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PRECONCENTRATION AND EXTRACTION OF COPPER(II) ON ACTIVATED CARBON USING ETHYL-2-QUINOLYL-β(*p*-CARBOXYPHENYL HYDRAZONE)DIOXO PROPIONATE

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ABSTRACT. Activated carbon modified method was used for the preconcentration and determination of copper content in real samples such as tap water, wastewater and a synthetic water sample by flame atomic absorption spectrometry. The copper(II) was adsorbed quantitatively on activated carbon due to its complexation with ethyl-2-quinolyl-β(*p*-carboxyphenyl hydrazone)dioxo propionate (EQCPDP). The adsorbed copper(II) ion on solid phase was eluted quantitatively by using nitric acid. The important parameters such as pH, amount of carrier, flow rate, amount of activated carbon and type and concentration of eluting agent for obtaining maximum recovery were optimized. The method at optimum conditions gives linear concentration range of 0.05-1.0 μg mL^{-1} of copper(II) with correlation coefficient of 0.9994 and the detection limit of 0.99 ng mL^{-1}. The preconcentration leads to enrichment factor of 175 and break through volume of 1750 mL. The method has good tolerance limit of interfering ions and selectivity and it has been successfully applied for determination of copper content in real sample such as blood, wastewater and river sample.

KEY WORDS: Copper(II), Solid phase extraction, Activated carbon, Flame atomic absorption spectrometry

INTRODUCTION

Considering biological research, the role of some trace and ultra-trace elements in the body is very rich and varied. Some of them are essential to life while others are toxic even at very low concentrations [1-3].

Copper has received considerable attention owing to its uses in metallurgy and chemical industries. Moreover, it is an essential constituent of about thirty enzymes and glycoproteins, is required for the synthesis of hemoglobin and for some biological processes and also promotes iron absorption from the gastrointestinal system. It is involved in the transport of iron from tissues into plasma, helps to maintain myelin in the nervous system, is important in the formation of bone and brain tissues and is necessary for other many important functions.

Due to the presence of copper(II) ion in environmental samples at low levels and matrix effects the low detection limit of copper with traditional flame atomic absorption spectroscopy (FAAS) requires its preconcentration in addition to separation from matrix elements. Preconcentration and separation can solve these problems and these difficulty can be overcome by caring out a separation step prior to analysis, and lead to simultaneously preconcentrate and separate the metal ions to be analyzed from the matrix [4]. The most widely used techniques for the separation and preconcentration of trace amount of copper are liquid and supported membrane transport [5, 6], solvent extraction [7, 8], co-extraction [9], liquid membrane extraction [10] and solid phase extraction [11, 12].

Among them, solid phase extraction due to advantages such as high efficiency, simplicity, rapidity, and low consumption of material has found increasing application in the enrichment of

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*Corresponding author. E-mail: m_ghaedi@mail.yu.ac.ir trace metal ions and elimination of matrix interference prior to FAAS analysis [13-23]. Use of various types of sorbents for separation and/or preconcentration of metal ions has been gaining popularity because of its high concentrating ability and simple operation.

Among them activated carbon with high adsorption capacity has wide application due to its ability to adsorb organic compounds and organic metal complexes as non-polar or little polar substances in aqueous solution after converting them to corresponding metal chelates or precipitates or metal hydroxides. Metal chelate could provide higher selectivity and high enrichment factors for such a preconcentration and separation. The mechanism of metal sorption on activated carbon is still under investigation and their adsorption could be explained using Langmuir and Freundlich equations. It was assumed that the sorption is quantitative when the chelate contains systems of π-electrons in the molecule and when the centers for binding on carbon and those for the metal ions are spatially separated so that their orbital do not have a substantial influence [24]. The adsorption equilibrium studies have revealed that pH is the dominant parameter controlling the adsorption [25]. Therefore, using activated carbon as collector permits the preconcentration and separation of low levels of analytes in several matrices [26-29].

The purpose of this work is preconcentration and determination of copper(II) ion content based on activated carbon modified with EQCPDP.

