نانو سیلیکای اصلاح‌شده توسط CTAB و لیگاند اکسیم جهت جداسازی و پیش‌تغلیظ مقادیر ناچیز یون مس (II) در نمونه‌های زیست-محیطی حقیقی

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Nano-SiO2 Modified by CTAB and Oxime Ligand for Separation and Preconcentration of Trace Amount of Cu(II) in Real Environmental Samples

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چکیده

یک روش ساده، جدید، صحیح و گزینش‌پذیر برای اندازه‌گیری مقادیر ناچیز یون مس در نمونه‌های آبی و خاک پیشنهاد شده است. روش بر اساس جداسازی و پیش‌تغلیظ یون مس بر روی نانوسیلیکای اصلاح‌شده توسط ستیل تری متیل آمونیوم برومید به عنوان عامل فعال‌کننده سطح و ایندان–۱و۲و۳-تری اون ۱و۲–دی اکسیم به عنوان عامل کمپلکس‌دهنده می‌باشد. مس جذب‌شده بر روی نانوجاذب با استفاده از ۱٫۵ میلی لیتر از محلول ۰٫۱ مولار نیتریک اسید شسته شده و سپس بوسیله دستگاه جذب اتمی شعله‌ای تعیین مقدار می‌شود. فرآیند سنتز این نانوجاذب تشریح شده و با استفاده از تکنیک‌های طیف بینی زیر قرمز تبدیل فوریه FTIR، پراش اشعه ایکس XRD و تصویربرداری میکروسکوپی روبشی گرمایی TEM تایید شده است. علاوه بر این، چندین پارامتر تجزیه‌ایی تاثیر گذار بر فرآیند بررسی و بهینه شده‌اند. تحت بهترین شرایط بهینه حاصله، بیشترین ظرفیت جذب، فاکتور غنی‌سازی و حد تشخیص روش به ترتیب ۷٫۰۴ میلی گرم بر گرم، ۳۳۳٫۳ و ۴٫۴ میکروگرم بر لیتر بدست آمدند. انحراف استاندارد نسبی روش پیش تغلیظ (RSD) برای ۷ تکرار ۰٫۲۸ ٪ حاصل شد و منحنی درجه‌بندی محدوده خطی خوبی با مقدار ضریب رگرسیون ۰٫۹۹۷حاصل شد. در پایان، انعطاف‌پذیری و کارآیی روش با استفاده از اندازه‌گیری یون مس (II) در چندین نمونه آب و خاک ارزیابی شده و نتایج رضایت‌بخشی بدست آمد.

واژه‌های کلیدی

نانوسیلیکای اصلاح‌شده؛ عامل فعال‌کننده سطحی ستیل تری متیل آمونیوم برومید؛ لیگاند ایندان؛ جداسازی؛ پیش تغلیظ؛ تعیین مقدار مس.

Abstract

A simple, novel, accurate and selective method for the determination of trace amounts of Cu^{2+} ions in water and soil samples is proposed. The method is based on the separation and preconcentration of Cu^{2+} on a nano-SiO2 modified by a cetyltrimethylammonium bromide as surfactant and indane-1,2,3-trione-1,2-dioxime as complexing agent. The retained copper on the nano-sorbent was eluted with 1.5 mL of 1.0 mol L^{-1} HNO_3 and measured by flame atomic absorption spectrometry. The synthesis of this nano-sorbent is also described and certified by FTIR, XRD and TEM techniques. Furthermore, several effective analytical parameters were evaluated and optimized. Under the best optimum conditions maximum absorption capacity, enrichment factor and limit of detection were 7.04 mg g^{-1}, 333.3 and 4.4 µg L^{-1}, respectively. The relative standard deviation of the preconcentration method was 0.28% (n=7) and calibration curve gave good level of linearity with correlation coefficient value 0.997. Finally, the feasibility and performance of the method was evaluated by determination of copper (II) ions in several water and soil samples with satisfied results.

