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Application of chitosan-graft-poly(itaconic acid) as adsorbent in dispersive solid phase extraction-atomic absorption spectroscopy for the determination of copper and lead ions in water

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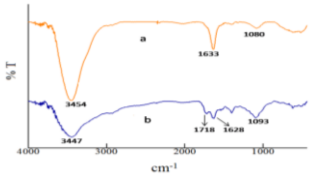
GRAPHICAL ABSTRACT



FTIR spectra of a) chitosan and b) chitosan-g-poly(itaconic acid)

ABSTRACT

This study aimed to investigate the application of chitosan-g-poly(itaconic acid)(CS-g-PIA) adsorbent for the dispersive solid phase extraction (dSPE) of copper (II) ion(Cu^{2+}) and lead (II) ion(Pb^{2+}) in water sample. The synthesized adsorbent was characterized by Fourier Transform Infrared Spectroscopy (FTIR) and Brunauer Emmet Teller (BET) analysis. Flame Atomic Absorption Spectroscopy (FAAS) was used to determine the amount of Pb^{2+} and Cu^{2+} after dSPE. The optimum extraction method parameters wereas follows: water sample pH 6, 100 mg of adsorbent, extraction time of 30 min, sulphuric acid as desorption solvent and desorption time of 7.5 min. The optimized method showed linearity with R^2 of 0.973 and 0.998 for Pb^{2+} and Cu^{2+}, respectively. Furthermore, the limit of detection (LOD) values were2.93mg/L and 0.12 mg/L for Pb^{2+} and Cu^{2+}, respectively.

Keywords: dispersive solid phase extraction, chitosan-g-poly(itaconic acid), heavy metals, atomic absorption spectroscopy

1. INTRODUCTION

During recent years the developments in adsorption of heavy metals from aqueous solutions have gained tremendous popularity among the scientific community as methods to treat industrial wastewater [1]. Heavy metals such as cadmium, iron, copper, chromium, nickel, lead and zinc are toxic to the environment. They are not biodegradable and depend to their high water solubility, can be easily absorbed by living organism. Due to their mobility in natural water ecosystems and their toxicity to living forms, they have been ranked as major inorganic contaminants in surface and ground water. The maximum allowable limit in drinking water of Pb^{2+} and Cu^{2+} ions as according by The U.S Environmental Protection Agency (USEPA) is 15 µg/L and 1300 µg/L, respectively [2].

Several techniques have been developed and applied to remove toxic metal ions from aqueous solutions [1]. These include adsorption, ion-exchange, chemical precipitation, coagulation-flocculation, membrane filtration, flotation and electrochemical method [3]. However, adsorption has proved as one of the most efficient methods to extract the heavy metals from aqueous media [3]. Extraction method has been made in the development to extract heavy metal in the water due to their process which is simply, automation and miniaturization.

Extraction techniques, which are defined as non-exhaustive sample preparation methods with a notably small volume of extraction medium in relation to the sample volume, play in important role in analytical chemistry [4]. Among the extraction methods, dSPE is a notably efficient extraction technique that can increase sensitivity of an analytical procedure and has been widely developed to analyze pesticides, polycyclic aromatic hydrocarbons, triazine, metal ions, and phytochemicals [5]. In this dSPE, the adsorbent (CS-g-PIA) will be dispersed in the sample solution that contain heavy metal ions. The adsorbent will attract metal ions while been dispersed in the solution. After all the analyte have been extracted onto the adsorbent, it will be desorbed with an eluent. dSPE method needs little quantity of sorbent and organic solvent, and less time consuming as compared to classic SPE method. Adsorption using natural polymer is one of the most effective method for extraction and preconcentration of heavy metal ions because it is biodegradable material.

