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Zeolite-like Arabinose-based Coordination Polymers: Synthesis and Characterization for Heavy-Metal Sequestration Applications

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[abstract]

L-Arabinose-based coordination polymers were synthesized by the oxidation of L-arabinose using warm HNO₃ to form arabinaric acid and allowing the resulting arabinaric acid to react with the different metal ions such as zinc(II), lead(II), copper(II), iron(III), and chromium(III). Only zinc(II) and lead(II) ions produced crystalline coordination polymers suitable for analysis while copper(II) produced a gummy solid.

Preliminary characterization of the coordination polymers was based on their solubility, melting points, UV-Visible spectra, and infrared spectra. The coordination polymers were insoluble in common organic solvents and in acidic aqueous solutions but soluble in moderately basic aqueous solutions (pH 12). The zinc(II) and lead(II) coordination polymers have melting points above 300 °C while the copper(II) polymer melts from 218–225 °C. UV-Visible spectra showed that these polymers have maximum absorption in the ultraviolet region. Zinc(II), lead(II), and copper(II) arabinarate coordination polymers had maximum absorbance at $\lambda_{\text{max}} = 217 \text{ nm}$, $\lambda_{\text{max}} = 240 \text{ nm}$, and $\lambda_{\text{max}} = 220 \text{ nm}$, respectively. The infrared spectra of the coordination polymers indicated the association of the arabinarate ligand with the metal ions.

Introduction and incorporation of molecular species such as azobenzene and molecular iodine to the coordination polymers were also investigated. Infrared spectra obtained from the azobenzene inclusion experiments showed additional infrared absorption bands below 1000 cm⁻¹ implying absorption of azobenzene within the polymers. Iodometric titrations also confirmed the inclusion of iodine in the coordination polymers.

The potential of the coordination polymers to incorporate lead(II) ions in aqueous solutions was also investigated using column elution of different sample concentrations of lead(II). Atomic Absorption Spectrometric analysis illustrated significant lead reduction of up to 80.70 ppm of lead(II) on the eluted samples.

[abstract]

[manuscript]

INTRODUCTION

Rapid industrialization in the modern world today causes severe pollution in the environment. This may be due to toxic, inorganic, or non-biodegradable materials released to the environment as waste products during industrial processes.

Heavy metals, like lead, are among the most harmful of the environmental elemental pollutants. Lead contamination from excessive exposure has been found to cause several health hazards and long term detrimental effects. Prominent conventional processes for the removal of lead from aqueous mixtures, such as sludge separation, chemical precipitation, and electrochemical treatments are relatively expensive and can cause secondary pollutants (Manahan, 1993 as cited in Acabal *et al.*, 2000).

Due to the problems of pollution, "green" industrial productions of compounds and their derivatives based on renewable starting materials and biodegradable products are developed (Kiely, 2001).

Carbohydrates are biodegradable, widely available, and generally economical. Hence, their study for chemical and industrial applications would be very sensible. Because of their ease in functionalization forming sugar derivatives, they could serve as valuable building blocks for potentially useful polymers (Abrahams *et al.*, 2003). Heavy metal sequestering properties of certain types of these polymers provide an alternative and potentially economical treatment process for heavy metal removal and recovery.

L-Arabinose, a monosaccharide aldose, can undergo terminal oxidation to produce L-arabinaric acid, a dicarboxylic aldaric acid. This acid is a potential metal-chelating agent of metal ions in aqueous solutions to form coordination polymers. Certain types of coordination polymers can serve as organic sieves or three-dimensional nets for heavy metal inclusion.

Carbohydrate-based coordination polymers have distinct chemical and physical properties arising from the multiplicity of the hydroxy groups. Determination of these properties through extensive characterization and structural elucidation prior to further specific chemical application is greatly necessary.

Coordination polymers derived from some aldaric acids were previously investigated. Previous researches on zinc D-glucarate and lanthanum D-galactarate polymers showed extraordinary properties of these polymers like the possession of hydrophilic and hydrophobic channels in the crystal lattice (Abrahams *et al.*, 2003). It was also reported that copper(II) D-glucarate has a linear polymeric structure shown to have a different structure from other copper complexes of bis(bidentate) ligands (Ferrier *et al.*, 1998). Reports about some alkali and alkaline earth metal derivatives of glucaric and galactaric acids were also presented (Taga *et al.*, 1994; Sheldrick *et al.*, 1989).