1. INTRODUCTION

Copper is widely used in many industries, such as electroplating, metal finishing, electrical, fertilizer, wood manufacturing and pigment industries. Rapid development of these industries has led to accumulation of copper(II) ion in environment.

Copper and some other toxic heavy metals are non-biodegradable and can exist for a long time in natural environment [1-2]. If the level of copper ions is beyond the tolerance limit, it will cause serious environmental and public health problems. Thus, it is necessary to remove copper ions from industrial effluents prior to their discharge. Up to now, numerous technologies have been developed, including chemical precipitation [3], ion exchange [4], liquid–liquid extraction [5], electrodialysis [6], biosorption [7] and so on. Considerable attention has been concentrated on the removal of copper (II) ions by adsorption method because it is simple, relative low-cost, effective and flexible in design and operation. Up to now, numerous adsorbents have been developed including activated carbon [8], carbon nanotubes [9], chitosan [10], lignocelluloses [11], synthetic porous inorganic materials [12], natural inorganic minerals [13], zero-valent iron [14] and functionalized polymers [15] and so on. However, most of these adsorbents show unsatisfied adsorption capacity due to diffusion limitation or the lack of enough active surface sites, and some problems, including high cost, difficulties of separation and regeneration of adsorbents from wastewater and secondary wastes, have to be faced. So, it is very important to develop novel adsorbents with large adsorptive surface area, low diffusion resistance, high adsorption capacity and fast separation for large volumes of solution. Considering these characteristics, nano-materials attracted much attention and various nano-adsorbents have been exploited to remove heavy metal ions from solution.

Because nanometer-sized silica (Nano-SiO$_2$) has high surface area, high sorption capacity and high chemical activity, it could be successfully applied for the separation and concentration of trace metal ions in environmental samples modification of silica surface relates to all the processes that lead to change in chemical composition of the surface [16]. Surface can be modified either by physical treatment (thermal or hydrothermal) that leads to change in ratio of silanol and siloxane concentration of the silica surface or by chemical treatment that leads to change in chemical characteristics of silica surface. By the modification the adsorption properties are significantly affected. Chemisorptions of chelating molecules on silica surface provides immobility, mechanical stability and water insolubility, thereby increases the efficiency, sensitivity and selectivity of the analytical application [17]. The most convenient way to develop a chemically modified surface is achieved by simple immobilization (or fixing) of the group on the surface by adsorption or electrostatic interaction or hydrogen bond formation [18-19] or other type of interaction. Simple impregnation of the solution of modifiers or covalent binding [20], so called, covalent grafting of the chelating molecule to the silica matrix is the common practice of developing a functionalized silica surface [21]. Nano-particles have received considerable attention because of their special physical and chemical properties [22-24]. Nano-silica is useful filler, polishing material, pigment, catalyst and reinforcement material, and has been widely used in many fields [25-29]. However, the hydroxyl group on the silica surface absorbs moisture and causes the nano-particles to be agglomerated. The agglomerations cause poor dispersion capacity in the organic polymer matrix, therefore the applications of nano-silica was largely limited. Fortunately, this problem could be resolved by using some surface modification methods with different surfactant agents [30-33]. Surfactants are used in coatings for a variety of reasons, including emulsification, emulsion polymerization, wetting and dispersion. According to the different chemical structure of surfactants, it can be divided into the following four categories: nonionic, anionic, cationic and so on. Cationic surfactants bear a positive charge on the polar portion of a solution, for example, CTAB is a typical cationic surfactant with sixteen long-chain carbons [34-35]. It is frequently used in the electrodeposition coatings as pigment grinding aids and/or flow control additives. In addition, the systems can be very effective with greater surface activity than either. A variety of methods for surface modifying nano-particles have been developed, including chemical vapor deposition, physical vapor deposition, plasma coating method, liquid precipitation method, sol-gel method and micelles method [36-38]. In all of those methods, the liquid-phase methods were widely used because of the easier operating conditions and the low experimental cost.

