Nigerian Research Journal of Chemical Sciences (ISSN: 2682-6054)
Volume 11, Issue 2, 2023

PREPARATION OF AGAROSE-GRAFTED-ETHYL ACRYLATE FOR THE DETERMINATION OF Cu^{2+} AND Pb^{2+} METAL IONS IN WATER SAMPLES

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ABSTRACT

In this work, a new extraction procedure based on Agarose grafted Ethyl Acrylate (AG-g-EA) was developed and used for the determination of Cu^{2+} and Pb^{2+} in water samples. Dispersive solid phase extraction (d-SPE) method was employed. AG-g-EA copolymer was used as extractant to adsorb Cu^{2+} and Pb^{2+} from water samples. The amount of the metal ions adsorbed on AG-g-EA were determined using FAAS. The metal ions on the AG-g-EA copolymer were desorbed by ultrasonication method. Important parameters, such as the effects of pH, mass of AG-g-EA, extraction time, desorption eluent and desorption time were studied. The calibration results showed linearity with the correlation coefficient (r^2) in the range of 0.9045 and 0.9917 for Cu^{2+} and Pb^{2+} respectively. Limit of detection (LOD) were found to be 0.15 mg/L and 0.18 mg/L, while the Limit of Quantification (LOQ) were found to be 0.44 mg/L and 0.58 mg/L for both Cu^{2+} and Pb^{2+} respectively. Based on the analysis of the sample, the relative recoveries were obtained in the range of 62.50% to 87.50% .

Keywords: AG-g-EA, Cu^{2+} and Pb^{2+} metal ions, dispersive solid phase extraction, adsorption, water sample

INTRODUCTION

Agarose, a natural polymer, which consists of alternating D-galactose and 3,6-anhydro-L-galactose, is extracted from seaweed. Agarose normally represents at least two-third of the natural agar. It is regarded as a green polymer because it is biodegradable and an environment-friendly material. Its chemical inertness and flexible pore sizes made it possible for it to have wider applications, such as a medium in gel electrophoresis [1], and as pervaporation membrane for dehydration of organics [2-3]. Lately, agar-agar powder has been modified and used as an adsorbent in solid phase extraction for the extraction and preconcentration of mercury in water and fish samples [4]. A simple approach termed agarose film liquid phase microextraction has also been demonstrated for the extraction and pre-concentration of PAHs from environmental water samples.

In this report, agarose film was utilized as a barrier between organic extractant and sample solution. This approach contributes substantially to green chemistry due to its microextraction format and the biodegradability of the agarose film.

Heavy metal contamination of various water resources is of great concern because of the toxic effects of heavy metals on human beings and other animals and plants in the environment, even at very low concentrations. Various methods, including chemical precipitation, ion exchange, and reverse osmosis, have been used to remove heavy metal ions from waste water. However, these processes may be ineffective or expensive, especially when the metals in solution are in the range of 1–100 mg L^{-1} [5].

Adsorption technology emerged as an attractive alternative technique for heavy metals removal from wastewater in recent years. The increasing demand for new and economic processes for the recovery of metal ions from industrial effluents has led many research groups to investigate the possibility of using natural polymer for metal uptake [5].

Dispersive Solid Phase Extraction (d-SPE) was previously used to determine pesticide residues in fruit and vegetable samples. As a clean-up step, the crude extract is cleaned up by addition of a small amount of Solid Phase Extraction (SPE) sorbent material to an aliquot of the extract to remove the matrix co-extractives. Basically, d-SPE is based on the SPE methodology, where the sorbent is directly added into the crude extract without conditioning. The clean-up is easily carried out by just shaking and centrifugation.

The method was described as QuEChERS, which is the abbreviation of quick, easy, cheap, effective, rugged and safe method [6].

Water sources contaminated with heavy metals have become subject of discussion due to the toxic effects of such metals on humans, animals, plants and the environment. Various methods have been used to remove heavy metal ions from water but most of those methods are expensive and inefficient. This work is carried out to establish a simple, inexpensive, green and efficient method utilizing modified Ethyl Acrylate as solid phase extraction adsorbent for the removal of metal ions in water.

MATERIALS AND METHODS

Previously synthesized AG-g-EA was used as adsorbent for metal ions extraction [6]. Doubly distilled deionized water (Milli-Q Millipore 18.2 MΩ cm^{-1}conductivity) was used throughout. Analytical grade of lead and copper from Merck were used without any further purification. The pH was adjusted by addition of appropriate amount of dilute nitric acid and sodium hydroxide to the solutions. Both stock and working standard solutions were stored in the refrigerator at 4 °C for further analysis.

