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Determination of copper(II) ion in water samples using sol-gel hybrid cyanopropyltriethoxysilane-methyltrimethoxysilane as sorbent in micro solid phase extraction

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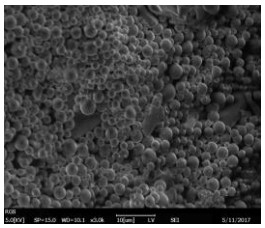
GRAPHICAL ABSTRACT



(a) SEM image of sol-gel hybrid CNPrTEOS-MTMOS at 3000 magnificent.

ABSTRACT

Column solid phase extraction sorbents have been used for metal ions analysis from various water samples. However, column SPE has its limitation such as channeling and it is rather expensive. The use of micro dispersive solid phase extraction (µ-D-SPE) offers a solution to channeling and it also cut cost as it only uses small amount of sorbent and no column as compared to SPE. In this study, a hybrid material, cyanopropyltriethoxysilane-methyltrimethoxysilane (CNPrTEOS-MTMOS) was successfully synthesized using sol-gel method. The sol-gel method is simple and can be carried out in room temperature. The synthesized sorbent was characterized using attenuated total reflectance (ATR) and scanning electron microscope (SEM). The as-synthesized material was applied as a new sorbent in dispersive-micro solid phase extraction (D-µ-SPE) of Cu(II) ion in different water sample namely sewage effluent, tap, bottled, zam-zam and UTM lake water. The results obtained were compared with Drinking Water Quality Standard, Ministry of Health Malaysia, (2010). Extracted Cu(II) ion was analyzed using flame atomic absorption spectroscopy (FAAS). The optimum µ-DSPE condition obtained were 20 mg CNPrTEOS-MTMOS as sorbent mass, 40 mL water sample volume, sample pH 10, and 8 min extraction time. Cu(II) was desorbed from the sorbent using 0.3 M HNO_3 as desorption solvent with vortex assisted. The calibration graph was linear in the range 100-1000 ppb with coefficient of determination (R^2) of 0.9994. Limit of detection (LOD = 3SD/slope) and limit of quantification (LOQ = 10SD/slope) obtained were 29 and 98 ppb respectively. The as-synthesized sol-gel hybrid CNPrTEOS-MTMOS showed a great potential as sorbent for µ-D-SPE for Cu(II) ion in various water samples (sewage effluent, tap, bottled, zam-zam and UTM lake water) with good recoveries (89-109%) and precision (2.33% RSD)..

Keywords: sol-gel technique, cyanopropyltriethoxysilane-methytrimethoxysilane, solid phase extraction, metal extraction

1. INTRODUCTION

Human organs, cells and tissues use water to maintain its temperature and make sure it function well. Water also plays an important role in helping human body in removing waste through perspiration, urination and defecation. Water used by the kidney and liver to help flush out waste. Rehydration by drinking fluid and eating food containing water is very important as human body can lose water through breathing, sweating and digestion. The amount of water needed varies depends on the individuals surrounding.

To maintain our health, drinking water from clean source and free from contaminant are very important. According to United State Environmental Protection Agency (EPA), contaminant is any physical, chemical, biological or radiological substance presence in water. It stated that water rationally expected to contain at least a very small amount of contaminant. Some of the contaminant may be harmful to human health, others may be harmless. Chemical contaminants that are presence in water include nitrogen, bleach, salts, pesticides, heavy metals, toxin produce by bacteria and human or animal's drugs.

Copper, (Cu) is the most common heavy metals contaminant that is present water. It is a byproduct of the corrosion of pipe, acid amine, drainage, iron and steel production and sewage treatment. The existence of highly toxic metal ions in ecosystem cause a threat to humans and other living organisms. It can cause various chronic or acute disease such as cancer and skin, cardiovascular and blood disorder (Shakerian et.al, 2016). High exposure to Cu can cause anaemia, digestive disturbance, liver and kidney damage. Therefore, it is very important to determine the presence of Cu in order to ensure the water is safe to consume.

