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Copper(II) ion determination in water samples using magnetite-calcium alginate sorbent and flame atomic absorption spectrometry analysis

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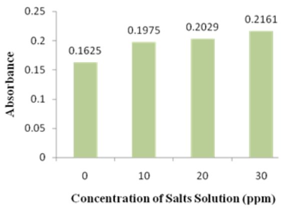
GRAPHICAL ABSTRACT



Effect of interfering ions on the extraction of Cu(II) ion using 50 mg adsorbent, 10 min extraction time, 10 mL of 0.1 M HNO_3, 5 min desorption time (sonication assisted), 100 mL volume of sample of pH 6.

ABSTRACT

Conventional technique such as liquid-liquid extraction (LLE) is widely used in the analysis of Cu(II) ions from water samples. However, LLE is time consuming, tedious, and consume lots of high purity organic solvents. Solid phase extraction (SPE) is an interesting alternative to LLE but it is prone to channelling and is rather expensive. A greener technique such as magnetic solid phase extraction (MSPE) avoids the use of column cartridge and overcome channelling problem. MSPE using magnetite-calcium alginate (Fe_3O_4-CaAlg) as sorbent is proposed for the extraction of Cu(II) ion from tap and lake water samples and analysis performed using flame atomic absorption spectrometry (FAAS). Characterization of the synthesised sorbent was performed using Fourier transform infrared spectroscopy and scanning electron microscope. The optimum conditions for Fe_3O_4-CaAlg MSPE of Cu(II) were achieved at a sample solution of pH 6 with 100 mL sample volume and the existence of interfering ions (Na^+, K^+, Mg^{2+}, and Cl^-) was found not to affect the extraction efficiency of the sorbent for Cu(II) ion significantly at the concentrations tested. Other MSPE parameters used were 10 min extraction time, 50 mg sorbent, 10 mL of 0.1 M HNO_3 as desorption solvent and 5 min desorption time (sonication assisted). The calibration graph was linear from 20 - 600 ppb with good coefficient of determination (R^2 = 0.9998). The LOD (3SD/slope) and LOQ (10SD/slope) of Cu(II) using Fe_3O_4-CaAlg MSPE with FAAS were in 6.75 and 22.5 ppb, respectively. The LOD achieved with the Fe_3O_4-CaAlg MSPE with FAAS is applicable to the determination of Cu(II) in real water samples (tap water and UTM lake water). Good relative recoveries and precision were achieved with this proposed method. The Fe_3O_4-CaAlg has great potential as an alternative sorbent for Cu(II) determination from water samples using the greener MSPE method.

Keywords: magnetite-calcium alginate, Cu(II) ion, magnetic solid phase extraction, flame atomic absorption spectroscopy

1. INTRODUCTION

Water is a very crucial element for living organisms. Human especially, consumed water for many purposes in order to continue their survival and progression. Today, it is very challenging to have freshwater which is free from any contamination. Example of toxic heavy metal which is common in water contamination is copper, Cu. Although Cu is beneficial for human such as to prohibit anaemia and ensure the other body systems healthy, however, if it is consumed at high levels, it will cause diarrhoea, nausea and abdominal pain. The sources of this heavy metal contamination in may come from various sources such as from mining, battery industry, pipe corrosion and household plumbing system. Thus, there is a need to inhibit excess vulnerability of Cu in order to ensure that the water supply is safe to be consumed.

In analytical technique, sample preparation and pre-treatment of heavy metal such as Cu in water are steps that are very crucial to be applied in analysis. This is because, during these steps, it aids to remove interferences coming from the matrix of the selected sample and thus, providing an easy pre-concentration of the desired metal ion (Zhu *et al*., 2013). For the past few years, various sample pre-concentration techniques have been applied for the purpose of analysis of metals. For example, ion exchange, co-precipitation, liquid-liquid microextraction (Feist and Mikula, 2014) as well as cloud point extraction (CPE), liquid-liquid extraction (LLE) and solid phase extraction (SPE). In conventional LLE technique, there exist several drawbacks such as it is tedious and its operation needs high purity of organic solvent which is costly and potentially toxic. As for SPE technique, albeit it does not consume much solvent as in LLE, it is laborious as it involves extra step to pre-concentrate the analyte (Xu *et al*., 2007). Magnetic solid phase extraction (MSPE) has been developed to overcome these shortcomings.