Certain studies about the extraction of lead in aqueous solutions through biosorption were studied. Immobilized root tissues of *Amaranthus spinosus* (Acabal, *et al.*, 2000) and dead *Saccharomyces cerevisiae* (Acabal and Patindol, 1999) have been found to absorb lead from aqueous solutions.

This study aimed to synthesize coordination polymers of an L-arabinose derivative and evaluate the potential of the coordination polymers to incorporate lead in aqueous solutions. Specifically, it was intended to synthesize arabinaric acid from L-arabinose, synthesize arabinarate coordination polymers from arabinaric acid, characterize the properties of each coordination polymer, test the crystalline structural features of each coordination polymer using the azobenzene and the molecular iodine inclusion techniques and evaluate the ability of the polymers to incorporate lead in aqueous solutions using column elution.

The scope of the study included the synthesis of arabinaric acid from L-arabinose. The study utilized zinc(II), lead(II), copper(II), iron(III), and chromium(III) ions to bind with the arabinaric acid ligand for the polymerization reactions. The characterization of the coordination polymers by ultraviolet-visible (UV-Vis) spectra and infrared spectra was done using the double beam Shimadzu UV-1601 UV-Vis Spectrophotometer and the Perkin Elmer Paragon 1000 Fourier Transform Infrared Spectrophotometer, respectively. Inclusion of lead in the polymers was evaluated using column elution. The above procedures were carried out at the Department of Chemistry of the University of San Carlos, Cebu City, Philippines. Effective lead removal was assessed through the analysis of the resulting eluted solutions for lead by Atomic Absorption Spectrometric (AAS) analysis using the SpectrAA Atomic Absorption Spectrometer in the

Chemistry Laboratory of the Department of Science and Technology Region 7 – Regional Standards and Testing Center (DOST7–RSTC) at Sudlon, Lahug, Cebu City, Philippines.

Further conditions that were investigated were the physical properties such as the solubility using different solvents and aqueous solutions at different pH, melting point using the Fisher-Johns Melting Point Apparatus, the ability to incorporate certain compounds such as azobenzene and molecular iodine, and the potential to incorporate lead in aqueous solutions.

REVIEW OF LITERATURE AND RELATED STUDIES

Aldaric Acids from Aldoses

Like other aldehydes, aldoses are easily oxidized to yield the corresponding monocarboxylic acids, called aldonic acids. Aldoses react with Tollens' reagent, Fehling's reagent, or Benedict's reagent to yield the oxidized sugar and a reduced metallic species from the reagents (McMurry, 2000).

If a more powerful oxidizing agent such as warm dilute nitric acid is used, aldoses are oxidized on both terminals to produce dicarboxylic acids, called aldaric acids. Another process, which yields a greater yield, uses 4-acetamido TEMPO (4-acetamido-2,2,6,6-tetramethyl-piperdinyloxy radical) as a catalyst, a commercial grade bleach, and sodium bromide (Merbouh, 2001). Oxidation reactions utilizing this process are termed as nitroxy radical-catalyzed reactions. Another method for the oxidation of aldoses is also adapted such as the Mehlretter's method (Ferrier *et al.*, 1998).

These aldaric acids, which are polyhydroxy dicarboxylic acids, could provide coordination polymers with interesting properties arising from the multiplicity of hydroxy groups and from the chirality (Abrahams *et al.*, 2003). Accordingly, typical aldaric acids such as D–glucaric acid (saccharic acid) and D–galactaric acid (mucic acid) from glucose and galactose, respectively, were reported earlier.

Aldaric acids are generally very soluble in water and other aqueous solutions. They have to be converted to their less soluble monopotassium salts for them to be precipitated and isolated for characterization (Bullock, 2002).

Nature of Arabinaric Acid

Arabinaric acid is a polyhydroxy dicarboxylic acid derivative of L–arabinose. It is very soluble in aqueous solutions and it needs to be converted to its monopotassium salt in order for it to be isolated (Figure 1). However, if quantitative analyses are not required, the isolation procedure is not necessary.

Some protocols include in the conversion the isolation and purification of the aldaric acid from other impurities. Due to the high solubility of arabinaric acid in water, this procedure is oftentimes neglected especially when arabinaric acid would still be used in further reactions using aqueous solutions or using water as the solvent.

