

Separation and Preconcentration of Heavy Metals through Nanocomposites in Real Samples

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ABSTRACT

In the present study, trace amount of copper (II) ions in real samples has been separated, preconcentrated and determined by a modified nanocomposite. The effective factors such as pH, nanocomposite amount, extraction time, eluent type, ionic strength and sample volume were optimized for quantitative determination of copper (II) ions. The linear range of the calibration graph was between 10 and 900 ng mL⁻¹ with limit of detection (LOD) 3.62 ng mL⁻¹. Relative standard deviations (RSD) was 1.8%. Modified nanocomposite was used for measurement of the trace amounts of Cu (II) ions in the real samples such as sea water, tap water, river water and well water with suitable fallouts.

Keywords: Copper ions, Nanocomposites, Extraction.

1. INTRODUCTION

Copper is one of the basic elements in nature and has been used by human in a wide range of crafts. Today, there are many industries that use copper including plating, oil refinery and mining extraction. On the other hand, using this element in industry causes the production of large amount of copper cations contains in form of wastewater and sludge and as this element is unsuitable to human life, which have negative impacts on the environment water [1]. The separation preconcentration techniques which has been employed to address the above mentioned barriers and problems consists of extracting the solvent, chelating sorbents, cloud point extraction, ion-exchange, using electro- analysis is methods, solid phase extraction, etc. [2–4]. On the other hands, there are some other alternatives that have more benefits than the ordinarily used solid phase extraction (SPE). This research proposes an nanocellulose coat which is improved by using CBIMMT ligand, as an alternative sorbent which could be efficiently used as a new sorbent in both the preconcentration function and detecting the Cu ions via FAAS in widely used targets which are used in every day life.

2. Materials and methods

2.1. Reagents and apparatus

Ethanol, CBIMMT ligand, copper (II) nitrate, acetone and sodium hydroxide have been purchased from Merck Corporation and α -cellulose were purchased from sigma Aldrich. Analytical grade nitrate salts of elements (all from Merck) were of the highest purity available and used without any further purification. pH meter model Metrohm 744 from Switzerland was used to measuring pH. Kokusan model H-11n centrifuge was used to precipitating nanocomposite. Measuring Copper ions was done by a Thermo M series (Model: M5) FAAS with a Cu hollow cathode lamp. The following conditions were used: λ_{\max} =249.0 nm; monochromator spectral bandpass=0.1 nm; lamp current=15 mA; burner head=50 mm; acetylene and air-flow rates were 0.8 and 10.0 L min⁻¹ respectively.

2.2. General Procedure of Extraction

50 mL of Cu (II) ions solution (100 ng mL⁻¹) was prepared and pH value was adjusted to 9 using ammonium buffer solution, then 0.1 g of modified nanocomposite was added to 50 mL of solution. The mixture was stirred for 15 min at room temperature, after centrifugation of the mixture (at 4000 rpm for 5 min) Cu (II) ions retained on nanocomposite



were eluted with 1.0 mL HNO_3 (0.5 mol L^{-1}). Finally, after stirring and centrifugation (at 5000 rpm for 5 min) the mixture acidic, Cu (II) ions determined by FAAS.

3. Result and discussion

3.1. Effect of pH on the extraction efficiency

To find the best pH for maximum extraction of Cu (II) ions, different values of pH (in the range of 2-11) were analyzed. As shown in Fig. 1, the maximum extraction can be found at pH=9. At low pH values, owing to the electrostatic repulsion between positively charged nanocomposite surface and positive charge of Cu (II) ions, the adsorption of Cu (II) ions will decrease. On the other hand, at high pH values, the charge of nanocomposite surface is negative owing to existing hydroxide ions; so, one can conclude an increase in the adsorption of Cu (II) ions because of electrostatic attraction between them.

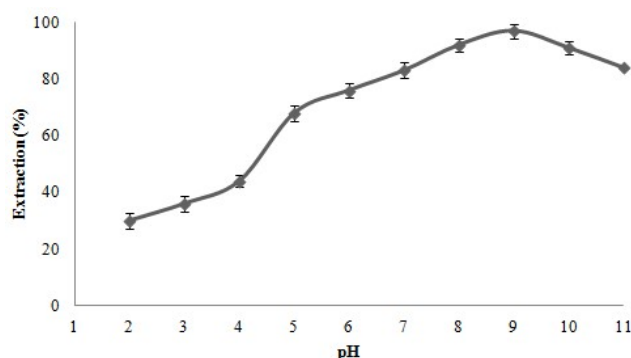


Fig. 1. Effect of pH on extraction of Cu (II) ions.

3.2. Effect of the amount of nanocomposite

Fig. 2 shows the effect of different amounts of nanocomposite in the extraction of Cu (II) ions. As can be seen in Fig. 2, for each amount of nanosorbent, the recovery of nanocomposite is much higher compared to nanocellulose, confirming the good performance of nanocomposite toward Cu (II) ions extraction. However, we can conclude from Fig. 2 that by increasing the amount of adsorbent up to 0.1 g, the extraction of Cu (II) ions increases owing to an increase in the surface of interaction. The amount of 0.1 g of nanocomposite gives the highest recovery percent and there is no significant increase in Cu (II) ions extraction by increasing the amount of adsorbent to 0.2 g. So, 0.1 g of nanocomposite was selected for further studies.