MSPE use magnetic properties on its sorbents for the extraction and pre-concentration of analyte (organic or inorganic) in a large volume of sample. When the magnetic sorbent particles are added to the sample solution, the analyte of interest will be adsorbed onto its surface and an external magnet is applied to separate the analyte from the solution. With the use of appropriate solvent, the adsorbed analyte is eluted and can then be analyzed with selected analytical instrument. MSPE is simple because it has facile magnetic separation, great surface area and sorption volume.

Common magnetic nanoparticles (MNPs) used as sorbent is magnetite, Fe_3O_4 because it is inexpensive and has low toxicity. Since pure Fe_3O_4 is easily oxidized, various coating materials have been developed in order to improve and modified it. For instance, inorganic substances such as silica and organic substances such as polymer have been used for functionalization of this material (Cao *et al*., 2014; Wan Ibrahim *et al*., 2012, Nodeh *et al*., 2016). Flame atomic absorption spectrometry (FAAS) is a relatively easy and frequently available technique that can be used for the determination of metal ion, although it does not offer an excellent sensitivity for the detection of metal ion. Thus, FAAS is usually coupled with a pre-concentration step.

In this study, a modification to the Fe_3O_4 MNPs was applied by encapsulating its surface with calcium alginate (CaAlg) and used as an MSPE adsorbent for the purpose of pre-concentration step and to extract Cu(II) ion in lake as well as tap water samples prior to FAAS analysis.

2. EXPERIMENTAL

2.1 Chemicals and Reagent

All materials used were of analytical reagent grade and used as received without further purification. A stock solution (1000 ppm) of Cu (Certipur®) was purchased from Merck (Darmstadt, Germany). $MgCl_2.6H_2O$, KCl, Na Alginate, NaOH pellets and nitric acid (HNO_3 65%) were purchased from QReC (Asia) Sdn. Bhd. (Selangor, Malaysia). NaCl and commercial ferrite (Fe_3O_4) were purchased from Bendosen Laboratory Chemicals (Selangor, Malaysia). $CaCl_2.2H_2O$ was purchased from HmbG® Chemicals. 0.1 M HNO_3 and/or 0.1 M NaOH were used to adjust the pH of sample solution. Working solutions were prepared with deionised water (DW) from Sartorius (Goettingen, Germany).

2.2 Instrumentation

The analysis for determination of Cu in water samples was performed using a PinA Acle 900T FAAS provided with background correction of deuterium and hollow cathode lamp (HCL) for the measurement of absorbance at wavelength 324.75 nm. It was conducted in air/acetylene flame. FT-IR spectra (4000 - 400 cm^{-1}) were recorded on a Perkin-Elmer TM 400 FTIR Spectrometer (Waltham, MA, USA) as KBr pellets. SEM analysis was performed to investigate the surface morphology of the adsorbent by using a JEOL JSM-6390LV (Massachusetts, USA) operated at 10 kV, with magnification ranging from 5000 to 7500.

2.3 Preparation of Standard Solution and Real Water Samples

The stock solution of Cu (1000 ppm)(Certipur®) was from Merck (Darmstadt, German). Serial dilutions were performed to prepare series of standard working solution of Cu (0.2, 0.4, 0.6, 0.8 and 1.0 ppm). Tap and lake water samples were obtained from UTM Skudai and filtered using a 47 mm, 0.45 μm nylon membrane filters from Whatman (Buckinghamshire, UK).

2.4 Preparation of Fe_3O_4-CaAlg sorbent

4.5 g of sodium alginate (NaAlg) was dissolved in 200 mL of DW with magnetic stirring. Calcium chloride ($CaCl_2$) solution was prepared by dissolving 3.3 g of $CaCl_2$ in 150 mL of DW water with magnetic stirring. For encapsulation process, firstly, 0.5 g of commercial Fe_3O_4 was mixed with NaAlg for the formation of Fe_3O_4-NaAlg solution and this solution was added dropwise (using a syringe) into the $CaCl_2$ solution to form beads of Fe_3O_4-CaAlg. The beads were rinsed with DW for the removal of any Ca and Cl ions residues. Oven drying of beads was performed for 24 h to remove any water residue.