Natural polymers, mainly polysaccharides, are biodegradable, cheap, fairly shear stable and easily available from renewable agriculture resources [8]. Graft copolymerization is one of the techniques employed for modifying the chemical properties of these polymers [6]. There are numerous approaches for the development of cheaper and more effective biosorbents that functionalized with natural adsorbents. Chitosan is one of the types of biosorbent. It is cheaper compared to other conventional sorbents. Besides, chitosan are the best option for removing heavy metals because they have functional group such as amino group and hydroxyl that could attract the heavy metal. For an acidic solution, chitosan will be soluble so it cannot be applied as an adsorbent[7]. However, chitosan can be modified with other polymer through the amino functional group to improve the surface, reactivity and stability of the chitosan [7]. The objectives of this study are to perform characterization of the newly prepared chitosan-g-poly(itaconic) acid (CS-g-PIA), to develop dispersive solid phase extraction method (dSPE) based on (CS-g-PIA) combined with atomic absorption spectroscopy (AAS) for the pre-concentration and determination of selected heavy metal ions in water and to validate the method and apply the validated method to the analysis of heavy metals in lake water.

2. EXPERIMENTAL

Lead (II) nitrate $Pb(NO_3)_2$ and Copper (II) nitrate solution $Cu(NO_3)_2$ (1000 ppm) was prepared and used as stocks solutions. The $Pb(NO_3)_2$ and $Cu(NO_3)_2$ was purchased from Sigma-Aldrich (Milwaukee,USA). Fourier Transformed Infrared (FTIR) Spectroscopy (Perkin Elmer) was used to investigate the functional groups and the comparison between chitosan and chitosan-g-poly(itaconic acid). The evaluation of metal ions content was carried out on a Perkin Elmer PinAAcle 900T atomic absorption spectrometer with a hollow cathode lamp and a deuterium lamp, background corrector, at respective resonance line using an air-acetylene flame. Micromeritics 3Flex Surface Characterization Analyzer was used to analyze the BET surface area of each adsorbent that has been prepared in single point mode. The pH values for all the sample was carried out on a Eutech Instruments. The dispersion of adsorbent (CS-g-PIA) was facilitated to the sample of solution by orbital shaker (Protech Orbital Shaker, Model 722) at 250 rpm. In dispersive solid phase extraction, CS-g-PIA was added into a vial containing 10 mL of sample solution comprising Pb^{2+} and Cu^{2+}. The pH was adjusted to 6.0 with sulfuric acid (0.1 M) and sodium hydroxide (0.1 M) solutions. The mixture of solution was then agitated using the orbital shaker (250 rpm) for 30 minutes to facilitate the dispersion of CS-g-PIA in the sample. After extraction, the mixture was decanted and only CS-g-PIA sorbent remained in the vial. To desorb the analytes 5mL H_2SO_4 (0.1 M) was added to the vial containing CS-g-PIA. The vial was ultrasonicated for 7.5 minutes. The solution was decanted again in order to analyze by AAS.

3. RESULTS AND DISCUSSION

The functional groups of chitosan and CS-g-PIA were characterized using FTIR. The spectrum of chitosan and chitosan-g-poly(itaconic acid) were compared as shown in Figure 4.1. They were recorded in the range between 4000 cm^{-1} to 400 cm^{-1}. The characteristic absorption band of the chitosan is the band at 1633 cm^{-1}, which is assigned to the stretching vibration of amino group. Another band is at 3454 cm^{-1} due to amine NH symmetric vibration. The broad peak at 1080 cm^{-1} indicates C-O-C stretching vibration. For the CS-g-PIA, Table 4.1 shows the absorption band which is 1628 cm^{-1} for the presence of amino group. NH symmetric vibration for CS-g-PIA is 3447 cm^{-1} showing different value with the chitosan and it can prove some compound has been attached. The value of the NH bending is different due to the attachment itaconic acid to the chitosan which is 1628 cm^{-1}.

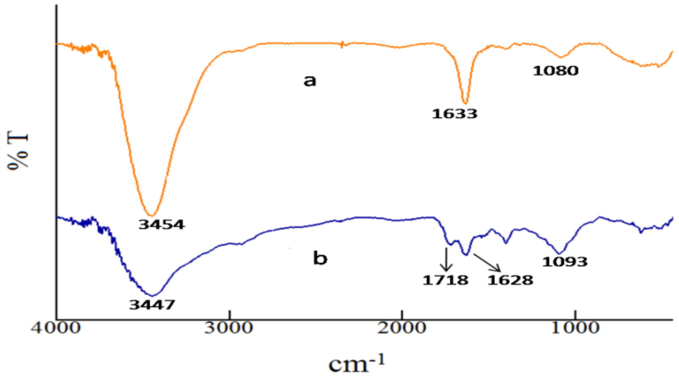


Figure 4.1 FTIR spectra of a) chitosan and b) chitosan-g-poly(itaconic acid)