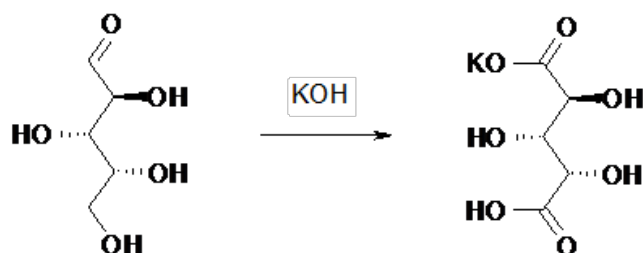


Figure 1. Conversion of Arabinose to Potassium Arabinarate (Salt of Arabinaric Acid)

COORDINATION COMPOUNDS OF ALDARIC ACIDS

Reaction of monopotassium D-glucarate with zinc acetate produces a three-dimensional coordination polymer of chiral zinc D-glucarate, which consists of pillars of zinc linked by glucarate ligands (Figure 2). Channels with square cross-section are formed with metals occupying the corners while the ligands on the sides and edges.

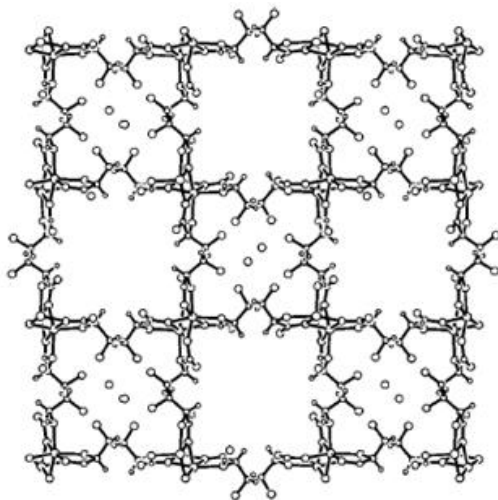


Figure 2. Zinc D-Glucarate (saccharate) viewed down the Channel Axis (Reproduced from Ref. Abrahams *et al.*, 2003 with permission from John Wiley and Sons)

The polymer contains two types of parallel channels with different chemical characteristics. The channels alternate like the black and white squares on a chessboard. The hydroxy groups attached to the two central carbons of the ligands surrounding the first channel are directed into that channel. This arrangement renders channels that are hydrophilic and others that are hydrophobic in character (Abrahams *et al.*, 2003).

Crystals of lanthanum galactarate also form from hot aqueous mixtures of lanthanum nitrate and monopotassium galactarate (Figure 3). The resulting coordination arrangement generates channels with hexagonal cross section (Abrahams *et al.*, 2003).

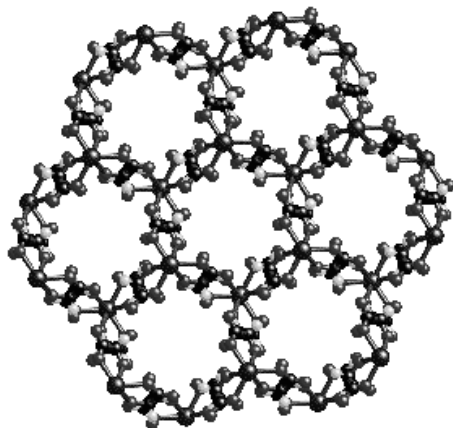


Figure 3. Lanthanum D–Galactarate (mucate) viewed down the Channel Axis (Reproduced from Ref. Abrahams *et al.*, 2003 with permission from The Royal Society of Chemistry)

Both polymers had a successful introduction and crystallographic detection of several small non-polar compounds such as I2, azobenzene, and cyclooctatetraene into the hydrophobic channels (Abrahams *et al.*, 2003).

Copper(II) D–glucarate was shown to have a linear polymeric chain structure that has a different structure from other copper complexes of bis(bidentate) ligands (Ferrier *et al.*, 1998) and the structures of the potassium and calcium salts were described earlier (Taga *et al.*, 1977) (Figure 4).

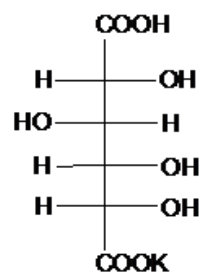


Figure 4. Potassium Glucarate (saccharate)

Galactaric acid has been found to generate salts with the sodium and potassium (Taga *et al.*, 1994) (Figure 5). Magnesium, barium, and calcium salts of galactaric acid were also investigated through crystallographic studies (Sheldrick *et al.*, 1989).