2.5 MSPE Procedure and Optimization Process

A 100 mL water sample containing 0.6 ppm of Cu from the Cu stock solution was added with 50 mg of the Fe_3O_4-CaAlg adsorbent. The mixture was shakened for 10 min for MSPE process. Then an external magnet was applied to the side of the beaker for separation from the water. The adsorbed Cu(II) ions were desorbed (sonication assisted for 5 min) from the Fe_3O_4-CaAlg adsorbent using 3 mL of 0.1 M HNO_3 solution. Eluate was collected and analysed using FAAS.
Optimization of MSPE process was performed by varying one parameter at a time. The extraction parameters optimized in this study were pH and volume of sample solution. Other MSPE parameters were based on previous studies (Shah Bani *et al*., 2015).

3. RESULTS AND DISCUSSION

3.1 FTIR Characterization

The FT-IR spectra in Figure 1.1 (a), (b) and (c) shows the spectra of Fe_3O_4, CaAlg beads and Fe_3O_4-CaAlg, respectively. An important peak in Figure 1.1 (a) at ~580 cm^{-1} is assigned to Fe-O bond stretching which comes from the crystalline lattice of Fe_3O_4 (Lopez *et al*., 2010). Spectrum of CaAlg in Figure 1.1 (b) shows three vital peaks at 3439.13, 1628.34 and 1424.91 cm^{-1} which indicates the bands for O-H and two C-O bonds, respectively (Daemi and Barikani, 2012). The prominent peaks in Figure 1.1 (c) are assigned to three types of bonds which are O-H, two C-O and Fe-O bonds that gives absorption bands at 3446.92, 1629.73,1384.39 and 617.73 cm^{-1} respectively (Covaliu *et al*., 2011).

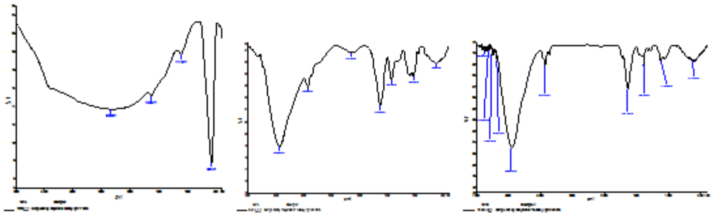
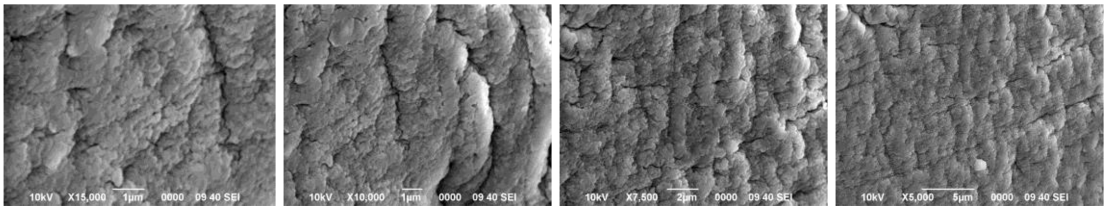

(a) (b) (c)

Fig. 1.1 FTIR spectra of (a) Fe_3O_4, (b) CaAlg and (c) Fe_3O_4-CaAlg

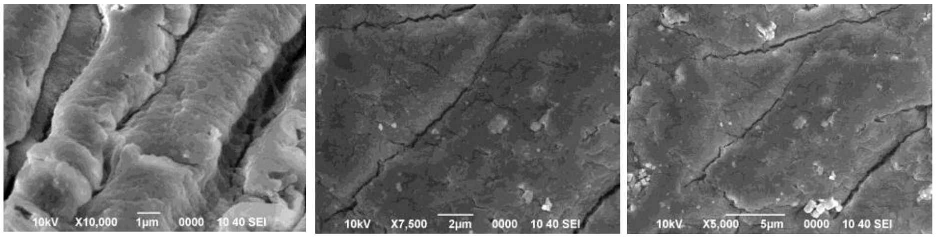
3.2 SEM Analysis

The SEM analysis of CaAlg was performed at a fixed accelerating voltage of 10 kV at various magnifications (Figure 1.2). The SEM images for Fe_3O_4-CaAlg are shown in Figure 1.3. The surface of the CaAlg adsorbent is rough with cauliflower-like structures. The structure of the Fe3O4-CaAlg adsorbent is smoother compared to the CaAlg surface.



