FERRITE-CALCIUM ALGINATE AS MAGNETIC SOLID PHASE EXTRACTION ADSORBENT OF COPPER(II) IONS IN WATER PRIOR TO FLAME ATOMIC ABSORPTION SPECTROSCOPY

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Abstract

A magnetic solid phase extraction (MSPE) procedure using ferrite-calcium alginate (Fe_3O_4-CaAlg) as adsorbent for Cu(II) ions prior to flame atomic absorption spectroscopy (FAAS) was developed. The extraction of Cu(II) ions using Fe_3O_4-CaAlg MSPE is simpler and faster than the conventional method such as solid phase extraction and traditional method such as liquid-liquid extraction. The simple extraction is based on the use of magnetisable adsorbent to extract Cu(II) ions, which can be readily isolated from water samples as a matrix with an external magnet. The adsorbent was prepared by mixing sodium alginate solution with Fe_3O_4 magnetic particles and calcium chloride solution to form magnetic alginate beads. Important parameters influencing the extraction and desorption process including type and volume of desorption solvent, agitation time, extraction time, weight of adsorbent and ample volume were optimized. Under the optimized conditions, calibration graph (external standard method) with coefficient of determination (R^2) of 0.974 in the linearity range 20-100 µg/L was observed. Good limit of detection (1.70 µg/L), and limit of quantification (5.6 µg/L) was obtained. Acceptable repeatability (n = 3) with RSDs 2.37% while reproducibility (n = 9) with RSD 5.15% were obtained for Cu(II) ions using the developed MSPE method. Finally, the proposed method was successfully applied for the determination of Cu(II) ion in tap water sample with relative recovery of 78.9% and 4.72% RSD. However, the proposed method was found to be less suitable for the determination of Cu(II) ion in river water sample with lower relative recovery (45.7% , 1.76% RSD) indicating that the method is sensitive to the matrix.

Keywords: Fe_3O_4-Calcium alginate, Magnetic solid phase extraction, Copper(II) ions, Water samples, flame atomic absorption spectrophotometry

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INTRODUCTION

Copper (Cu) are extensively used in industry field such as electroplating, manufacture of electrical wire and industrial machinery since it has good resistance to corrosion, low thermal expansion and tensile strength. As well as for industry uses, Cu also has been recognized as an essential trace metal for living organisms and important for human`s growth and development. However, the amount of consumption has to be limit to 1–3 mg per day as an adequate and safe level of intake (Ndlovu et al., 2012) since it will affect human`s health and causing several disease if excessive. According to Guidelines for Drinking-water quality of the World Health Organisation, the limit for copper content in drinking water is 2.0 mg/L (Jana et al., 2011). Above this healthy limit, copper will accumulates in the liver and become toxic to human which causing diarrhoea, vomiting and neurological illness such as schizophrenia, depression, autism and epilepsy (Shrivas & Kumar, 2013). Since Cu has been widely used in industry and household plumbing, it will easily enter the environmental and water systems in a form of ion causing high exposure of people to Cu(II) ion residue by drinking water. Thus, method to remove Cu(II) ion from water supplies need to be developed to ensure the concentration is below the safety limit.

A simple, efficient and green sample preparation technique is required to replace conventional extraction techniques. In recent years, an alternative solvent minimization sample preparation approach, magnetic solid phase extraction (MSPE), has gained considerable attention. The advantages of the MSPE method are that this procedure is simpler and faster than LLE and SPE by the use of only an external magnetic force to isolate the adsorbent and analyte/s from sample matrix. Besides that, MSPE technique only requires small amount of organic solvent. With the advantages of MSPE, the development of modified Fe_3O_4 MNPs has to be developed and progress rapidly in order to improve the adsorption quality of the adsorbent and obtain the most efficient extraction results.