EXPERIMENTAL

Chemicals

Acids and bases were of the highest purity available from Merck (Darmstadt, Germany) and were used as received. Doubly distilled deionized water was used throughout. Nitrate salts of copper, lead, cadmium, mercury, cobalt, nickel, zinc, magnesium, calcium, strontium, barium, silver, sodium and potassium (all from Merck) were of the highest purity available and used without any further purification. The pH adjustment was carried out by addition of dilute nitric acid or sodium hydroxide to the solution. Activated carbon (gas chromatographic grade, 40–60 mesh from Merck), were soaked in hydrochloric acid for 2 days, it was then washed with water and dried at 110 °C for one day. The ligand ethyl-2-quinolyl-β(*p*-carboxyphenyl hydrazone)dioxo propionate (EQCPDP) was synthesized according the described procedure [30].

Pre-treatment of natural water samples

Water samples were collected from Gachsaran, Iran. Before the analysis, the samples were filtered through a cellulose membrane filter (Millipore) of pore size 0.45 mm. The organic content of the water samples were oxidized in the presence of 2 mL of 1 % H_2O_2 and addition of 5 mL of concentrated nitric acid. The samples were filtered through a filter paper and stored in polyethylene bottles. For the preconcentration procedure, 800 mL of water samples was heated until its volume was reduced to 250 mL. After adjustment of desired pH by the addition of appropriate amount of dilute sodium hydroxide or nitric acid, SPE experiment was carried out. The retained Cu(II) ions on modified activated carbon were eluted with 10 mL of 1 M HNO_3. The effluent was subjected to FAAS for evaluation of Cu(II) ions content.

Apparatus

The metal content determinations were carried out on a Shimadzu 680 AA atomic absorption spectrometer with a hallow cathode lamp and a deuterium background corrector at wavelength of 324.8 nm (copper resonance line) and the air-acetylene flame were adjusted according to standard recommendations. A Metrohm 691 pH/Ion meter was used for the pH measurement.

The amounts of ligand loaded on activated carbon were measured using UV-Vis 160 Shimadzu spectrophotometer. Extractions were performed with solid phase suspended in a tube while a piece of glass wool put in the end to inhibit loss of solid phase and sample were passed throughout for preconcentration and separation of the copper(II) ion.

Preparation of the solid phase

Ligand loaded on activated carbon (AC) was prepared by dissolving 15 mg of the ligand EQCPDP in 0.005 M NaOH and adding to the 0.3 g of activated carbon. After 18 h, solutions were filtered through the filter paper and activated carbons were washed with distilled water until the filtrate was no longer alkaline. The solid phase columns were initially preconditioned with solution with desired pH. For the final optimum experiments the solid phase was prepared as follow: 15 mg EQCPDP per 300 mg of AC.

Measurement of the amount of ligand loaded on the activated carbon (AC)

A 0.3 g AC was placed in a 10 mL vial and 5 mL of 0.005 M NaOH containing weighed amount of ligand were added and shaken. After 18-20 h while shaking, a portion of the supernatant liquid was diluted to the appropriate volume and the absorbance of the solutions was measured at maximum wavelengths using a UV-Vis spectrophotometer. Results show that the ligand was adsorbed on activated carbon quantitatively.

Preconcentration

The pH of standard water solutions containing 0.01–1.5 µg mL^{-1} of copper was adjusted to the desired pH value, i.e. pH 5.7 ± 0.2 by adding appropriate amount of dilute sodium hydroxide or nitric acid to the sample solution. The sample was passed through the ligand loaded activated carbon column with flow rate lower than 5 mL min^{-1}. The concentration of copper was determined in the final solutions by FAAS.

Loading capacity

To investigate the loading capacity, 100 mL of 5.0 µg mL^{-1} or various volume of 0.2 µg mL^{-1} of copper(II) solution at pH 5.7 were passed through the solid phase columns containing 15 mg EQCPDP per 300 mg of AC. After loading and elution by nitric acid as stripping agent, effluent was sent into the FAAS to measure the copper content.