In present work, we have prepared Nano-SiO$_2$ modified by CTAB and Indan-1,2,3-trione-1,2-dioxime, as a new and effective adsorbent for the preconcentration and determination of ultra-trace amount of copper ions by flame atomic absorption spectrometer (FAAS) in several environmental samples with satisfactory results.

2. EXPERIMENTAL
2.1. Apparatus
The copper determination was carried out on a flame atomic absorption spectrometer (Varian, SpectraAA-220, Australia) with a hollow cathode lamp at a wavelength of 324.7 nm using an air–acetylene flame and a deuterium background corrector. The burner height and the gas flow rates were adjusted to obtain the maximum sensitivity. A Metrohm 692 pH/Ion meter with a combined

glass-calomel electrode was used for measurement of test solution pH. A peristaltic pump (040D model, made in IRAN) was used to propel the solutions.

2.2. Chemicals

All chemicals and solution with highest purity available from Sigma (St. Louis, MO, USA) and Merck (Darmstadt, Germany) were used and received. Doubly distilled water was used throughout. The stock standard solution of copper (1000 mgL^{-1}) prepared from Cu(NO$_3$)$_2$ salt. The pH adjustment was done by addition 0.1 mol L^{-1} of hydrochloric acid (pH range of 1-3.5), acetic acid/sodium acetate (buffer solution for pH range of 3.5-6.0) and 0.1 mol L^{-1} of sodium hydroxide solution (pH range of 7-8) to prepare the desired pH solution. The Nano-SiO$_2$ mesh 20-30 was purchased (from US Research Nano Materials) used and received. The cetyltrimethylammonium bromide (CTAB) was purchased from Merck (Darmstadt, Germany). Indane-1,2,3-trione-1,2-dioxime as complexing agent (L) was synthesized as literature [39] at our laboratory (phase separation and FIA-Labratuare) and its solution was prepared in ethanol.

2.3. Synthesized of nano-sorbent

At first about 5 g of nano-SiO$_2$ was activated by stirring and refluxing in 50 mL of 6 mol L^{-1} hydrochloric acid for 4 h. Active nano-SiO$_2$ particles was filtered, washed several times with doubly distilled water to discard Cl$^-$ in solution and dried in an oven at 150 ^{0}C for 6 h. After that, 2.9 mg of CTAB added to 100 mL of water solution containing 0.5 g of nano-SiO$_2$ particles and pH was adjusted to 8 with NaOH 0.1 mol L^{-1} to form ad-micelles on nano-SiO$_2$ particles. Then 5 mL of ligand solution (0.1 mol L^{-1}) was added while shaking the suspension was continued for 4 h. Next, suspended content filtered and washed several times with distilled water and dried at 50 ^{0}C for 8 h. Finally, white-yellow solid precipitated and then dried at 60 ^{0}C for 24 h. Then, synthesized powder prepared to take TEM image and XRD patterns (Fig. 1 and Fig. 2, relatively).