Alginates are natural anionic polysaccharide of brown algae which is composed of linear binary copolymers of (1-4)-linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) monomers (Figure 1) (Draget et al., 2005). Due to high stiffness of gelling properties (Fuhrer & McHugh, 2003), high porosity and small size providing larger surface area (Paques et al., 2014), alginate has been applied as the adsorbent which encapsulate the Fe_3O_4 MNPs during the extraction of analyte. The polymer also consist of many carboxyl and hydroxyl groups which acts as potential adsorption sites for metal ions to bind (Draget et al., 2005).

In this study, a green MSPE analytical method was introduced by utilizing ferrite-calcium alginate (Fe_3O_4-Ca Alg) as the adsorbent. Calcium alginate (CaAlg) has the potential to be an effective adsorbent while MSPE is a simple and fast technique that contributes to minimize the time consuming, and use of organic solvent.

Thus, we consider this Fe_3O_4-CaAlg MSPE approach as it is effective and gives higher relative recoveries of Cu(II) ion.

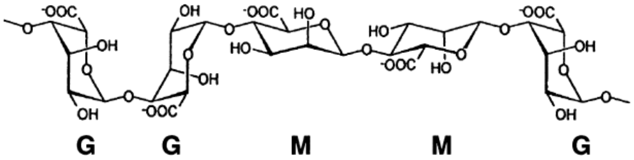

Figure 1: Chain conformation of (1-4)-linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) polymer (Draget et al., 2005)

EXPERIMENTAL

Chemicals and Reagents

Water samples used were tap and river water from Sungai Skudai, Skudai, Johor. The glassware used in this project was washed with deionized water (DW) and have been sterilized. The Fe_3O_4-CaAlg adsorbent was obtained (previously synthesised) from the analytical laboratory in Universiti Teknologi Malaysia, Johor. Deionized water was used all the time when preparing stock and standard solution. Cu stock solution (1000 mg/L) was prepared from $CuSO_4$ obtained from analytical laboratory in Universiti Teknologi Malaysia, Johor. Then, Cu standard solution of 1, 2, 3, 4, and 5 mg/L were prepared from the stock solution. The desorption solvents used were nitric acid (HNO_3), hydrochloric acid (HCI) and sulphuric acid (H_2SO_4). Nitric acid, 65% was purchased from QRec (Asia) Sdn Bhd (Selangor, Malaysia), hydrochloric acid 36.5-38.0% was purchased from J.T. Baker (Philipsburg, USA) and sulphuric acid 95-97% was obtained from Merck (Darmstadt, Germany). All desorption solvents namely 0.1 M of each of HNO_3, HCI, H_2SO_4 and 1:1 mixture of HCI + HNO_3 were prepared by appropriate dilution of the concentrated solution.

Analytical Instrumentation

A PinA Acle 900T FAAS equipped with deuterium background correction and a copper hollow cathode lamp was used for absorbance measurements at 324.75 nm. All measurements were carried out in an air/acetylene flame. Instrumental parameters used were those recommended by the manufacturer.

Preparation of stock, standard solutions and real water samples

The Cu stock solution (1000 mg/L) was prepared by dissolving 0.25 g of copper sulphate ($CuSO_4$) in DW. The solution was made up to the 100 mL mark in a volumetric flask. Then, a series of standard solutions (1.0, 2.0, 3.0, 4.0, 5.0) mg/L were prepared by appropriate dilution of the stock solution. River water sample and fresh tap water sample were collected in bottles pre-cleaned with acetone. For the river water samples, the samples were filtered through a Whatman filter paper No. 1 (Maidstone, England) to remove any non-soluble particles. The samples were stored in freezer at 5ºC until analysis.