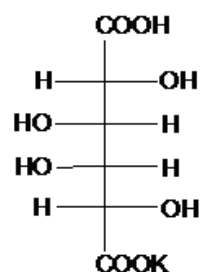


Figure 5. Potassium Galactarate (mucate)

Extraction of Heavy Metals

Several “green” methods for extracting heavy metals from aqueous solutions or wastewater systems have been proposed in the past years. As cited in Acabal *et al.*, heavy metals have been extracted from aqueous solutions through biosorption, a process used to describe the removal of metals and other related elements or compounds from a solution by biological materials. Fungal and yeast biomasses have been used for the recovery of uranium, strontium and cesium. The higher metal capacity of nonliving biomass for the uptake of copper, zinc, cadmium, and uranium has been described for the biomass of *Saccharomyces cerevisiae* (yeast). The roots of *Lycopersicon esculentum* (tomato) and *Nicotiana tabacum* (tobacco) were also shown to adsorb strontium from an aqueous solution of SrCl₂.

The adsorption of lead by organic tissues could be due to the cellulose and lignin contained within the tissues. Lignin together with cellulose and hemicellulose are the major cell wall constituents of the fibers of most plant species. Previous investigations have shown that heavy metals bind to natural materials, particularly of a carbohydrate-based nature. Batch adsorption studies showed that ground powders of dead *S. cerevisiae* (Acabal and Patindol, 1999) and root tissues of *Amaranthus spinosus* (spring amaranth/kulitis) (Acabal *et al.*, 2000) possessed the property of binding lead from aqueous solutions. Moreover, immobilized dead *S. cerevisiae* and *A. spinosus* has been found to extract significant amounts of lead using a continuous process of the aqueous solution.

EXPERIMENTAL

Synthesis of the L-arabinose-based coordination polymers and the extraction procedures were done at the Chemistry Research Laboratory, characterization at the Instrumentation Room of the Department of Chemistry, and the extraction analysis at the Chemistry Laboratory of the Department of Science and Technology Region 7 – Regional Standards and Testing Center (DOST7–RSTC) at Sudlon, Lahug., Cebu City, Philippines.

All the chemicals used in this study were reagent grade or better and were used as received.

Synthesis of Arabinaric Acid

L-Arabinose (5.00 g, 33.3 mmol) was dissolved using 50 mL of distilled water in an Erlenmeyer flask. The resulting solution was added with 10 mL of concentrated HNO₃ solution and was heated over a water bath for 3 hours until the resulting volume reached approximately 25 mL. Occasional swirling was also done during the heating period. The solution was then allowed to cool and diluted to 75 mL.

Synthesis of Arabinarate Coordination Polymers

Zinc Arabinarate Polymer. A 5-mL portion of the diluted arabinaric acid solution was added with 0.50 g (2.22 mmol) of zinc acetate dihydrate. It was swirled until all the solid had dissolved. The resulting solution was heated at 60°C for 16 hours in an oven.

After 16 hours, the crystals formed were separated from the solution through decantation, dried and stored in a desiccator.

Lead Arabinarate Polymer. For the reaction of arabinaric acid with lead(II), 0.80 g (2.22 mmol) of lead(II) acetate dihydrate was dissolved in a 5-mL portion of the arabinaric acid solution. It was then heated in the oven for 16 hours at 60°C and the resulting crystals were separated and dried.

Synthesis of Other Coordination Polymers. The succeeding procedures were carried out exactly as stated above. For the reaction with copper(II), 0.50 g (2.22 mmol) of copper(II) acetate dihydrate was used. For iron(III), 0.90 g (2.22 mmol) of iron(III) nitrate nonahydrate was used. For chromium(III), 0.45 g (2.22 mmol Cr) of basic chromium(III) acetate, Cr₃(CH₃COO)₇(OH)₂, was used.

Characterization of Arabinarate Coordination Polymers

The characterization of the obtained coordination polymers included the determination of the melting point and two spectroscopic analyses using Fourier Transform Infrared Spectrometry and Ultraviolet–Visible Spectrometry.

Solubility. The solubility of the coordination polymers obtained using the different metal ions in different organic solvents was determined by adding approximately 0.05 g of the coordination polymers to 3 mL of ethanol, dichloromethane, acetone, and diethyl ether.

