁₈-silica adsorber and chelating cation exchanger. Each species of Cu is retained in one of the columns; anionic complexes in the first column, neutral complexes of N, N'-disalicylideneethylenediamine modified Nano Graphene in the second, and the free ions in the third. The results of passing certain volumes of different water samples through the columns are listed in Table 4. According to the results, it is indicated that Cu present only as cations. On the other hand, the t-test comparing the obtained mean values of the present work with those published indicate no significant difference between them. We have proposed a method for determination and preconcentration of Cu in water samples using surfactant coated C₁₈ impregnated with a Sciff's base. The proposed method offers simple, highly sensitive, accurate and selective method for determination of trace amounts of Cu (II) in water samples.

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