2.4. Column preparation

The mini-column was prepared by firmly packing 50 mg modified nano-adsorbent in a polyethylene syringe tube (40 mm length and 2 mm inner diameter) plugged with glass wool at both ends. The prepared mini-column washed with several reagents such as nitric acid, ethanol and distilled water respectively for several times. The performance of the mini-column was stable at least over 20 separation/concentration cycles.
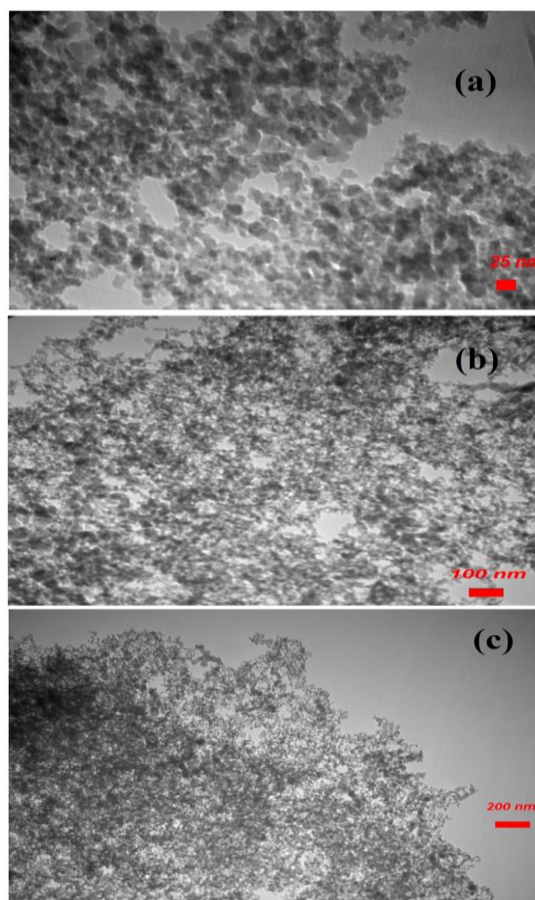
Fig. 1. TEM of nano-SiO$_2$ modified with CTAB and Indane-1,2,3-trione-1,2-dioxime at 25 nm(a), 100 nm(b) and 200 nm(c)
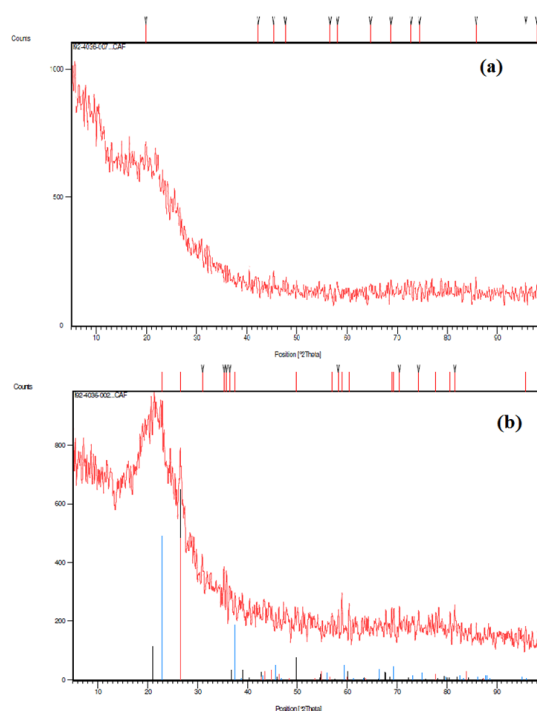
Fig. 2. XRD pattern of (a) nano-SiO$_2$ and nano-SiO$_2$ modified by CTAB and complexing agent (Indane) (b)

2.5. Analytical procedure

After pH of sample solution adjusted to 6.0, about 10 mL of sample solution containing copper ions (2 mg L^{-1}) was passed through the mini-column containing 50 mg of modified nano-SiO$_2$ at a flow rate of 4.2 mL min^{-1} with the aid of a suction pump. Afterwards, the absorbed copper ions on the mini-column was then eluted from the adsorbent with 1.5 mL of 1 mol L^{-1} nitric acid at a flow rate of 8.2 mL min^{-1} and then determined by FAAS.

*2.6. Pretreatment of water and soil as real samples*

Analysis of water samples for determination of copper ions content was performed as following route: 400 mL of sample was poured in a beaker and 10 mL concentrated HNO$_3$ (63% v/v) and 5 mL of H$_2$O$_2$ (30% v/v) for elimination and decomposition of organic compound were added. The samples, while stirring was heated to one tenth volume. After adjustment of samples pH to desired value the column SPE were performed according to general described analytical procedure.

Homogenized soil sample 20 g was weighed accurately and in a 200 mL beaker was digested in the presence of an oxidizing agent with addition of 10 mL concentrated HNO$_3$ (63% v/v) and 2 mL HClO$_4$ (70% v/v) was added and heated for 1 h. The content of beaker was filtered through a Whatman No. 40 filter paper into a 250 mL calibrated flask and its pH was adjusted to desired value and diluted to mark with deionized water. Then the general analytical procedure given at 2.6 section was applied.