The solubility of the coordination polymers in aqueous solutions at varying pH was also determined by adding 0.05 g of the polymers in 20 mL water and adding 6 M HNO₃ and 6 M KOH to make the suspension acidic and basic, respectively. The pH of the suspension was monitored using the Orion pH meter during the addition of the acid and base.

Melting Point. The melting point was obtained using the Fisher-Johns Melting Point Apparatus. The sample was placed between two 18–mm microscope cover glasses that were placed in the depression of the aluminum block. The temperature was regulated by means of a variable transformer, and the melting point was obtained with the aid of an illuminator and a magnifying glass.

Spectroscopic Analysis. Spectral analyses were done using the Perkin Elmer Paragon 1000 Fourier Transform Infrared (FTIR) Spectrometer using the KBr disks. About 1 part of the sample and 10 parts of KBr were mixed, ground, and pressed into a transparent pellet. The pellet was placed in the sample compartment of the FTIR Spectrometer and the infrared spectrum was obtained.

Spectral analyses were also done using the double beam Shimadzu UV-1601 UV–Vis Spectrometer. An aqueous solution containing 200 ppm of the sample was prepared. The absorbance of the solution was taken at wavelengths 200–800 nm at 40 nm increments using distilled water as the reference. The absorbance readings were also taken at 10–nm increments within the 50 or 100 nm range where the absorbance was at maximum. A spectral absorption curve from the plot of absorbance vs. the wavelength was made and λ_{max} was determined from the graph.

Azobenzene Inclusion

A 0.0600–g portion of the arabinarate coordination crystal polymers was suspended in an excess of molten azobenzene in an evaporating dish and heated at 96°C for 4 hours. The resulting crystals were separated from the excess molten azobenzene and were thoroughly washed first with toluene, then pentane, and then dried in air. The residue was collected, weighed and analyzed using FTIR Spectrometric analysis. An infrared spectrum for the resulting crystals is obtained and analyzed for the inclusion of azobenzene.

Iodine Inclusion

Approximately, a 0.050–g portion of the arabinarate coordination crystal polymers was exposed to iodine vapor in a sealed jar containing excess iodine crystals. It was left undisturbed for 140 hours at room temperature until the crystals became dark red. The crystals were weighed immediately and added with 20 mL of water.

The resulting solution was titrated using a standard 5.0×10^{-4} M Na₂S₂O₃ solution using starch as an indicator. The amount of iodine present was then analyzed using the amount of the Na₂S₂O₃ solution consumed.

Lead Inclusion through Column Elution

Approximately 0.6 g of each of the arabinarate coordination polymers was ground until enough to produce a fine powder, which was then packed into a column measuring about 10 cm in length, between slugs of cotton and glass wools, and using a thin burette. Three lead concentrations: 25 ppm, 50 ppm, and 100 ppm, were allowed to run through the three different columns. A completely randomized design (CRD) with three replicates was employed. Blanks utilizing only cottons and glass wools were prepared for each experimental condition.

Distilled water was first allowed to run to the different columns. Exactly 20.0 mL of the lead solutions of different concentrations were then added in 2.0–mL portions to the columns. The lead solutions were allowed to flow by gravity until all the solution was eluted. The eluted liquid samples were placed in volumetric flasks and diluted to 250.0 mL.

The diluted samples were transferred to plastic containers and were stored in the refrigerator until analyzed with AAS analysis.

The quantity of metal ions incorporated in the column was calculated from the concentration of metal in the solution before and after contact with the coordination polymers according to:

$$q = (C_0 - C_f)(V/M) \quad (\text{Eq. 1})$$

where: q is the quantity of metal uptake by the absorbent, C₀ and C_f are the initial and final concentrations, respectively, V is the volume of the sample solution, and M is the mass of the coordination polymer added.

Atomic Absorption Spectrometric (AAS) Analysis

Levels of excluded lead were determined by AAS analysis at a wavelength of 217.0 nm of the air/acetylene flame type. Absorbance of the samples was read and the concentration of lead was calculated from the absorbance readings of the standard solutions using the external calibration method (ECM) of analysis.

