

## Multiwall carbon nanotube-encapsulated alginate micro-beads for extraction of lead(II) and methylene blue from water samples

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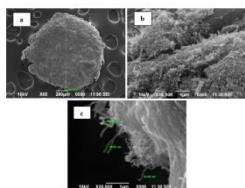
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### GRAPHICAL ABSTRACT



SEM image of MWCNT-Alg (a) x 65 magnification, (b) x 15k magnification and (c) x 25k magnification

### ABSTRACT

Aquatic heavy metals and dyes have been extensively-studied due to their toxicity that threatens human health and the environment. However, most of the methods are technologically disadvantageous and not cost effective from an economic point of view. This study investigates the application of multiwall carbon nanotube encapsulated alginate (MWCNT-Alg) micro-beads as adsorbent in solid phase microextraction ( $\mu$ SPE) for the determination of selected heavy metal ion, Pb(II) and methylene blue in water samples. MWCNT-Alg micro-beads were prepared by dissolving sodium alginate in warm water and add appropriate amount of MWCNT. The mixture was stirred until it turned into a viscous black mixture. The mixture obtained was added dropwise into a stirred 500-mL  $\text{CaCl}_2$  solution (1% v/w) using a syringe and solid gel was immediately formed. The material was characterized using scanning electron microscopy (SEM) and attenuated total reflection (ATR) spectroscopy. Three parameters were optimized for the extraction of metal and the condition were: sample solution of pH 7, extraction time, 60 min and hydrochloric acid solution (0.05 M) as desorption solvent. Metal ion was determined using atomic absorption spectroscopy (AAS) while ultraviolet-visible spectroscopy (UV-Vis) was used to determine methylene blue in the water sample. For dye, the optimized extraction parameters were 4 min extraction time, 4 min desorption time and acetyl nitrile as a desorption solvent. Pb(II) ions were successfully extracted from the water samples. The method shows good linearity for Pb(II) and methylene blue with  $r^2 > 0.9965$ . Overall, the proposed MWCNT-Alg- $\mu$ SPE combined with AAS and UV-Vis has proved satisfactory for the determination of aquatic heavy metal ions and dyes with good linearity  $r^2 > 0.9969$  and satisfactory LODs of 0.20 and 0.43 ppm for lead(II) and methylene blue, respectively.

*Keywords:* MWCNT-Alg, lead(II), methylene blue, micro solid phase extraction, water samples.

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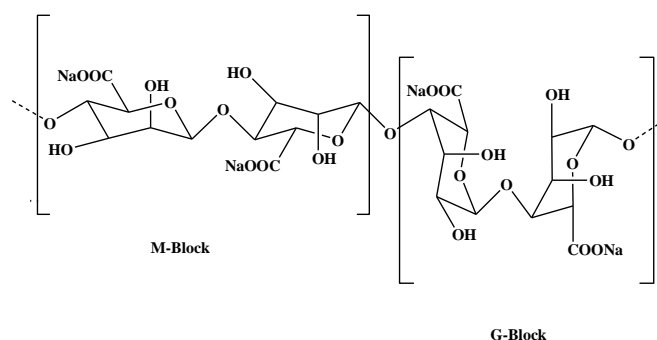
## 1. INTRODUCTION

The increase of industrial activities has given a huge impact to our environmental well-being due to their waste discharge containing chemicals such as heavy metals, dyes, synthetic compounds, nuclear wastes and others that leads to the environmental pollution and deterioration of ecosystem [1]. Heavy metal pollution in water has been threatening human health and aquatic organisms. Furthermore, heavy metals are not biodegradable and tend to accumulate in living organisms which lead to several disorders. Lead, being the most significant toxin of the heavy metals can cause the malfunctions in the kidney, joints and reproductive system, cardiovascular system and chronic damage to the central nervous system [2]. Zinc also reported to cause the same signs of illness as lead and can easily be mistakenly diagnose as lead poisoning [2, 3].

Dyes are discharged from the paper, textile, leather and food industries. At low concentration, dye can be visually detected and can affect the aquatic life. Other than esthetic unpleasing of colored compound, it also will inhibit sunlight into streams and affecting photosynthetic reaction [4]. The most common use of dye is methylene blue. Azo dyes are hazardous for the environment because their toxicity affect aquatic life and mutagenic to humans [5]. Therefore, the release of dyes to environment has become a threat to ecosystems and humans.