Preparation of Fe_3O_4-CaAlg Adsorbent

An amount of 4.5 g of sodium alginate was accurately weighed and dissolved in 200 mL deionized water with magnetic stirring. A calcium chloride solution was prepared by mixing 33 g of the salt with 1.5 L of DW, with magnetic stirring. For encapsulation process to form Fe_3O_4-CaAlg adsorbent, 4.0 g of the Fe_3O_4 MNPs were mixed with sodium alginate solution forming Fe_3O_4-NaAlg solution. Then the Fe_3O_4-NaAlg solution was slowly dropped into the calcium chloride solution. Fe_3O_4-CaAlg beads were formed immediately in the calcium chloride solution. Lastly, the Fe_3O_4-CaAlg beads were thoroughly rinsed with distilled and deionized water to eliminate any residues of calcium and chloride ions. Fe_3O_4-CaAlg beads were placed in the oven for 12 h to dry the water residue.

Fe_3O_4-CaAlg Magnetic Solid Phase Extraction Process and Optimization

The MSPE process is illustrated schematically in Figure 2. Briefly, 10 mL of water sample containing 1 mg/L of Cu(II) analyte from the prepared stock solution was added with 50 mg of Fe_3O_4-CaAlg adsorbent. Initially, the mixture was shakened for 30 min to allow adsorption process of Cu(II) ion onto the Fe_3O_4-CaAlg adsorbent. The adsorbent was then collected easily and quickly by applying an external magnet on the beaker wall, and the supernatant was decanted directly. For desorption of Cu(II) ion from the Fe_3O_4-CaAlg adsorbent, 3 mL of approximately 0.1 M solution of the desorption solvent was added into the beaker containing the adsorbent, and agitated for about 5 min. The adsorbent was then collected with an external magnet outside and the eluent was collected eluent for analysis using FAAS.

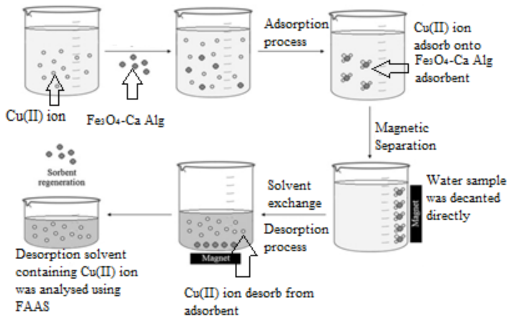

Figure 2: Schematic of Fe_3O_4-CaAlg MSPE process for Cu(II) ions from aqueous solution

In this study, three extraction and three desorption conditions were systematically optimized. Optimization of MSPE process was performed by varying one parameter at a time. The extraction parameters optimized were extraction time, weight of adsorbent and volume of sample while the desorption parameters optimized were types of desorption solvent, volume of desorption solvent and agitation time. Initally

RESULTS AND DISCUSSIONS

Effect of Desorption Solvent

In order to maximize the desorption of Cu(II) ion from Fe_3O_4-CaAlg adsorbent, a suitable solvent is required. Four different solvents namely 0.1 M HNO_3, 0.1 M HCI, 0.1 M H_2SO_4 and 0.1 M of a 1:1 mixture of HNO_3: HCI were used. During desorption of the Cu(II) ions, hydrogen ions were dissolved from the acid desorption solvent used and displaced the Cu(II) ions on the adsorbent. It was found that all the solvents examined showed almost equal desorption efficiency with recovery of Cu(II) ion in the range of 57.6%-61.6% but the highest percentage recovery was obtained with 1:1 mixture of HNO_3: HCI as the desorption solvent (Figure 3). Thus 1: 1 mixture of HNO_3: HCI was selected for further analysis.

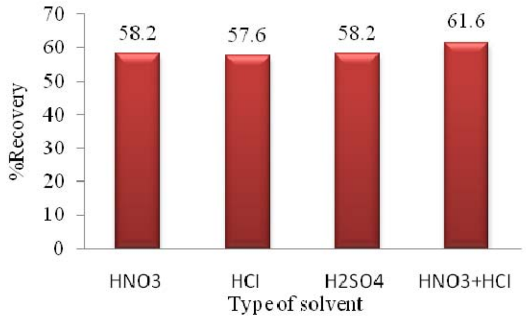

Figure 3: Effect of types of desorption solvent on Fe_3O_4-CaAlg MSPE of Cu(II) ion from water sample. Extraction conditions: 10 mL volume sample; 50 mg adsorbent weight; 30 min extraction time; Desorption conditions: 3 mL solvent volume with 5 min agitation time.