(a) (b) (c) (d)

Fig. 1.2 SEM images of CaAlg at different magnifications



(a) (b) (c)

Fig. 1.3 SEM images of Fe_3O_4-CaAlg at different magnifications

3.3 MSPE Optimization

To improve the analysis of Cu(II) ion, two parameters were optimized namely pH and volume of sample solution in combination with previous optimized parameters (Shah Bani *et al*., 2015): 50 mg adsorbent, 10 min extraction time, 3 mL of 0.1 M HNO_3 (selected in this study as it is a single solvent) desorption volume, 5 min agitation time during desorption. Selectivity study of the sorbent was conducted by the addition of salt solutions of NaCl, KCl, and $MgCl_2$, each at 10, 20 and 30 ppm concentration.

3.4 Effect of Sample Volume

A large volume of sample solution is required to achieve a higher preconcentration factor. In our previous study, 150 mL sample volume was used (Shah Bani *et al*., 2015). In the current study the volumes studied were 50, 100, 150, 200 and 250 mL of DW. These solutions were spiked with 0.6 ppm of standard Cu(II) solution. The highest absorbance was observed with 100-150 mL sample solution (Figure 1.4). Further increase of sample solution to 200 mL and finally 250 mL decrease the response observed. This observation can be explained from the combination of two equations which are mass-balance equation and partition equation, which stated that the response (recovery) will decrease when phase ratio is increased (Abd Ali *et al*., 2016). Thus, a sample volume of 100 mL was selected for the extraction of Cu(II) ion for the next experiment. This is in agreement with the findings from Shah Bani *et al*. (Shah Bani *et al*., 2015)

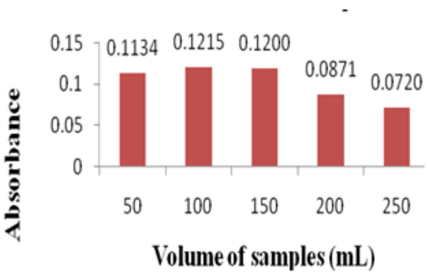


Fig. 1.4 Effect of sample volume on the extraction of Cu(II) ion using 50 mg of Fe_3O_4-CaAlg adsorbent, 10 min extraction time, 10 mL of 0.1 M HNO_3 as desorption solvent and 5 min desorption time (sonication assisted)

3.5 Effect of sample solution pH

The effect of sample solution pH on the extraction of Cu(II) ion using Fe_3O_4-CaAlg was investigated at pH 2, 4, 6 and 8 for optimization process (Figure 1.5). At pH 2, the extraction of Cu(II) ion produced the lowest absorbance reading. This might be due to the competition that occur between Cu(II) and hydrogen ions for adsorption sites on the adsorbent (Abd Ali *et al*., 2016; Liu *et al*., 2013). The absorbance of Cu(II) increased significantly at pH 4 and remained almost constant till pH 8. Since the pH of environmental water is usually around pH 6, this pH was selected for subsequent experiment since less acid or base is needed to change the pH of water, reducing cost for mass application.

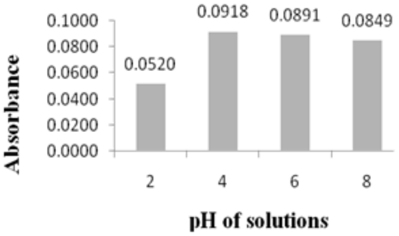


Fig. 1.5 Effect of sample solution pH on the extraction of Cu(II) ion using 50 mg of Fe_3O_4-CaAlg adsorbent, 10 min extraction time, 10 mL of 0.1 M HNO_3 as desorption solvent, 5 min desorption time (sonication assisted) and 100 mL sample volume