RESULTS AND DISCUSSION

The analytical parameters that are thought to affect the enrichment and measurement step in this procedure are pH, amount of EQCPDP, flow rate, amount of activated carbon and type and concentration of eluting agent and these parameters were optimized by using the univariate method for obtaining maximum recovery and efficiency for copper(II) ion. The optimum values or range of a parameter were studied using a solution of 250 mL of 0.2 µg mL^{-1} copper(II) ion.

Effect of activated carbon amounts on extraction recovery

In the adsorption step, an appropriate amount of activated carbon should be used in order to obtain quantitative retention of metal ions. On the other hand, an excess amount of the sorbent also prevents the quantitative elution of the retained metals by a small volume of eluent. For this reason, the effect of the amount of activated carbon and the eluent volume were examined. Therefore, the amount of activated carbon has an important role on recovery of extraction and must be optimized. The results show that sorption were quantitative with increasing amount of activated carbon until 300 mg and further addition lead to decrease in extraction efficiency, probably due to irreversible adsorption of metal ion (instead of its chelate) on activated carbon. So 300 mg of activated carbon were used for further studies.

Effect of pH on recovery

As is well known, pH value of the solution has significant influence on the overall performance of the retention of the copper(II) ion on activated carbon. The effect of pH on the preconcentration of copper(II) ion on AC loaded with EQCPDP was studied by determining 50 μg (250 mL of 0.2 μg mL^{-1}) of copper(II) ion which were preconcentrated in the pH range of 2.0-8.0 by introducing 15 mg of EQCPDP on the 0.3 g activated carbon. The results in Figure 1 show that optimum pH for maximum recovery of the Cu(II) ion are belonging to the pH from 5.0-6.5. Due to the presence of nitrogen atom in the ligand structures, which are weakly acid, at low pH they are not available to form chelate complexes and hydrogen ion compete with copper ion to these active sites, while in basic media due to hydroxide precipitation extraction efficiency would be reduced.

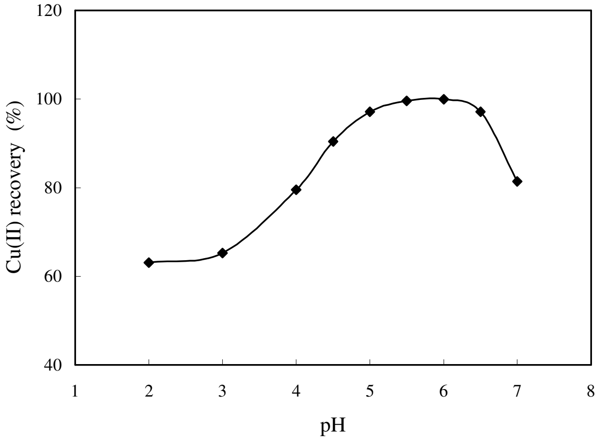

Figure 1. Effect of pH on recovery of Cu(II) ion.

Influence of amounts of ligands on copper ion recovery

To investigate the role of sorbent concentration on the recovery efficiency of Cu(II) ion, a series of preconcentration procedures under previously optimized conditions were carried out as following: 250 mL of 0.2 μg mL^{-1} of copper(II) ions was passed through the column comprises of the various amount of EQCPDP loaded on constant value of activated carbon (0.3 g). The data are shown in Figure 2. The data show that the recovery of Cu(II) ion gradually increased with increasing concentration of ligands, reaching the maximum extraction efficiency at 15 mg of EQCPDP causes increase in recovery and further increase lead to decrease the efficiency, probably due to formation of soluble charged complexes.