Instrumentation

The evaluation of metal ions content were carried out on a Perkin Elmer AAcle 900T Atomic Absorption Spectrophotometer (AAS) with a hallow cathode lamp and a deuterium background corrector, at respective resonance line using an air–acetylene flame. Selected spectral lines (nm) for Cu and Pb were 324.75 and 283.31 respectively. A Mettler Toledo pH meter with a combined glass–calomel electrode was used for monitoring of sample solution. An ultrasonic bath, S100 Elmasonic was employed for desorption process of metal ions.

d-SPE Procedure

In this procedure, 100 mL of water sample containing the analyte was transferred into a conical flask. After adjusting the pH of the water sample, AG-g-EA was dispersed into the sample. The extraction of analyte was conducted by continuous shaking using orbital shaker (250 rpm) at specified time. After equilibrium was achieved, the sample was withdrawn and decanted. Ultrasonication method was used to desorb metal ions from AG-g-EA adsorbent. Five (5) mL sulphuric acid was added to the separated AG-g-EA and sonicated to desorbed all the metal ions. After this process, the sample was decanted again and the acid containing the desorbed metal ions was taken for FAAS analysis (Figure 1) to determine how much metal ions are desorbed from AG-g-EA [4].

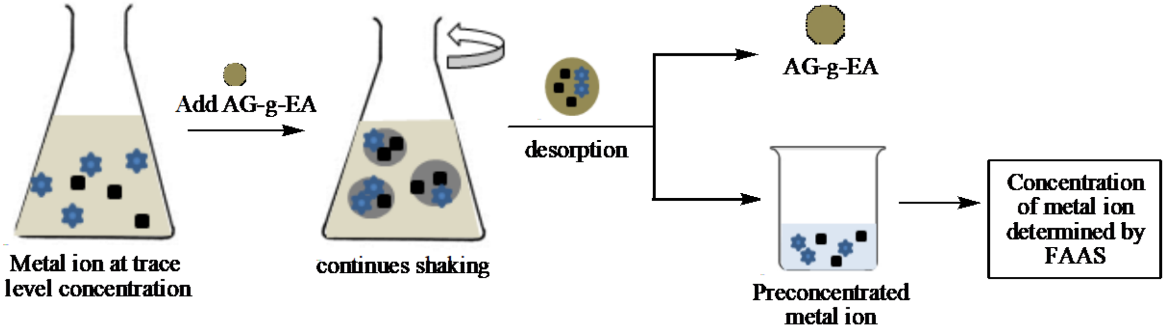

Figure 1: Representation of the disperive solid phase extraction methodology

Validation of Analytical Method and Sample Analysis

The extraction method was assessed for linearity in limit of detection and limit of quantification before sample analysis. For the water sample analysis, tap water and river water collected in polyethylene bottles were acidified with nitric acid after the sampling process. The water samples were filtered prior to the analytical procedure and kept in the refrigerator at 4 °C before use.

Optimization of Extraction Parameters

To obtain an efficient separation of the metal ions, the following extraction parameters were optimized:

Effect of pH on Sample Soluions

To study the effect of pH sample solution on AG-g-EA adsorption capacity, extractions were carried out at a pH range of 3 – 9.

Extraction Time

The effect of extraction time for optimum results was considered in the range of 0–3.5 h. Other parameters optimized were effect of adsorbent dose, selection of eluent, effect of and desorption time.

RESULTS AND DISCUSSION

Tables 1 and 2 present analytical performance of AG-g-EA in spiked water samples and concentrations of Cu^{2+} and Pb^{2+} in river and tap water respectively.

Table 1: Analytical performance of AG-g-EA in spiked water samples

Metal ions	Correlation coefficient r^2	LOD (mg/L)	LOQ (mg/L)
Cu^{2+}	0.9045	0.15	0.44
Pb^{2+}	0.9917	0.18	0.58

Table 2: Data for analysis of Cu^{2+} and Pb^{2+} in river and tap water

Sample	Analyte	Spiked concentration (mg/L)	Percentage Recovery (%)
Tap water	Cu^{2+}	0.4	77.5
	Pb^{2+}	0.4	85
River water	Cu^{2+}	0.4	62.5
	Pb^{2+}	0.4	87.5

Adsorption Mechanism

Adsorption of metal ions onto AG-g-EA is possible due to the presence of hydroxyl and ester group which can form ionic exchange reaction as well as metal complexation. An ionic exchange reaction takes place as the Cu^{2+} and Pb^{2+} ions replace H^+ ions and bind to the negatively charged functional group. Meanwhile, metal complexation of Cu^{2+} and Pb^{2+} by AG-g-EA could be due to the negatively charged hydroxyl and acrylate surrounding the metal ion and bound to the metal ion by a coordinate covalent bond (Figure 2).