In order to protect the environment, animals and humans from the increasing of toxicity in water from metals, there are many conventional methods to remove heavy metals from wastewater such as chemical precipitation, electrowinning, evaporation, ion exchange resin and membrane separation. The conventional methods for removal of dyes from wastewater are photocatalysis, oxidation, coagulation and membrane separation. However, these methods are technologically disadvantage and not cost effective from an economic point of view. To reduce the cost from an economic point of view, inexpensive natural material such as alginate biopolymer can be developed as sorbents for the adsorption of metals and dyes to be competitive with other conventional technologies [6]. Adsorption is considered to be most effective method because of the simple design and low cost [7].

Alginate is a linear copolymer of  $\alpha$ -L-guluronic acid (G) and  $\beta$ -D-mannuronic acid (M). Alginate also known as alginic acid, consists of three types of block, namely M-block that include only M fragments, G-block that include only G fragments and MG-heteroblock that include both M and G fragments [8]. G-blocks are responsible for the gelling properties of alginate while M-blocks and MG-heteroblocks are responsible for the solubility of alginic acid regulation in acid sorption or desorption properties of the material [9].



**Figure 1:** Molecular structure of sodium alginate

## 2. EXPERIMENTAL

### 2.1 Chemicals and Reagents

Sodium alginate was obtained from QReC Asia (Selangor, Malaysia). Multiwall carbon nanotubes (MWCNTs) was purchased from Sun Nanotech (Jiangxi, China). Nitric acid (65%) and acetonitrile were from Merck (Darmstadt, Germany). Hydrochloric acid (37%) and acetic acid glacial were from QReC Asia (Selangor, Malaysia). Methanol (HPLC Grade) was obtained from J.T. Baker (Center Valley, USA). Isopropanol was from System (Selangor, Malaysia). Methylene blue was from Sigma-Aldrich (St. Louis, USA) and lead standard solution (1000 mg/L) was obtained from Merck (Darmstadt, Germany). Working standard solutions were prepared by dilution of stock solution with 0.05 M nitric acid. All reagents and solvents were analytical grade from various suppliers and used as received.

### 2.2 Preparation of the MWCNT-Alg beads

The beads were prepared using a simple method by dissolving 3 g of sodium alginate in 85 mL of warm distilled water and add 1 g of MWCNT. The mixture was stirred until it turned into a viscous black mixture. Thereafter, the mixture obtained was added dropwise into a stirred 500-mL  $\text{CaCl}_2$  solution (1% v/w) using a syringe and solid gel was immediately formed. The beads were dried at 50 °C in a vacuum oven for 24 hours.

### 2.3 Procedure for extraction

#### 2.3.1 Lead(II)

A 3 ppm of sample lead solution was prepared in 250 mL volumetric flask. The pH of analyte was adjusted to pH 7. MWCNT-Alg beads (50 mg) was put in an Erlenmeyer flask containing the sample and then shaken at 250 rpm in 60 min. After that, the sample was filtered and the MWCNT-Alg beads were transferred into a 50 mL centrifuge container. HCl (0.05 M) (4 mL) was added and the mixture was vortexed at 120 rpm in 2 min. After that, the MWCNT-Alg beads were filtered and the solvent was transferred into another 50-mL centrifuge container. The solvent was analyzed by using AAS.

#### 2.3.2 Methylene blue

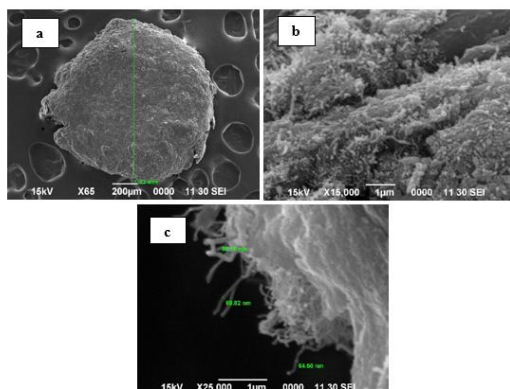
Analyte (3 ppm) was prepared in 50 mL volumetric flask. Sample (30 mL) was poured into 50 mL centrifuge container and 50 mg of MWCNT-Alg beads was added into the centrifuge container containing the analyte. The mixture was vortexed at 120 rpm in 4 min. After that, the sample filtered and transferred into another 50-mL centrifuge container and added with 4 mL of acetonitrile. The mixture was vortexed at 120 rpm in 4 min. Then the MWCNT-Alg beads were filtered and the filtrate was transferred into a 50-mL centrifuge container for UV-Vis analysis.