Effect of desorption solvent volume

In order to study the effect of desorption solvent on the recovery of Cu(II) ion, different volumes of the 1:1 HNO_3-HCl desorption solvent were optimized. This is to ensure quantitative recovery with minimum volume of desorption solvent. Thus, the 0.1 M 1:1 mixture of HNO_3+HCI solvent was set (3, 4 and 5 mL). Figure 4 shows that the percentage recovery of Cu(II) decreases as the desorption solvent increases from 3 to 5 mL. Desorption of Cu(II) ion from the Fe_3O_4-CaAlg adsorbent was most effectively achieved using 3 mL of the optimized solvent. This indicates that 3 mL of the desorption solvent was sufficient to desorb adsorbed Cu(II) ions from the adsorbent. Thus, 3 mL of the 1:1 mixture of HNO_3+HCI solvent was selected for further analysis.

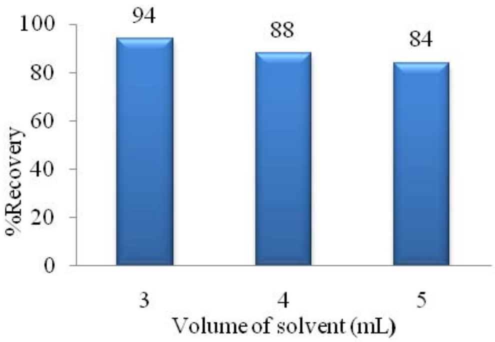

Figure 4: Effect of desorption solvent volume on Fe_3O_4-CaAlg MSPE of Cu(II) ion from water sample. Extraction conditions: 10 mL volume of sample; 50 mg mass of adsorbent; 30 min extraction time; Desorption conditions: 1:1 mixture of HNO_3+HCI desorption solvent with 5 min agitation time

Effect of extraction time

Generally, sufficient time is required to achieve adsorption equilibrium for the analyte on the adsorbent. In this study, the effect of extraction time on the extraction efficiency of Cu(II) ion on Fe_3O_4-Ca Alg adsorbent was investigated by changing the extraction time from 1 to 60 min under the optimum conditions. Five sample solutions were continuously shakened using an orbital shaker at room temperature at 250 rpm. From the results obtained (Figure 5), it can be seen that equilibrium was reached within 5 min extraction time by showing recovery 104.5%. Decrease of percentage recovery was observed starting from 10 to 60 min extraction time. This might due to back-extraction of Cu(II) ion from Fe_3O_4-CaAlg adsorbent into sample solution since ion exchange between cation group of adsorbent and Cu(II) ion in the water sample is reversible and the bond formed is just temporary (Wierucka & Biziuk, 2014). Thus, 5 min was selected for further analysis.

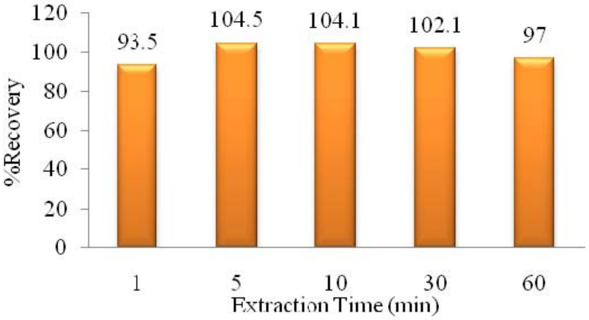

Figure 5: Effect of extraction time on Fe_3O_4-CaAlg MSPE of Cu(II) ion from water sample. Extraction conditions: 10 mL volume of sample; 50 mg mass of adsorbent; Desorption conditions: 3 mL of 1:1 mixture of HNO_3+HCI desorption solvent with 5 min agitation time