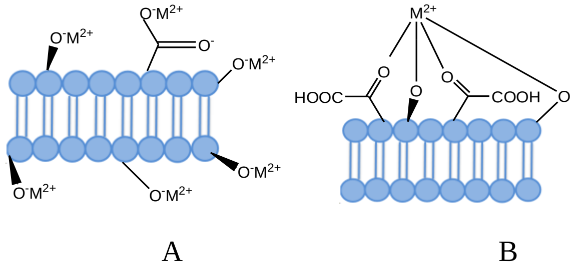

Figure 2: Possible adsorption mechanism on the AG-g-EA. (A) ion exchange mechanism (B) metal complexation by AG-g-EA.

Effect of pH on Sample Solution

The pH value of the metal ion solution is an important factor which controls the uptake of the metal ions by the AG-g-EA. At very low pH, the protonation of hydroxyl and acrylate functional groups gives an overall positive charge to the copolymer molecules, hence unable to adsorb positively charged ions. Thus, adsorption is reduced. Increasing the sample pH gradually reduced the electrostatic repulsion, exposing more negatively charged functional groups to a subsequent attraction of metal ions. Thus, adsorption increased as the pH increases. High percentage adsorption at pH 7-9 could be due to precipitation of $Pb(OH)_2$ and $Cu(OH)_2$ and not because of adsorption process. From Figure 3, it was clear that AG-g-EA performed well in the case of Pb^{2+} *as* compared to Cu^{2+}. At pH 6, the adsorption of Pb^{2+} reached almost 27%, while Cu^{2+} adsorption was 18% .

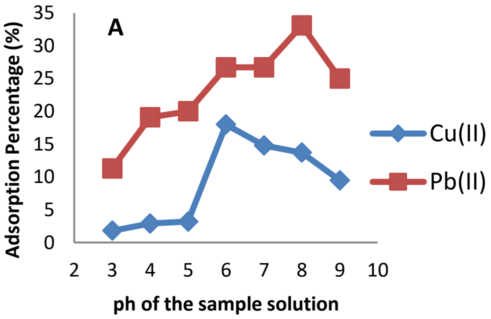

Figure 3: Extraction at various pH values for 100 mL water sample, AG-g-EA mass 100 mg, extraction time 1 h, desorption eluent nitric acid, desorption time 10 min.

Extraction Time

The effect of extraction time was analyzed in the range of 0–3.5 h with constant experimental conditions (Figure 4). Metal ion adsorption on AG-g-EA is a slow process, where the adsorption takes place after 1 h and equilibrium is attained within 3 h. Beyond the equilibrium time, the adsorption was decreased. This could be attributed to the availability of unfilled surface sites at the initial stage of adsorption,, and once the equilibrium is attained, the remaining unfilled sites are difficult to be access. This could be probably due to the repellent forces between the heavy metal molecules on the AG-g-EA and bulk solution. Also, it may indicate that the saturation point of adsorption has been achieved. The optimum extraction time for AG-g-EA was 3 h.

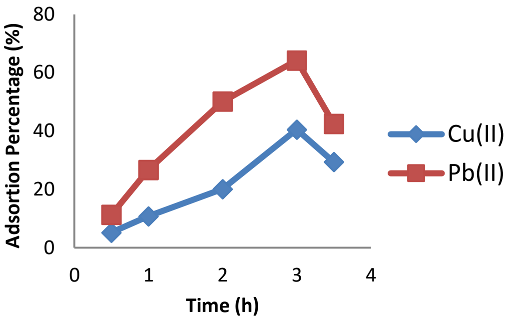

Figure 4: Extraction at various extraction time for 100 mL water sample, AG-g-EA mass 100 mg, pH 6, desorption eluent nitric acid, desorption time 10 min.

Effect of Adsorbent Dosage

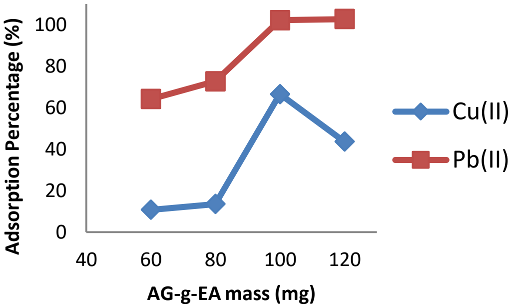

Figure 5: Extraction at various AG-g-EA mass for 100 mL water sample, extraction time 3 h, pH 6, desorption eluent nitric acid, desorption time 10 min

Results presented in Figure 5 indicate the mass of AG-g-EA for maximum adsorption of Pb^{2+} and Cu^{2+} ions as 100 mg. The percentage adsorption of Pb^{2+} increase from 64.20% to 100% with the increase in adsorbent dosage from 60 mg to 100 mg. Higher adsorbent dosage can give extra adsorption sites for metal ion adsorption. For 100 mg AG-g-EA, the amount of Pb^{2+} extracted is about 40 percent higher than Cu^{2+} . Pb^{2+} has the higher ionic radius (1.19A°) compared to Cu^{2+} (0.69A°). For the large non hydrated ions, since the charge is more dispersed, hydration water is held less strongly. The bigger the ionic radius, the stronger the adsorption of the ion since the hydration capacity of that ion is smaller, resulting in weaker binding of the ion and water phase [7].