The most common analytical instrument used in determination of heavy metals content in environmental samples are flame atomic absorption spectroscopy (FAAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) (Zhu et.al, 2013). These instrument usually limited with restricted sensitivity, therefore, preconcentration and sample pretreatment is needed. Sample pretreatment procedures usually necessary in order to remove the heavy matrix interferences and facilitate the preconcentration of copper (Zhu

et.al, 2013). There are various sample preparation and preconcentration method namely liquid-liquid extraction (LLE), solid phase extraction (SPE), cloud point extraction (CPE), co-precipitation, physical preconcentration by the evaporation of sample and chemo filtration. These method are widely been used as preconcentration and separation method of trace metal in various sample (Mikula and Feist, 2014). Modern technique nowadays is towards the miniaturization of sample preparation and preconcentration technique with the objective to reduce the usage of organic solvent.

Sol-gel synthesized materials have been shown to be highly effective in solvent free or solvent minimized sample preparation for wide variety of analyte such as in biological, environmental, food, pharmaceutical, bio-analytical and forensic, (Kabir et.al, 2013). Shamsuddin, 2017 stated that sol-gel method produced high degree of homogeneity and purity product with low processing temperature and inexpensive operation. Sol-gel technique can be categorized as environment friendly.

In this study, sol-gel method is used to synthesize hybrid cyanopropytriethoxysilane-methytriethoxysilane (CNPrTEOS-MTMOS) and the successfully synthesized material was used as an adsorbent in the determination of heavy metals in water samples. Cu(II) ion was selected as a target analyte by using micro dispersive solid phase extraction (μ-D-SPE). Sol-gel technology offers versatile pathway for preparing hybrid material and the procedure is simple and inexpensive (Kabir at.al, 2013).

2 EXPERIMENTAL

2.1 Synthesis of sol-gel hybrid CNPrTEOS-MTMOS

Sol-gel hybrid CNPrTEOS-MTMOS were prepared using the method by Wan Ismail. Solution A was prepared by mixing 0.48 mL of CNPrTEOS in 0.54 mL of deionized water. Solution B was prepared by mixing 0.28 mL of MTMOS in 0.54 mL of deionized water. 0.36 mL of deionized water and 0.85 mL of ammonium solution was mixed in a beaker. Solution A was added drop wise followed by solution B. The mixture was stirred to homogenize. The resulting particles were washed with deionized water for (2 × 5 mL) to remove any residual catalyst. The washed particles were dried at 80˚C for a day. The sorbents were ground using mortar before used.

2.2 Standard and reagent

The chemicals use in this study are methyltrimethoxysilane (MTMOS, 95%), cyanopropyltriethoxysilane (CNPrTEOS, 98%), ammonium hydroxide (28%), copper stock solution (1000ppm), nitric acid (HNO_3, 65%) and sodium hydroxide pellets (NaOH). Both MTMOS and CNPrTEOS were purchased from Sigma Aldrich (USA). Ammonium hydroxide 28%, HNO_3 65% and NaOH pellets were obtained from Qrec® Asia Sdn Bhd (Selangor, Malaysia). Copper standard were obtained from Sigma Aldrich (USA). Cu (1000 ppm) stock solution was used to prepare intermediate solution of Cu (100 ppm). Different volume of 100 ppm of Cu solution were pipetted into volumetric flask to prepare series of standard solution of Cu with concentration of 0.2, 0.4, 0.6, 0.8 and 1.0 ppm. All Cu solution were prepared using 1% of acid water, (1% of HNO_3). 1.0 M of NaOH and HNO_3 were used to adjust the pH of sample solution. Solution were prepared using ultrapure water from Milli-Q® Integral Water Purification System (Millipore USA).

2.3 Characterization of CNPrTEOS-MTMOS

The raw CNPrTEOS, MTMOS and synthesized sol-gel CNPrTEOS-MTMOS were characterize using attenuated total reflectance (ATR) on Perkin-Elmer TM 400 FTIR Spectrometer (Waltham. MA. USA) in the range of 600-4000 cm^{-1}. Scanning electron microscope (SEM) was done to determine the surface morphology of the sol-gel hybrid CNPrTEOS-MTMOS using a EM-30AX at 5 kV with magnification of 3000.

2.4 Real sample analysis

Developed μ-D-SPE method using sol-gel hybrid CNPrTEOS-MTMOS was applied in the application of Cu(II) analysis in water samples. Sewage effluent, tap, bottled, zam-zam and UTM lake water were used in the analysis. Both sewage effluent and UTM lake water were filtered to obtain clear solution and to remove any large particle that may affect FAAS analysis. The pH of water sample were adjusted and fixed at pH 10 by using 1.0 M HNO_3 and NaOH solution. Each of water samples was spiked with standard solution of Cu(II) and volume made up to give a final concentration of 200 ppb of Cu(II).