3. RESULT AND DISCUSSION

3.1. Effect of pH

The pH of sample solution plays an important role in meta-chelate formation and subsequent preconcentration. Therefore a series of 2 mg L^{-1} of copper ion sample solutions with different pH values from 1.0 to 8.0 were introduced into the packed mini-column and copper ions were adsorbed. The initial pH of the sample solution was adjusted by solutions of HCl or NaOH (0.1 mol L^{-1}) and measured by a calibrated pH meter. As showed in Fig. 3 maximum absorbance was obtained at pH of 6.0. The progressive decrease in the retention of this metal ion at a low pH is due to the competition of the H$_3$O$^+$ ions with Cu^{2+} ions for complexation with ligand, and because of high amount of hydronium ions, its won and complex of metal-ligand decreased. To achieve high efficiency and good selectivity, a pH of 6.0 was selected for subsequent work and in all experiments the pH of solution was fixed at pH of 6.0.
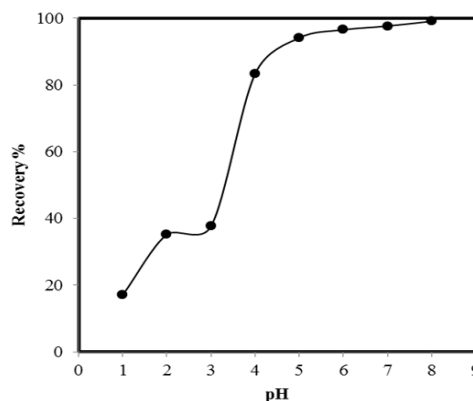
Fig. 3. Effect pH of sample solution, conditions: 10 mL of sample solution containing 2 mg L^{-1} of copper ions, pH is varied, amount of adsorbent 50 mg, and sample flow rate is 4.2 mL min^{-1}.

3.2. Effect of amount of nano-SiO$_2$

In order to investigate the effect of the amount of sorbent on the quantitative extraction of copper ions, the extraction was conducted by varying the amounts of the sorbent from 10 to 100 mg. The results indicated that the quantitative recovery (>95%) of copper ions was obtained with increasing of modified nano-SiO$_2$ amount up to 50 mg (Fig.4). Hence 50 mg of the modified nano-SiO$_2$ was used for further experiments due to the greater availability of the surface area at high amounts of the sorbent and to account for other extractable species.
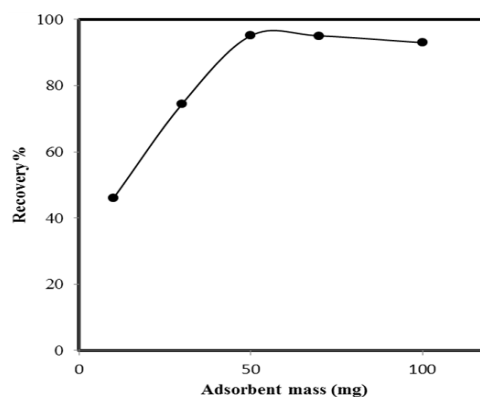
Fig. 4. Effect amount of nano-SiO$_2$ (adsorbent), conditions: 10 mL of sample solution containing 2 mg L^{-1} copper ions, pH is 6.0, amount of adsorbent is variable, and sample flow rate is 4.2 mL min^{-1}.

3.3. Sample flow rate and volume

The retention of copper ions on the sorbent depends on the flow rate of the solution loaded on the mini-column. The influence of flow rate of sample solution on amount of copper ions sorption on sorbent was investigated. The results showed the retention of the copper ions increased up to 4.2 mL min^{-1} and then slowly decreased. Hence, a flow rate of 4.2 mL min^{-1} was employed. Also

sample solution volume is an important parameter for evaluate of concentration factor and to obtaining high preconcentration factor (PF). For that reason, the volumes of sample solution containing 0.02 mg of copper ions were varied from 10 to 500 mL. The copper ions were absorbed on the sorbent by applying the proposed procedure. As obtained results, quantitative recovery (>95%) was obtained up to 500 mL of sample solution, thus concentration factor about 333.3 could be obtained.