## 3. RESULTS AND DISCUSSION

### 3.1 Characterization of MWCNT-Alg beads

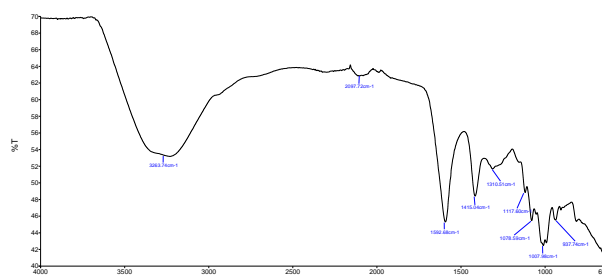
#### 3.1.1 Morphology Analysis

The morphology of MWCNT-Alg was characterized by using SEM. Figure 2a shows an image of whole sized bead having a diameter of 1.23 mm. The unique MWCNT network over alginate is clearly visible in Figure 2b. Because of the unique networking ability, the MWCNT could enhance the alginate encapsulation keeping the exact spherical shapes of beads.



**Figure 2:** SEM image of MWCNT-Alg (a)  $\times 65$  magnification, (b)  $\times 15k$  magnification, (c)  $\times 25k$  magnification

### 3.1.2 Attenuated Total Reflection (ATR)-FTIR Spectroscopy Analysis

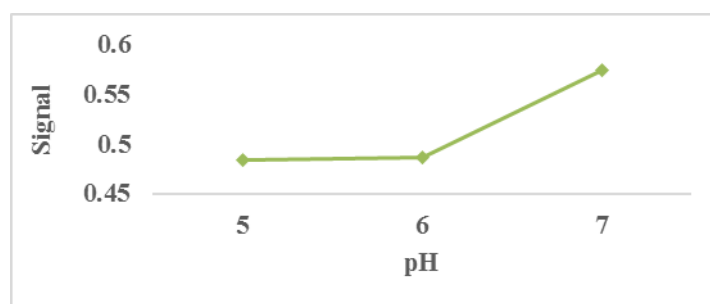


**Figure 3:** ATR-FTIR spectrum for MWCNT-Alg

The alginate fraction has shown bands in the region  $950\text{--}815\text{ cm}^{-1}$  ( $940.75\text{ cm}^{-1}$ ,  $904.50\text{ cm}^{-1}$  and  $816.48\text{ cm}^{-1}$ ) which were due to polyguluronic acid and polymannuronic acid sequences in the alginate backbone. Figure 3 shows the vibration at  $937.74\text{ cm}^{-1}$ , that prove the existence of alginate compound in the adsorbent

## 3.2 Extraction of lead(II) Optimization

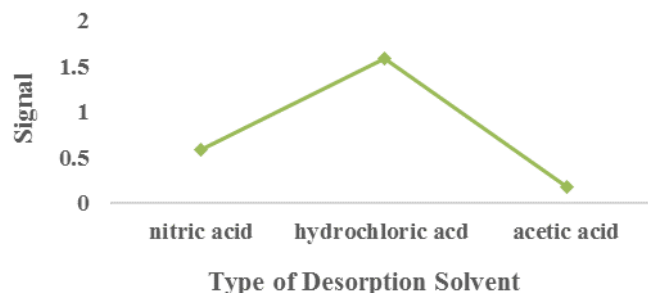
### 3.2.1 Effect of pH of analyte



**Figure 4:** Optimization of pH. Extraction conditions: 10 mL of water sample, 4 min extraction time, 0.05 M of  $\text{HNO}_3$  as desorption solvent

The pH was optimized in range of pH 5-7 for determination of extraction efficiencies for the analytes to be adsorbed. The acidic condition was not selected in this study because the proton in acidic condition will compete with lead ion for adsorption sites on the adsorbent. However, it was observed that the adsorption activity kept increasing as the pH increased (Figure 4). Lead (II) tends to form salts in alkali condition. Hence, pH 7 was chosen as it showed the best extraction efficiencies for all analytes.