Preparation of Standard Solutions

Standard solutions of lead with concentrations ranging from 0 to 10 ppm at 2.50 ppm intervals were prepared from a Spectro-grade lead(II) nitrate solution (Ajax) having a concentration of 1000 ppm by dilution method. The formula used was:

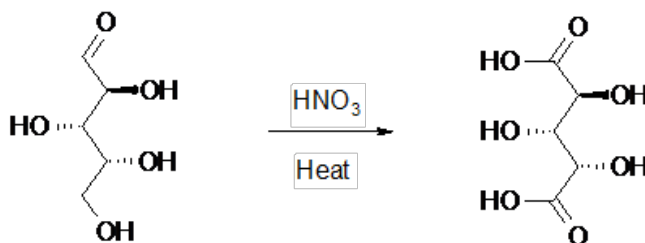
$$C_1V_1 = C_2V_2 \quad (\text{Eq. 2})$$

where: C₁ is the concentration of the stock lead solution (1000 ppm), C₂ is the concentration of desired solution, V₁ is the volume (mL) of stock lead solution, and V₂ is the volume of desired solution.

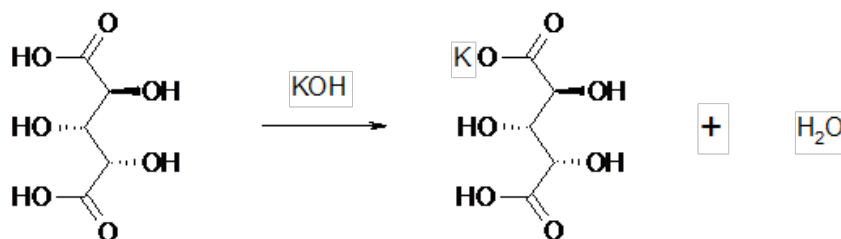
RESULTS AND DISCUSSION

Synthesis of Arabinaric Acid

Upon treatment with warm nitric acid, L-arabinose is oxidized at both terminal ends of the carbohydrate molecule producing a polyhydroxy dicarboxylic acid called arabinaric acid according to the equation below (Eq. 3):



Inherently, L-arabinose (Figure 6) is very soluble in polar solvents like water since it is a small polyhydroxy aldehyde. Approximately 1 gram of L-arabinose dissolves in 1 mL of water. Upon conversion to the dicarboxylic acid, the molecule is made more soluble because now it contains more oxygen atoms that would interact intermolecularly with water molecules to form hydrogen bonds. In order for the acid to be precipitated and purified, it should then be converted to its less soluble monopotassium salt (Eq. 4):



Unfortunately, arabinic acid and its monopotassium salt are extremely soluble in aqueous solution that none of them precipitated even in concentration, cooling, addition of 95% ethanol, and in salting out processes using KOH. Due to this difficulty, the succeeding procedures after the initial oxidation were done directly without further isolation and purification of the arabinic acid produced.

Upon concentration of the arabinic acid solution containing the KOH solution however, long colorless slender crystals were obtained. Unfortunately, the relatively simple infrared spectra of these crystals indicate that these are not arabinarate salts. Rather, they are merely inorganic nitrate salts and are believed to be KNO_3 (Figure 7). It was really possible that the solution got too concentrated that caused the supersaturation of the dissolved salts. Upon cooling, some salts, possibly KNO_3 , crystallized. One gram of KNO_3 dissolves in 2.8 mL and 0.5 mL of water at 25°C and 100°C , respectively.