3 RESULTS AND DISCUSSION

3.1 Characterization of CNPrTEOS-MTMOS

The ATR overlay spectra of CNPrTEOS-MTMOS are shown in Figure 3.1. The spectrum of raw CNPrTEOS shows absorption band of C≡N at 2246 cm^{-1} and CH stretching can be observed at 2888 cm^{-1}. The spectrum show Si-O-CH_2-CH_3 stretching at 1165 cm^{-1} as well. Stretching of C-H can be observed at 2972 cm^{-1} with medium intensity and at 1080 cm^{-1}, Si-O-CH_3 strong absorption band can be seen for the spectrum of MTMOS. Hybrid sol-gel CNPrTEOS-MTMOS shows medium intensity of C-H stretching at 2939 cm^{-1}. C≡N stretching can be observed at 2246 cm^{-1} with medium intensity. At 1016 and 1106 cm^{-1}, stretching of Si-O-Si can be observe and this indicate that the hybridization of CNPrTEOS and MTMOS was successful.

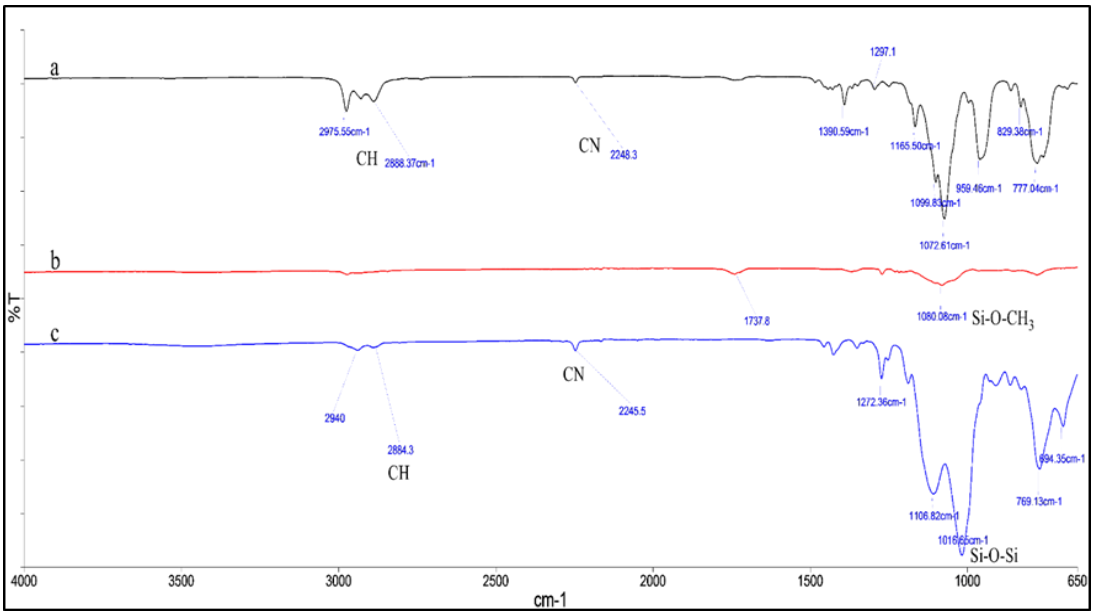


Figure 3.1: Overlay ATR spectra of a) CNPrTEOS, b) MTMOS and c) CNPrTEOS-MTMOS

Table 3.1 Wavenumbers of CNPrTEOS, MTMOS and CNPrTEOS-MTMOS

Stretching	Wavenumber (cm^{-1})			Intensity
	CNPrTEOS	MTMOS	CNPrTEOS-MTMOS	
C-H	2888	2972	2939	Medium
C≡N	2248	-	2246	Medium
Si-O-CH_3	-	1080	-	Strong
Si-O-CH_2CH_3	1165	-	-	Strong
Si-O-Si	-	-	1016 1106	Strong
OH	-	-	3434	Weak

The SEM analysis of CNPrTEOS-MTMOS were done in accelerating voltage of 5 kV with spot size of 10 µm. Sphere shape of synthesized CNPrTEOS-MTMOS can be observed from the SEM image in Figure 3.2.