3.6 Effect of Interfering Ions

Salts solution of NaCl, KCl and $MgCl_2.6H_2O$ were used to study the selectivity of the Fe_3O_4-CaAlg adsorbent on the extraction of Cu(II) ion in the presence of these interfering ions (Na^+, K^+, Mg^{2+}, and Cl^-). Different concentration of each salts (10, 20 and 30 ppm) were investigated. These salts were mixed (each with the same concentration) and added into the optimized sample solution. It can be seen that the presence of 10 ppm of each of the salts showed some effect on the extraction performance of the adsorbent for Cu(II) ion (Figure 1.6) but remained almost constant on further increase from 20-30 ppm. This suggest that the Fe_3O_4-CaAlg is a selective sorbent for the extraction of Cu(II) ion in the presences of these four ions (Na^+, K^+, Mg^{2+}, Cl^-).

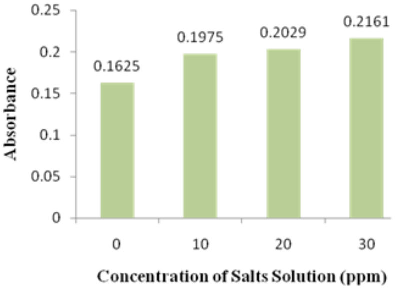


Fig. 1.6 Effect of interfering ions on the extraction of Cu(II) ion using 50 mg adsorbent, 10 min extraction time, 10 mL of 0.1 M HNO_3, 5 min desorption time (sonication assisted), 100 mL volume of sample of pH 6.

3.7 Method Validation

Based on the optimization results, the MSPE technique was validated for linearity, limit of detection (LOD), limit of quantitation (LOQ), precision (repeatability) and accuracy (recovery) (Table 1.1). LOD and LOQ at ppb level were achieved using the Fe_3O_4-CaAlg method. This indicates that the Fe_3O_4-CaAlg-FAAS method lends itself to real sample analysis of

Cu(II) in water samples (Maximum residue limit of Cu(II) in drinking water is 0.1 ppm). Good repeatability of the method was obtained within the linear range of 20-600 ppb.

Table 1.1 Validation of MSPE technique using Fe_3O_4-CaAlg sorbent

Linear range (ppb)	R^2	LOD (ppb)	LOQ (ppb)	Repeatability (±%RSD, n =3)
20-600	0.9998	6.75	22.5	3.46

3.8 Applications of Fe_3O_4-CaAlg sorbent in Tap and Lake Water Samples

The developed (Fe_3O_4-CaAlg) MSPE method was used for the determination of Cu(II) ions in real water samples taken from UTM lake and tap water from the laboratory. Good relative recoveries of Cu(II) were obtained from both samples analysed with the proposed MSPE –FAAS method (Table 1.2). Lower recoveries were obtained from lake water samples suggesting that matrix effect might play a role.

Table 1.2 Determination of Cu(II) ion in tap and lake water samples using the developed Fe_3O_4-CaAlg sorbent MSPE method.

Sample	Spiked Cu (ppb)	Found (ppb)	Relative recovery (%)	Precision (*n* = 3, %RSD)
Laboratory tap water	-	0.25	-	8.66
	80	92.25	115	9.15
	200	172	85.9	0.35
UTM lake water	-	2.25	-	2.82
	80	63	75.9	3.48
	200	173.25	85.5	1.11

4. CONCLUSION

The magnetite-calcium alginate sorbent (Fe_3O_4-CaAlg) was successfully synthesized and applied as a magnetic adsorbent for the extraction and preconcentration of Cu(II) ions in UTM lake and tap water samples and analysis using FAAS. The optimized condition that aids the extraction efficiency were achieved by using 100 mL sample volume at pH 6 and the adsorbent selectivity for cu(II) ions in the presences of co-existence of interfering ions was not significantly affected. Good relative recoveries and RSDs (76-115%, RSD 0.4 - 9.2%) were obtained for Cu(II) ions from both laboratory tap and UTM lake water samples analysed. Fe_3O_4-CaAlg-FAAS method offer an alternative analytical method for Cu(II) analysis from water samples. The method lend itself to analysis of Cu(II) in drinking water at levels below the MRL of 2 ppm (Jana et al., 2011).

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