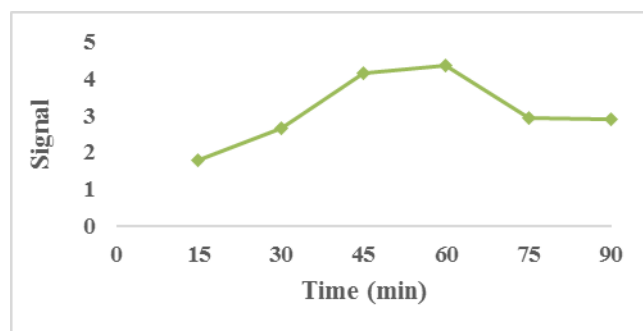
### 3.2.2 Effect of desorption solvent



**Figure 5:** Optimization of type of desorption solvent. Extraction conditions: 10 mL of water sample, 4 min extraction time and pH 7

Three type of desorption solvent was use which is HCl (0.05 M), HNO<sub>3</sub> (0.05 M) and acetic acid (0.05 M) It was found that HCl gave the most efficient desorption of the analyte (Figure 5). Thus, HCl was chosen as desorption solvent.

### 3.2.3 Effect of extraction time

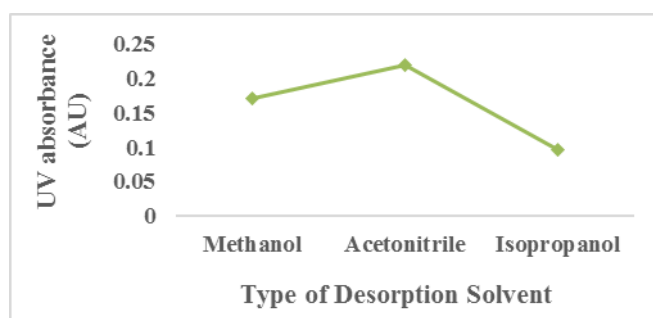


**Figure 6:** Optimization of extraction time. Extraction conditions: 200 mL water sample, pH 7 and 0.05 M of HCl as desorption solvent

The extraction time between 15-90 min were evaluated in this study to determine the equilibrium time required for the analytes to be adsorbed. It was found that the signal increased with time up to 60 min where the peaks tended to slightly decreased (Figure 6). This was due to loss of acceptor to sample solution that will result to poor reproducibility. Thus extraction time of 60 min was chosen as it showed the best extraction efficiencies for all analytes.

## 3.3 Extraction of methylene blue

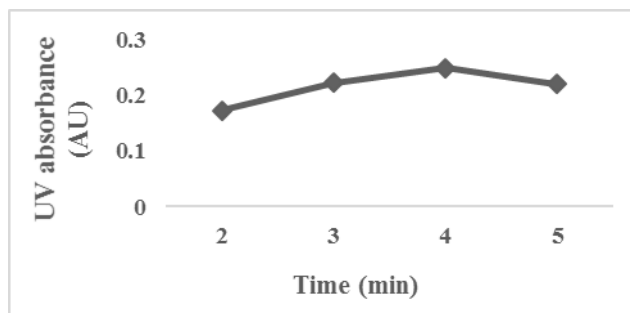
### 3.3.1 Effect of desorption solvent



**Figure 7:** Optimization of type of desorption solvent. Desorption conditions: 10 mL of water sample, 4 min extraction time and 2 min desorption time

The type of desorption solvent was optimized were methanol, acetonitrile and isopropanol. Since the methylene blue is polar molecule, isopropanol showed poor extraction efficiency (Figure 7). Acetonitrile was chosen as desorption solvent as it shows the best efficiencies in desorption than other solvents.

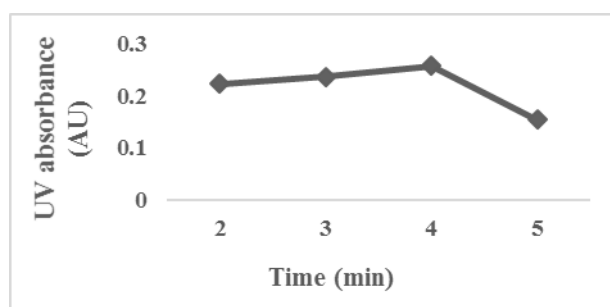
### 3.3.2 Effect of extraction time



**Figure 8:** Optimization of extraction time. Conditions: 30 mL of water sample, acetonitrile as desorption solvent and 2 min desorption time

The extraction time between 2 to 5 min were optimized in this study to determine the equilibrium time required for the analytes to be adsorbed. From figure 8, the extraction time of 4 min was chosen as it showed the best extraction efficiencies for all analytes.