Table 4.1 Comparison of FTIR Spectra between CS and CS-g-PIA

Type of vibrations	Wavenumber (cm^{-1})	
	Chitosan	Chitosan-g-poly(itaconic acid)
NH stretching	3454	3447
NH bending	1633	1628
C=O stretching	-	1718
C-O-C stretching	1080	1093

Nitrogen absorption-desorption analysis was used to determine Brunauer Emmett Teller (BET) surface area and pore size of the adsorbent which is CS-g-PIA. CS-g-PIA exhibited a BET surface area of 1.6011m^2/g which was slightly smaller than bare CS (2.0487m^2/g). As we compared the surface area above, CS-g-PIA gave smaller surface area than chitosan because the attachment of the itaconic acid. Thus, due to their attachment onto the surface of chitosan the surface area become smaller.

Table 4.2 Optimum extraction condition for Cu^{2+} and Pb^{2+} after optimization works.

Parameter	Cu^{2+} and Pb^{2+}
pH	6
Mass of adsorbent (mg)	100
Extraction time (min)	30
Type of eluent	H_2SO_4
Desorption Time (min)	7.5

From Table 4.2, it shows summary for the optimum extraction condition for both metal ions (Pb^{2+} and Cu^{2+}). This table stated the pH of the sample is 6, mass of adsorbent (100 mg), for an extraction time (30 min), the type of eluent is H_2SO_4, and for the last extraction parameter which is desorption time (7.5 min). This optimum condition will be applied to the method validation and for the real sample analysis.

The analytical procedure employed for this extraction method need to be confirmed with the method validation process. The optimized extraction method were pH 6 of the sample, 100 mg of adsorbent, 30 minutes of extraction time, H_2SO_4 as eluent and 7.5 minute of desorption time. To validate the applicable of the CS-g-PIA as metal ion adsorbent, the linearity and LOD for both Cu^{2+} and Pb^{2+} were determined. The linearity for this work was studied by constructing the calibration curve for both metal ions. LOD obtained from this work is 2.93mg/L and 0.12mg/L for Pb^{2+} and Cu^{2+} respectively.

The developed extraction method was applied to the analysis of real water sample which was lake water. The lake water was obtained from one of UTM lake and was subjected to dSPE. Cu^{2+} was detected in the water sample while $Pb^{2+}$was not detected. The concentration for the $Cu^{2+}$was 0.41 mg/L. As mentioned earlier, Cu^{2+}may come from the treatment of waste and combustion that will be released to the environment. From this statement, the Cu^{2+} was found in the lake water of UTM and suspected to be coming from that source. This might be due to the fact that most of pollutants entered the lake water by rain. Cu^{2+}detected in the lake water may harm people because it was above the US EPA stated maximum allowable limit contamination for the Cu^{2+}which was 1300 μg/L.

4. CONCLUSION

In this study, CS-g-PIA was successfully utilized for the analysis of metal ions in water samples due to the proven of characterization by FTIR. From the FTIR characterization, this material which is chitosan presence the amino group in the structural unit caused complexing capacity that can attracted metal ions. In this work chitosan was grafted to the polymer for preventing its dissolution in acidic medium. For this work, dSPE method was applied. There was several parameters that influences the adsorption of metal ions on the adsorbent which are pH of the sample, mass of adsorbent, extraction time, type of desorption solvent and desorption time.

The optimum conditions for the extraction process were water sample pH 6, 100 mg mass of adsorbent, 30 min extraction time, sulfuric acid as a desorption solvent and 7.5 min for desorption time for the both metal ions (Pb^{2+} and Cu^{2+}).

The calibration graph was plotted according to the optimum condition was obtained. From the calibration graph, the optimized method indicated the linearities with R^2 of 0.973 and 0.998 for Pb^{2+} and Cu^{2+} respectively. The limits of detection (LOD) values were 2.93 and 0.12 for Pb^{2+} and Cu^{2+}. The developed method has been applied to the analysis of lake water. The amount of Cu^{2+} that has been adsorbed in the lake water is 0.41 mg/L. Meanwhile the developed method does not adsorb the amount of Pb^{2+} in the lake water.

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