Effect of agitation time

In order to examine the influence of desorption time on the recovery of Cu(II) ions, different desorption time in the range of 30 to 300 s were optimized to ensure quantitative recovery of Cu(II) ions. The percentage recovery of Cu(II) ions increase as the desorption time increase from 30 s to 60 s but slightly decrease was observed at 120 s and 300 s. This might due to re-adsorbed of analyte by the adsorbent (Figure 6).Therefore, desorption time of 60 s was selected for further analysis for maximum desorption of analyte from adsorbent.

Effect of weight of adsorbent

Various weight (5 to 100 mg) of the Fe_3O_4-CaAlg adsorbent were used to study its effect on adsorption of Cu(II) ions. Based on the results obtained (Figure 7), increase in weight of adsorbent increase the extraction efficiency probably due to more adsorption sites or surface area available for Cu(II) ions to be adsorbed. However, a further increase in the weight of adsorbent higher than 50 mg did not cause significant improvement in the adsorption of Cu(II) ions. This might due to the adsorption of Cu(II) ions onto the adsorbent was completed (Paques et al., 2014). Thus, higher weight of adsorbent was not necessary to reduce analysis cost. Thus, 50 mg adsorbent was used for further analysis.

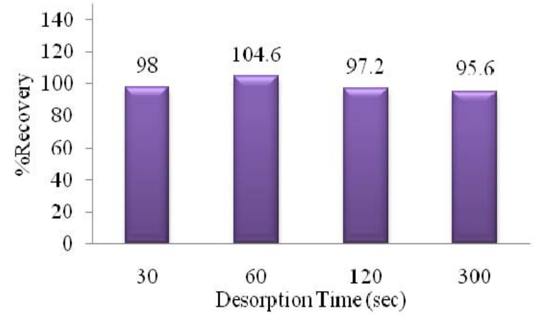

Figure 6: Effect of desorption time on Fe_3O_4-CaAlg MSPE of Cu(II) ion from water sample. Extraction conditions: 10 mL volume of sample; 50 mg mass of adsorbent; 5 min extraction time; Desorption conditions: 3 mL of 1:1 mixture of HNO_3+HCI desorption solvent

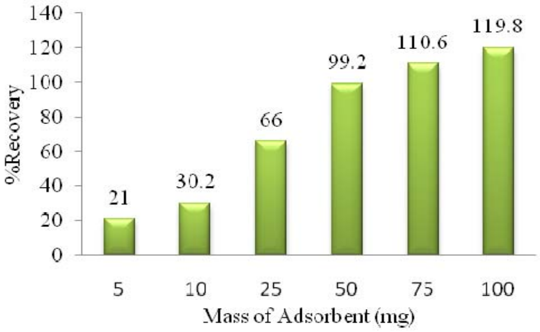

Figure 7: Effect of weight of Fe_3O_4-CaAlg adsorbent on MSPE of Cu(II) ions from water sample. Extraction conditions: 10 mL sample volume; 5 min extraction time; Desorption conditions: 3 mL of 1:1 mixture of HNO_3+HCI desorption solvent with 1 min agitation time

Effect of sample volume

In order to study the ability of the optimized weight of adsorbent in adsorbing Cu(II) ions different sample volumes were optimized. A series of 150 - 400 mL sample solutions containing 20 µg/L of Cu(II) ions were prepared. Based on the results obtained, 50 mg of adsorbent was found to sufficient to adsorb the highest Cu(II) ions from 150 mL sample (Figure 8). Increase in the sample volume was found to decrease the % recovery. This might due to breakthrough volume of adsorbent which have been exceeded. Thus, 150 mL sample volume was selected for further analysis.