3.4. Effect of elution condition

For the elution of adsorbed copper ions on the mini-column, some parameters, such as type, volume, concentration and flow rate of eluent were investigated and optimized. The nature and concentration of eluting agents were found to have a significant effect on the elution process of the adsorbed ions from the solid phase.

The acidic eluents is the best solution for obtaining efficient extraction. Due to this point, various eluent solutions such as acetic acid, nitric acid, sulfuric acid and hydrochloric acid were used in order to find an appropriate eluent for desorbing of copper ions from adsorbent surfaces. Based on the results showed in Fig. 5, the recovery was better in the presence of nitric acid as an eluent it was used as an appropriate eluent for desorbing of copper ion.
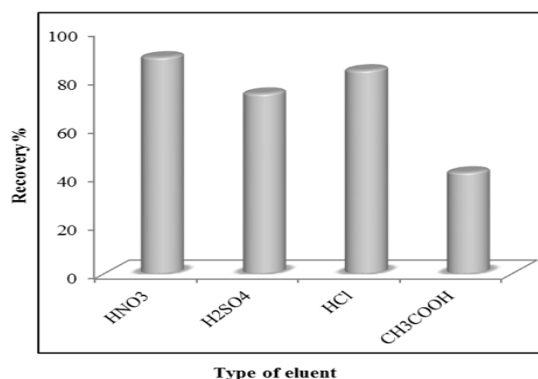
Fig. 5. Effect type of eluents, conditions: 10 mL of sample solution containing 2 mg L^{-1} copper ions, pH is 6.0, amount of adsorbent is 50 mg, sample flow rate is 4.2 mL min^{-1}, type of eluent is variable.

In order to find optimum volume of the elution solvent different, volumes of nitric acid from 1.5 to 6 mL were investigated. The results showed the quantitative elution was obtained using volume 1.5 mL at flow rate of 8.2 mL min^{-1}.

The influence of nitric acid concentration on the elution of copper ion from the adsorbent was also examined and the results are showed that the copper ions were quantitatively eluted from the column with 1 mol L^{-1} nitric acid.

In column solid phase extraction, flow rate of eluent is important parameter that affected recovery amount of desorbed analyte. So, a volume of 10 mL of the sample containing 2 mg L^{-1} of copper ions was passed through the column at 4.2 mL min^{-1}. Elution of the SPE mini-column was performed with 1.5 mL of 1 mol L^{-1} nitric acid at different flow rates between 2.2-8.2 mL min^{-1}. As results obtained, the amount of recovery increases and quantitative recovery was observed at flow rates 8.2 mL min^{-1}.

3.5. Effect of foreign ions

To assess the possible applications of the procedure, the effect of foreign ions which may interfere with the determination of copper ions by the presented method or/and often coexisting in various real samples was examined with the optimized conditions presented above. A 10 mL of copper ion 2 mg L^{-1} was taken with different amounts of foreign ions and the recommended procedure was followed. The recoveries of copper ions were higher than 95%. Tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding 5% in the determination of investigated copper ions by the combination of the SPE procedure and the FAAS method. The results are summarized in Table 1. As can be seen, large numbers of ions used have no significant effect on the determination of copper ions.