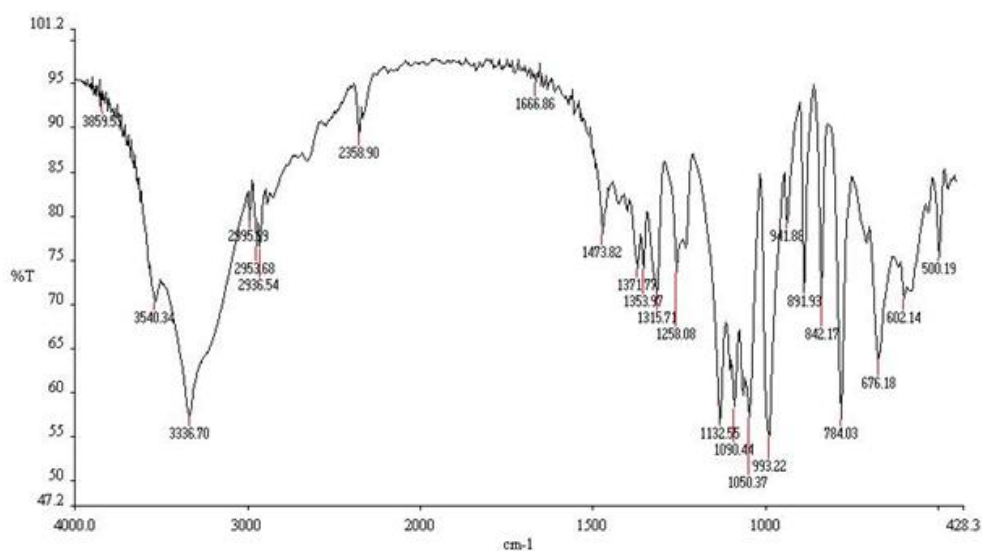


Figure 6. Infrared Spectrum of L-Arabinose

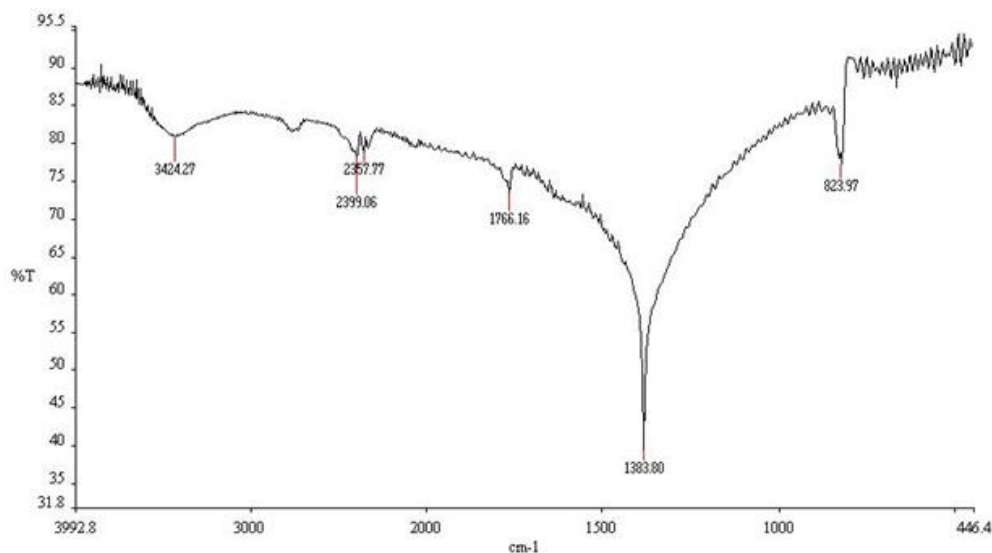
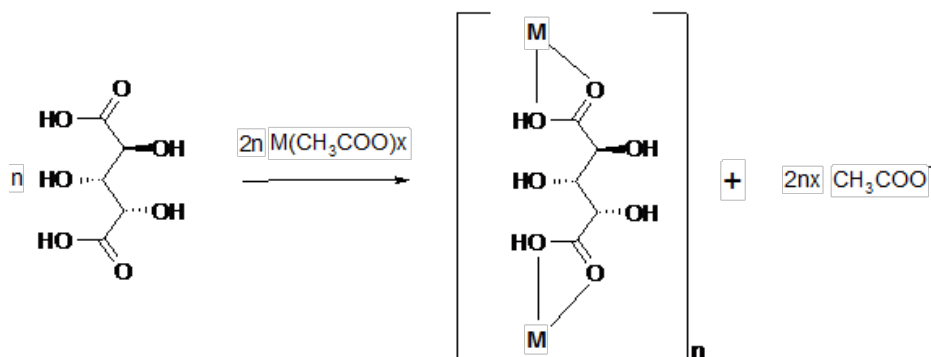


Figure 7. Infrared Spectrum of the Possible Nitrate Salt

Inorganic Synthesis of Arabinarate Coordination Polymers

Reactions with zinc(II), lead(II), copper(II), iron(III), and chromium(III) comprised the inorganic reaction synthesis of the coordination polymers (**Eq. 5**):



Reaction with Zinc(II). The reaction of arabinaric acid with zinc(II) acetate produced a white to light flesh compact crystalline solid (Figure 8). Though the solid might be perceived not as pure slender crystals in the macroscopic level, microscopic analyses indicate the presence of numerous large cubic colorless crystals. Further, microscopic analysis shows that the solid is composed of two distinct substances, the colorless crystals and the opaque powdery gummy solid material.