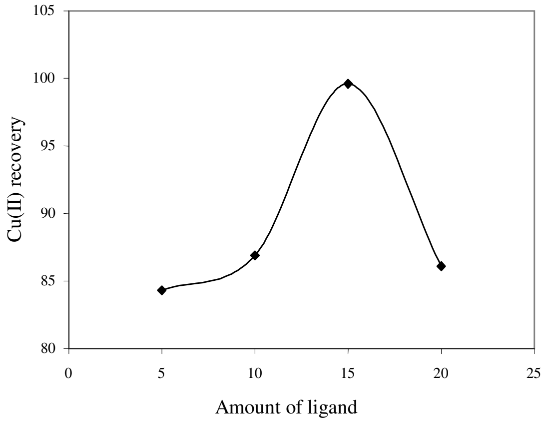

Figure 2. Effect of amount of ligand on recovery of Cu(II).

Flow rate has a great effect on the extraction efficiency, because lower flow rate lead to increasing residence and retention time of analyte in column, and so increasing interaction (complexation) between ions and sorbents. Therefore, different flow rate were examined and it was found that until 5 mL min^{-1} recovery is constant and after that gradually reduce. Therefore, flow rate of 5 mL min^{-1} was used for further studies.

Effect of type and concentration of eluting agent on recovery

The elution of a group of analytes could be sometimes troublesome owing to irreversible binding of some elements. An appropriate eluent for metal desorption was selected by taking into account the following considerations: (i) the eluent should desorb the metals or chelate complexes and (ii) should be suitable for the subsequent determination technique. Organic solvents and inorganic acids have been found to meet the requirements.

For investigating the effect of eluting agent and its concentration on recovery, a set of experiments under previously established conditions were undertaken. Different acids with various concentrations were selected as eluting agents for quantitative desorption of retained copper(II) ions. Results are given in Table 1 which show that when we used every eluting agent with concentration lower than 1.0 M except nitric acid recovery of copper(II) ion is low, < 70 %, but, when nitric acid was used, recovery of the copper(II) ion was increased. Hence, for further studies 10 mL of 1 M nitric acid were used for further studies for column modified by EQCPDP. Different volume of 1 M nitric acid was used as eluting agent. Results (Figure 3) show that with increasing nitric acid volume until 10 mL recovery increased and after that it remained constant.

Table 1. Effect of type and concentration of eluent on recovery of Cu(II).

Type and concentration of eluent	Recovery of Cu(II) (%)
1.0 M HCl	35.9
1.0 M HNO_3	99.5
1.0 M H_2SO_4	67.3
0.2 M Histidine	34.8
0.4 M HNO_3	55.8
0.8 M HNO_3	89.3
1.5 M HNO_3	99.4
2.0 M HNO_3	99.6

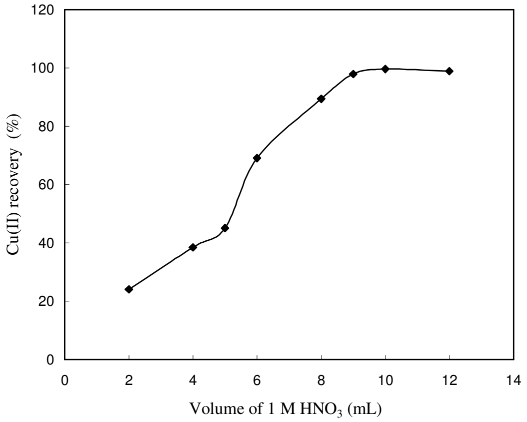

Figure 3. Effect of HNO_3 volume on Cu(II) ion recovery.

Reproducibility

The reproducibility of the method was evaluated at optimum condition by passing 250 mL solution of 0.2 µg mL^{-1} copper(II) ion through the modified columns and the effluent was sent to FAAS for evaluating Cu(II) ions content. The experiment was repeated six times using the same sorbent. The reproducibility of modified columns based on EQCPDP is 99.9 ± 0.6 that indicate repeatable results.

Interferences

Preconcentration/separation procedures for trace elements in the high salt content samples can be strongly affected by the matrix constituents of the sample. The influences of some alkaline and alkaline-earth ions and transition metal ions on the copper ion recovery were investigated. The results are given in Table 2. The tolerance limit is defined as the ion concentration causing a relative error smaller than ± 5 % related to the preconcentration and determination of copper(II) ion. Cu(II) ion was quantitatively recovered in the presence of large amounts of alkaline and alkaline-earth ions and some transition metal ions. The matrix ion contents in the eluent solutions were found to be significantly lower and suitable for atomic absorption spectrometric determinations.