Table 1. Effect of the interference of diverse ions on the recoveries copper ions (N=3)

Foreign ion[a]	Tolerance limit (mole foreign ion/mole copper ion)	Recovery (%)
Na$^+$, K$^+$, Ca^{2+}, Mg^{2+}, Ba^{2+}	>1000	95.8
Fe^{2+}	200	95.5
Mn^{2+}	250	96.5
Cd^{2+}, Pb^{2+}	100	94.4
Ni^{2+}	5	92.3
Zn^{2+}	100	95.0
Co^{2+}	5	92.2
NO$_3^-$, Cl$^-$, SO$_4^{2-}$	500	94.2
Br$^-$	1000	94.6

[a]All values of RSD is between 2.0-4.5%

3.6. Analytical figures of merit

According to the description of International Union of Pure and applied Chemistry, limit of

detection (LOD) for the copper ions was calculated based on $3S_b/m$ (where m is the slope of the calibration curve and S_b is the standard deviation for 7 blank measurements) was obtained 4.4 μg L^{-1}. Accuracy of the method was predictable based on the recovery while precision of the method was estimated as the relative standard deviations (RSD) of the replicate sample determinations. RSD% of the method for determination of the copper ion (2 mg L^{-1}) was 0.28%. These results indicated that the method had good precision for the analysis of trace amounts of copper ions.

The capacity of the adsorbent is an important factor that determines how much sorbent is required to remove a specific amount of copper ions from the solution quantitatively. To study the adsorption capacity of modified nano-SiO$_2$, was calculated as equation 1:

$$a_E=(C_0-C_E)Vm^{-1} \qquad (1)$$

At equation 1, C_0 and C_E are the initial and equilibrium concentrations (mg L^{-1}) of copper ions in the solution, respectively. Maximum amounts of copper ion that can be adsorbed by modified nano-SiO$_2$ were found to be 7.04 mg per g adsorbent.

Prencentration factor that reveal an ability of adsorbent to concentrate of copper ions in order to determination with detection system calculated by $CF=V_{sample}/V_{eluent}$ equation, maximum volume of sample solution is 500 mL and therefore the concentration factor of 333.3 could be obtained (Table 2).

Table 2. Analytical figures of merit for determination of copper ions.

Type of parameter	Value
Linear range	5-2000 (μg L^{-1})
Limit of detection	4.4 (μg L^{-1})
Loading capacity	7.04 (mg g^{-1})
RSD	0.28 (%)
Maximum retention	99.5 (%)
Concentration factor	333.3

3.7. Determination of copper ions real samples

We have explored the feasibility of the methodology given with modified nano-SiO$_2$ for determination of copper ions in water samples (Zanjan City, IRAN) by the standard addition method. The results are presented in Table 3 for several water and soil sample. The recovery of spiked samples is satisfactory reasonable and was confirmed using the addition method, which indicates the capability of the system in the determination of copper ions. A good agreement was obtained between the added and measured amounts. The recovery values calculated for the added standards were always higher than 96%, thus confirming the accuracy of the procedure and its independence from the matrix effects.

Table 3. Determination of copper ions in real environmental samples.

Real sample	Added (μg/mL)	Founded (μg/mL)	Recovery (%)
Tap water	0	0.1±2.1	-
	10	9.9±0.9	98.1
	50	50.1±1.8	100.1
	100	98.2±2.0	98.2
Well water	0	1.8±0.8	-
	10	11.1±1.3	94.1
	50	51.3±2.0	99.0
	100	102.0±1.0	100.2
Soil sample	0	6.8±1.7	-
	10	17.0±1.7	101.2
	50	56.9±1.2	100.2
	100	107.0±0.9	100.2

4. CONCLUSIONS

A modified nano-SiO$_2$ in presence of cationic surfactant (CTAB) as surfactant and Indane-1,2,3,-reione 1,2-dioxime as complexing agent was synthesized and prepared. The extraction/concentration method is simple, fast, accurate and economical and for the determination of copper ions in environmental samples at ultra-trace amounts. The system showed reproducibility and reliability in analytical data, with an RSD value of lower than 1% for seven experiments. About 50 mg of modified nano-SiO$_2$ can be used as high as greater than ten experiments without any loss in its adsorption behavior. The system was successful in separation/concentration and determination of copper ions from large sample volumes (~500 mL).

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