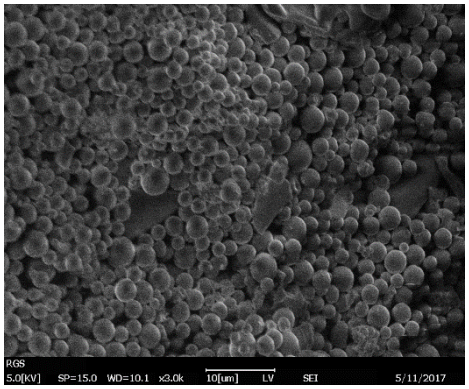


Figure 3.2: SEM image of sol-gel CNPrTEOS-MTMOS

3.2 Method validation

The CNPrTEOS-MTMOS µ-D-SPE method was validated for limit of detection (LOD), limit of quantification (LOQ), precision and accuracy (recovery). The LOD and LOQ obtained were 29 and 98 ppb respectively. The intra-day precision of CNPrTEOS-MTMOS µ-D-SPE method study was conducted for one day (n=3) which give RSD value of 2.33%.

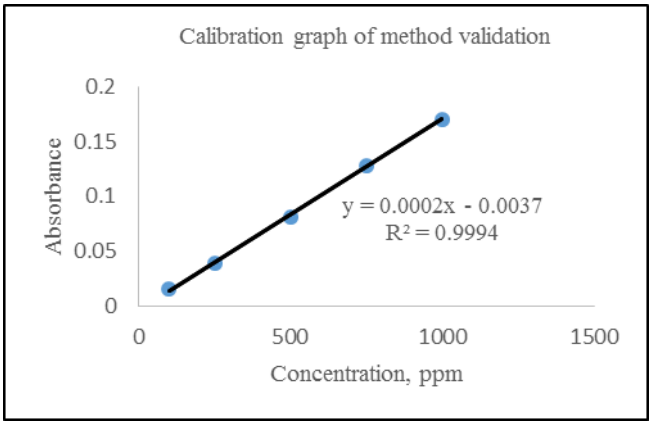


Figure 3.3: Calibration graph of µ-D-SPE technique

3.3 Application of µ-D-SPE for Cu(II) in sewage effluent, tap, bottled, zam-zam, UTM lake water

The successfully developed µ-D-SPE method using sol-gel hybrid CNPrTEOS-MTMOS was applied in the application of Cu(II) analysis in water samples. Sewage effluent, tap, bottled, zam-zam and UTM lake water were used in the analysis. Both sewage effluent and UTM lake water were filtered to obtain clear solution and to remove any large particle that may affect in FAAS analysis. The pH of water sample were adjusted and fixed at pH 10 by using 1.0 M HNO_3 and NaOH solution. Each of water samples was spiked with standard solution of Cu(II) ion and volume made up to give a final concentration of 200 ppb of Cu(II) ion. The recovery of Cu(II) ion is shown in Table 3.2. Lower recoveries of Cu(II) ion were observed from sewage effluent water samples indicating that matrix effect might play a role in the process.

Table 3.2 recovery of Cu(II) ion spiked at 200 ppb in various water sample using CNPrTEOS-MTMOS µ-D-SPE method

Water samples	Recovery (%)
Tap water	94.5
UTM lake water	108.5
Bottled water	102.0
Zam-zam water	94.0
Sewage effluent	89.0

4. CONCLUSION

The sol-gel hybrid cyanopropyltriethoxysilane-methyltrimethoxysilane (CNPrTEOS-MTMOS) was successfully synthesized, characterized and applied in micro dispersive solid phase extraction (μ-D-SPE) for extraction of Cu(II) ion in sewage effluent, tap, bottled, zam-zam and UTM lake water. From ATR results, the hybridization of CNPrTEOS-MTMOS was successfully carried out. The optimum CNPrTEOS-MTMOS μ-D-SPE conditions for extraction of Cu(II) ion were achieved using 40 mL of sample volume at pH 10, 8 minute extraction time, 10 mL of 0.3 M HNO_3 as desorption solution (vortex assisted) with 20 mg sorbent. Low limit of detection and limit of quantification in the ppb level were achieved using CNPrTEOS-MTMOS μ-D-SPE method. Good relative recoveries and precision were achieved at (89-109%, 2.33% RSD) from various water samples. In conclusion, CNPrTEOS-MTMOS showed a great potential as sorbent in determination of Cu(II) ion in water samples.

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