### 3.3.3 Effect of desorption time

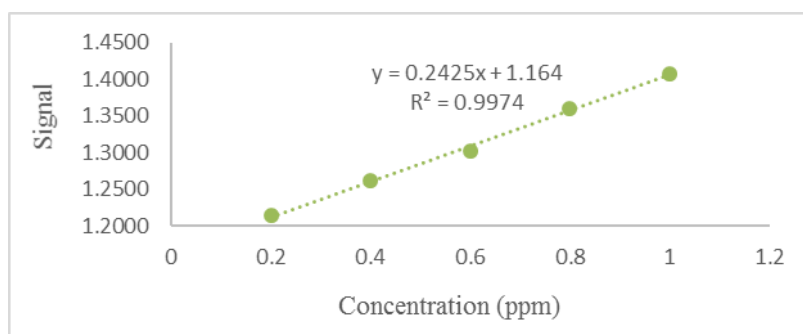


**Figure 9:** Optimization of desorption time. Condition: 30 mL of water sample, acetonitrile as desorption solvent and 4 min extraction time

Desorption times in the range of 2-5 min were investigated in this study to determine the equilibrium time required for the analytes to be desorbed (Figure 9). The desorption time of 4 min was chosen the optimum value as it showed the best desorption efficiencies for all analytes.

## 3.4 Analytical Parameters Validation

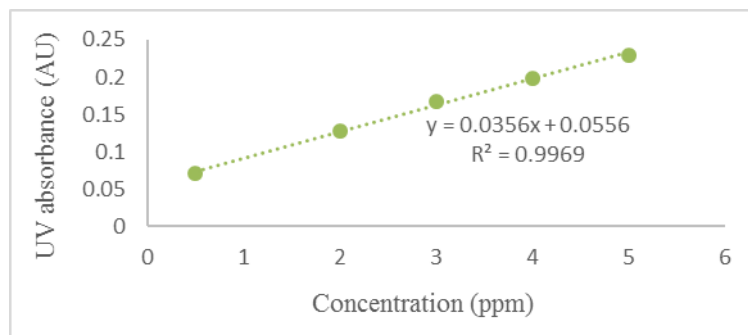
### 3.4.1 Lead(II) extraction



**Figure 10:** Extraction calibration plot for lead(II)

In order to construct a matrix matched calibration curve for the extraction of lead(II), extractions were carried out using lake water sample spiked with targeted analytes at different concentrations in the range 0.2-1 ppm. Figure 10 shows a good linearity was obtained with coefficient of determination ( $r^2$ ) of 0.9974. The limit of detection (LOD) and limit of quantification (LOQ) were 0.20 and 0.67 ppm, respectively.

### 3.4.2 Methylene blue extraction



**Figure 11:** Extraction calibration plot for methylene blue

In order to obtain a matrix matched calibration for the extraction of methylene blue, experiments were carried out using industrial wastewater sample spiked with targeted analytes at concentrations in the range of 0.5-5.0 ppm. Figure 11 shows a good linearity was obtained with coefficient of determination ( $r^2$ ) of 0.9969. The LOD and LOQ were 0.43 and 1.43, respectively.

## 4. CONCLUSION

In this study, Pb(II) and methylene blue have been successfully extracted from water samples by using MWCNT-Alg- $\mu$ SPE. Several parameters were optimized in  $\mu$ SPE. The optimum parameters were used in analysis or real sample. The optimum conditions for lead(II) extraction were as follows: pH 7, 60 min extraction time and HCl (0.05 M) as desorption solvent. The optimum conditions for methylene blue extraction were as follows: acetonitrile as desorption solvent, 4 min extraction time and 4 min desorption time. The analytes were successfully extracted using  $\mu$ SPE under identical conditions with good linearity  $r^2$  of 0.9974 and 0.9969 for lead(II) ion and methylene blue respectively. The proposed method showed good LOD of 0.20 and 0.43 ppm for lead(II) and methylene blue, respectively.

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