Selection of Eluent

To increase desorption percentage of metal ions, 5 mL of eluents, which is nitric acid, hydrochloric acid, and sulfuric acid with different concentrations were analyzed (Figure 6). The effectiveness of desorption depend on the binding strength of eluent cations to the adsorbent. It has been reported that the high concentration of hydrogen ions is responsible for the displacement of adsorbed metals through the ion exchange mechanism [8]. In this work, sulfuric acid has the highest desorption percentage and it is chosen as proper eluent for next steps. Using sulfuric acid as an eluent, resulted to the formation of sulfates.

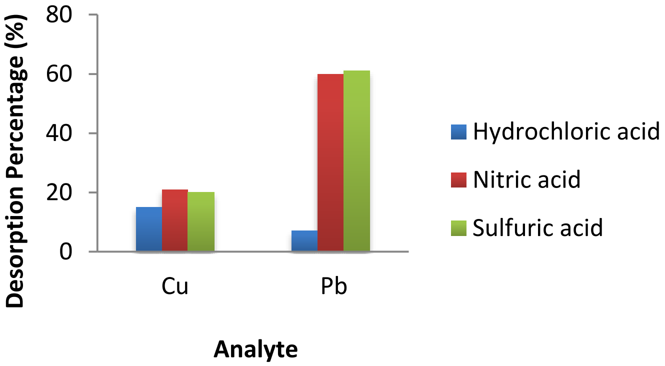

Figure 6: Selection of desorption eluent for d-SPE. Water sample volume, 100.00 mL; sample pH,6; extraction time, 3 h; desorption eluent (hydrochloric acid, nitric acid, sulphuric acid); eluent volume, 5.00 mL; desorption time, 10 min; adsorbent mass, 100 mg; stirring rate, 250 rpm.

Effect of Desorption Time

Influence of time on desorption of metal ions from AG-g-EA were investigated. As seen in Figure 7, copper and lead ions (Cu^{2+} and Pb^{2+}) desorption percentage gradually increased at the early desorption process. This could be due to the H^+ from sulfuric acid which started to exchange with metal ion located on the surface of the adsorbent. After 12 min, 100 percent of the Pb metal ions were successfully desorbed from the surface of AG-g-EA. As for copper metal ions, the highest desorption percentage was recorded at 9 min.

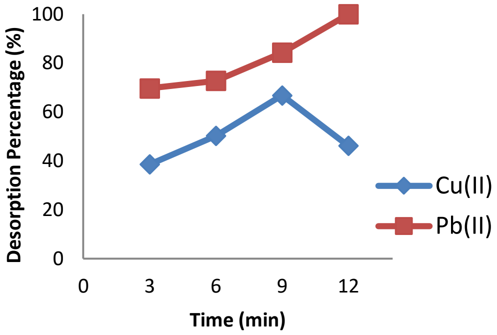

Figure 7: Extraction at various desorption time, AG-g-EA mass 100 mg, extraction time 3 h, pH 6, desorption eluent sulfuric acid.

Validation of AG-g-EA Adsorbent

The AG-g-EA method was validated for linearity, sample calibration, LOD and LOQ. The obtained correlation coefficients (r^2) were in the range of 0.9045 – 0.9917 for all the analyzed metal ions. The results are summarized in Table 1.

Analysis of Sample

Blank determinations were carried out on both river and tap water samples and were found to contain Cu^{2+} and Pb^{2+}. Recovery studies were conducted by spiking the water samples using 0.4 mg/L analyte and the results depicted in Table 2.

Tap water was used for the optimization and method validation while the river water was employed as the main sample for the extraction in this study

CONCLUSION

The study revealed that AG-g-EA is suitable for extraction of Cu^{2+} and Pb^{2+} from environmental water sample. By dispersing AG-g-EA into the water sample, the metal ion will be adsorbed on the AG-g-EA surface. In addition, the green and low cost nature of AG-g-EA could be added advantage for the removal of heavy metal ions as compared to conventional method.

ACKNOWLEDGEMENT

The authors would like to thank Universiti Teknologi Malaysia for the Postdoctoral Fellowships to Dr. Abdulganiyu Umar; and the Ministry of Education Malaysia for financial support through research grant number Q.J130000.2509.09H84.

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