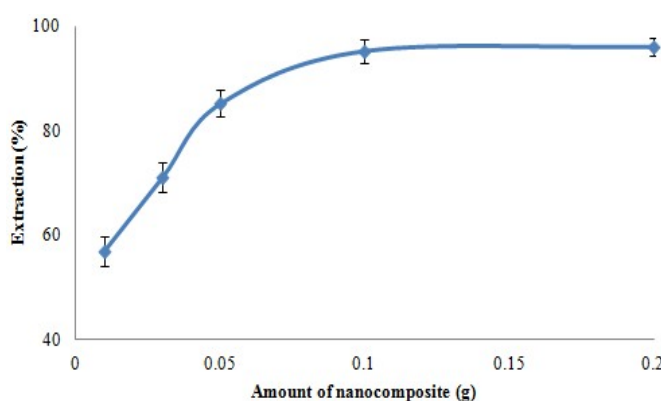


Fig. 2. Effect of different doses of nanocomposite for extraction of Cu (II) ions.

3.3. Effect of the shaking time

The rate of adsorption of Cu (II) ions by modified nanocomposite was studied with 0.1 g of the sorbent over a series of varying shaking times (5-20 min). It was observed (Fig. 3) that after 15 min, absorbance of the Cu (II) ions had no significant variation; thus, the extraction time of 15 min was selected for further studies.

3.4. Application of the proposed method to real samples

This technique was applied to determine copper ions in natural water samples. In order to test the ability of suggestion strategy, tap water, sea water, river water and mineral water samples were analyzed. For this purpose, 50 mL of each of the samples were pre-concentrated with modified nanocomposites, in accordance with the proposed method. The results are shown in Tables 1. The obtained data in these tables confirm the ability of suggestion method for determination of Cu (II) ions.

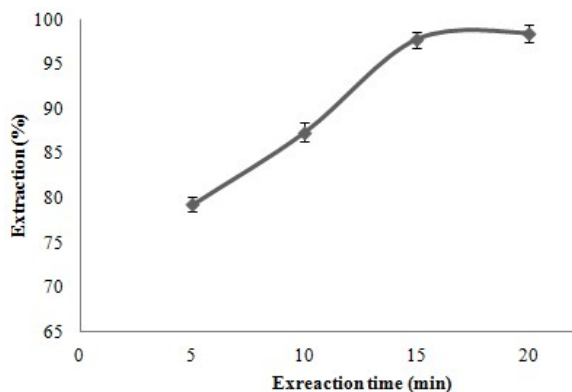


Fig. 3. Effect of different doses of nanocomposite for extraction of Cu (II) ions.

Table 1. Determination of Cu (II) in different water samples.

Sample	Cu (II) spiked (ng mL ⁻¹)	Cu (II) detected (ng mL ⁻¹)	Recovery (%)
Tap water	—	43.4 (2.7)	—
(From the drinking water system of Qaemshahr, Iran)	50	90.8 (1.9)	97.2
	100	137.5 (2.4)	95.9
Sea water	—	98.7 (3.1)	—
(Caspian sea water, Iran)	50	142.1 (2.8)	95.6
	100	189.7 (3.1)	95.5
River water (Tejen River, sari, Iran)	—	76.8 (2.6)	—
	50	121.4 (2.5)	95.7
	100	172.1 (2.3)	97.3
Mineral water	—	49.3 (3.4)	—
(From Abali mineral water, Tehran, Iran)	50	96.1 (1.8)	96.8
	100	146.5 (2.6)	98.1

4. Conclusion

In this research, nanocellulose functionalized with CBIMMT as modified nanocomposite was prepared. SPE method was used due to the vast surface, high thermal and chemical stability and good performance of the modified nanocellulose. As it's known, SPE is a powerful method to preparing samples. The advantage of such a method is its reproducible results, the need of less technical skills, low consumption of organic solvents and extraction cleaner, and its high speed and low cost. Using modified nanosorbent for copper ions extraction, not only increases absorption capacity but also Cu (II) ions show low resistance against mass transition and then they are rapidly absorbed. In this research, that was to analyzing by FAAS, the results showed that nanocomposite is very sensitive and selective to detecting low concentration of Cu (II) ions and has good accuracy in real samples analysis. The SPE suggested method has small RSD, suitable linear range, limit of detection, preconcentration factor and enrichment factor. The method was verified with real samples and it was proven satisfactory for determination of Cu (II) ions in natural water samples.

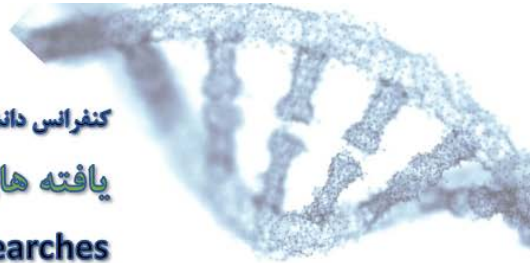


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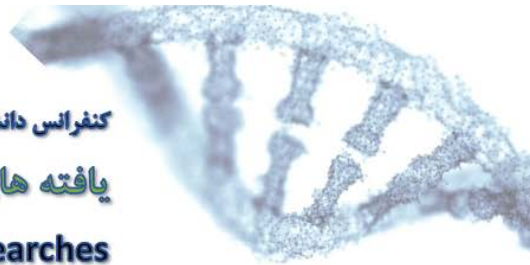


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