Table 2. Investigation of tolerance limit of interfering ion.

Interfering ion	[Interfering ion]/[Cu(II)]	Recovery of Cu(II) (%)
Ag^+	1000	99.4
Hg^{2+}	1000	98.9
Cd^{2+}	1000	99.6
Ni^{2+}, Co^{2+}	1000	98.9
Zn^{2+}	1000	99.1
Fe^{2+}, Fe^{3+}	1000	99.5
K^+	1000	99.6
Ba^{2+}	1000	99.6
Mg^{2+}	1000	99.5
Pb^{2+}	1000	98.8

Calibration graphs and precisions

The calibration curve was obtained by using 250 mL of 0.01-2.0 µg mL^{-1} copper(II) solutions at pH = 5.8 ± 0.2 at the optimum conditions. The eluting solution was introduced to FAAS for evaluating copper(II) ion content. The calibration curve was linear for copper(II) ion in the range of 0.05-1.0 µg mL^{-1} with calibration curve equation of $A = 0.25\ C_{Cu(II)} + 0.002$. Relative standard deviations of measurements were found to be 0.6 % for 0.2 µg mL^{-1} of copper. Detection limits for the copper(II) ion was found to be 0.99 ng mL^{-1}.

Accuracy and applications

To ensure that the method is valid and has reasonable accuracy and precision, recovery of the copper(II) ion in tap water, waste water and synthetic water samples were determined. The results are given in Table 3. Results, which obtained with reference standard addition method, express that reproducible and quantitative recovery for copper(II) ion can be obtained.

Table 3. Investigation of accuracy and precision of method for real samples analysis.

Sample	Added value	Found value
Waste water	0.0 0.800	0.169 ± 0.004 0.972 ± 0.002
Tap Water	0.0 0.200	0.08 ± 0.005 0. 283 ± 0.003
Synthetic mixture, Cu (1), Hg (4), Ni (4), Co (4), Pb (6), Zn (8), Fe(II) (5)	0.0	0.997 ± 0.002

Number in parenthesis is ion concentration (µg mL^{-1}).

Investigation of break through volume, enrichment factor and loading capacity

For the investigation of enrichment factor and break through volume various volumes (mL) of 0.2 µg mL^{-1} of copper(II) ion was passed through column and then the effluent was sent to FAAS for evaluating copper(II) ion content. The results in Figure 4 show that up to 1750 mL of 0.2 µg mL^{-1} of copper(II) ion adsorbed quantitatively on activated carbon and can be eluted by 10 mL of 1 M nitric acid leading to enrichment factors of 175.

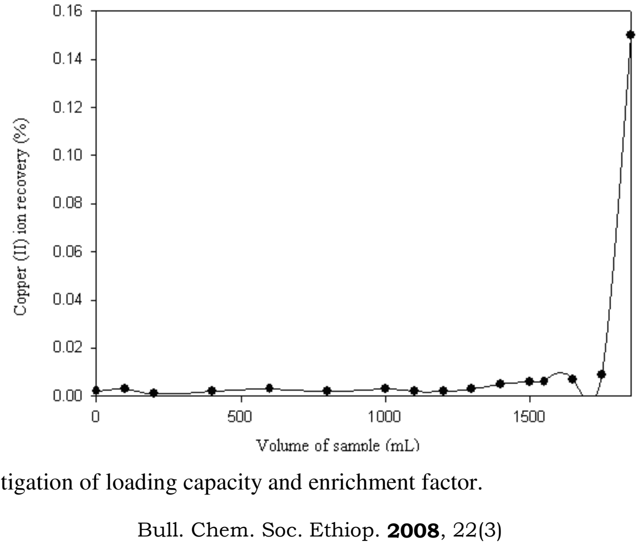

Figure 4. Investigation of loading capacity and enrichment factor.

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