Method Validation

The Fe_3O_4-CaAlg MSPE method was validated using the optimized conditions (50 mg adsorbent, 150 mL sample volume, 5 min extraction time, 3 mL of 1:1 mixture of HNO_3+HCI as desorption solvent with 1 min agitation time) for linearity, limit of detection (LOD), limit of quantification (LOQ), precision (repeatability and reproducibility) and accuracy (recovery). The results obtained are summarized in Table 1. Acceptable linearity from the linearity range of 20-100 µg/L was obtained with good coefficient of determination ($R^2 = 0.974$). LOD (3 S/N) and LOQ (10 S/N) obtained were 1.70 µg/L and 5.6 µg/L respectively. The precision studies were performed for one day ($n = 3$) and for three consecutive days ($n = 9$). Concentration of Cu(II) ion used was 100 µg/L. Satisfactory RSDs were obtained; 2.37% for repeatability and 5.15% for reproducibility showing good precision of the Fe_3O_4-CaAlg MSPE method.

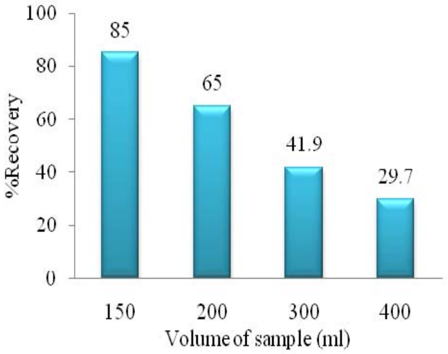

Figure 8: Effect of sample volume on % recovery of Cu(II) ions from water sample using Fe_3O_4-CaAlg MSPE. Extraction conditions: 50 mg adsorbent; 5 min extraction time; Desorption conditions: 3 mL of 1:1 mixture of HNO_3+HCI desorption solvent with 1 min agitation time

Table 1: Validation of Fe_3O_4-Ca Alg MSPE for Cu(II) ion

Linear range (µg/L)	R^2	LOD (µg/L)	LOQ (µg/L)	Repeatability (± %RSD, $n = 3$)	Reproducibility (± %RSD, $n = 9$)
20-100	0.974	1.70	5.6	2.37	5.15

Application of the developed Fe_3O_4-Ca Alg MSPE for Cu(II) ions from Tap and River Water Samples

In order to investigate the practicality of the proposed Fe_3O_4-CaAlg MSPE method, it was applied to the analysis of Cu(II) ions in tap and Sungai Skudai water samples. For tap water sample, the concentration of Cu(II) ion was found to be 11.84 µg/L while for river water sample, the concentration of Cu(II) ion found was 7.2 µg/L. Relative recovery studies were conducted by spiking tap water and river water samples to give a final concentration of 20 µg/L. Results showed that the relative recovery of tap water sample was 78.9% and for river water sample, 45.7% with RSDs < 4.72% ($n = 3$) for both (Table 2). The lower recovery of Cu(II) ions from the river water might be due to some external factor which affects the adsorption process such as the existence of cationic components in the river water sample as interferences. These components might compete with Cu(II) ions for the available adsorption sites thus decrease the extraction efficiency of Cu(II) ions (Paques et al., 2014). The alginate also may not be selective enough to adsorb Cu(II) ions in the complex sample. Besides, the pH of the river water sample should be taking into consideration as it may affect the extraction efficiency of metal ions. More acidic water sample contained more hydrogen ion which might also compete with the Cu(II) ion to adsorb onto the adsorbent.

Table 2: Relative recovery studies of Cu(II) ions from spiked tap and river water samples using the developed Fe_3O_4-CaAlg MSPE method

Sample	Spiked level (µg/L)	Concentration of Cu((II) ions found (µg/L)	% Relative Recovery (± % RSD, $n = 3$)
Tap Water	0	11.84	-
	20	15.78	78.9 (4.72)
River Water	0	7.20	-
	20	9.14	45.7 (1.76)