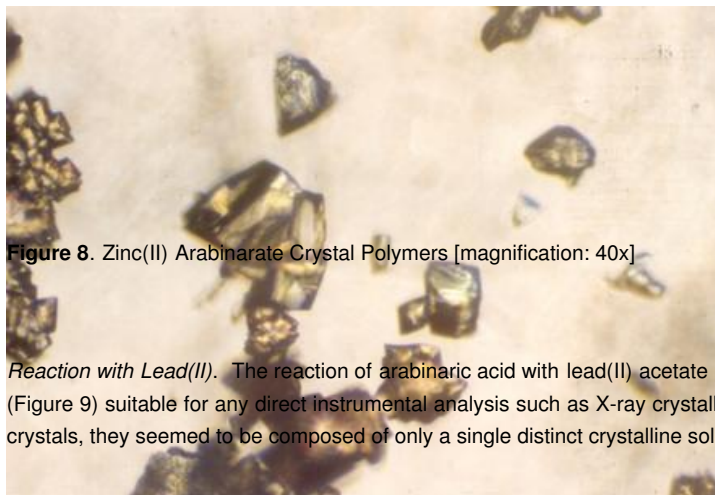


Figure 8. Zinc(II) Arabinarate Crystal Polymers [magnification: 40x]

Reaction with Lead(II). The reaction of arabinaric acid with lead(II) acetate produced good long slender white crystals (Figure 9) suitable for any direct instrumental analysis such as X-ray crystallography. In a microscopic analysis of the crystals, they seemed to be composed of only a single distinct crystalline solid.



Figure 9. Lead(II) Arabinarate Crystal Polymers [magnification: 16x]

Reaction with Copper(II). The reaction of arabinaric acid with copper(II) acetate yielded blue powdery gummy precipitate that tends to stick to the glass surface when dry. However, no distinct crystals were found with microscopic analysis.

Reaction with Chromium(III) and Iron(III). No crystalline or powdery solid was produced after heating the arabinaric solution containing chromium(III) and iron(III) for several hours. The solutions containing chromium(III) and iron(III) remained clear dark green and intense yellow, respectively.

It is possible that arabinaric acid will react with copper(II) to produce fine crystals and with chromium(III) and iron(III) to

produce crystalline solids at different syntheses conditions. However, the study is limited only to using aqueous solutions and common strong oxidizing agents like concentrated HNO₃. Unfortunately, with these conditions and with the metal ions investigated, only the zinc(II) and lead(II) coordination compounds produced suitable results.

Unlike the zinc(II) and lead(II) complexes, the copper(II) arabinarate coordination polymer produced a different solid since copper(II) produces unique linear polymeric structures or complexes with carbohydrate derivatives (Ferrier *et al.*, 1998).

Characterization of the Arabinarate Coordination Polymers

The arabinarate coordination polymers show several distinct properties.

Solubility. The polymers show little or almost no solubility in aqueous solutions even in appreciable amounts of water. Moreover, they do not tend to dissolve in any common organic solvents such as ethanol, dichloromethane, acetone, and diethyl ether. Though this property is beneficial for bioremediation applications since this would avoid or lessen contamination, this basically adds to the difficulty in the purification or recrystallization of the polymers.

The coordination polymers however, are soluble in basic solutions. Raising the pH of the coordination polymer suspension to approximately 12, a clear solution was obtained. Lowering the pH caused the appearance of turbidity and precipitates that later settled.

This property manifests the stability of the coordination framework which is due to the several hydrogen bonds, which act as "mortars" between arabinarate "bricks", per arabinarate molecule (Abrahams *et al.*, 2003).

Melting Point. The melting points of the coordination polymers were determined using the Fisher-Johns Melting Point Apparatus. The melting point of the zinc(II) arabinarate coordination polymer is above 300°C, which is beyond the temperature range of the Melting Point apparatus. However, the crystalline solid gradually changed in color from light flesh to reddish brown starting from 185°C. Similar with the zinc complex, the lead(II) arabinarate coordination polymer also has a melting point greater than 300°C and gradually changed in color from white to brown starting from 185°C. The copper(II) arabinarate coordination polymer has a melting point range of 218–225°C. Moreover, its color gradually changed from blue to green starting at 180°C.

It is possible that at approximately 180–185°C, the coordination polymers started to change from the original solid phase to another solid phase with different solid or crystalline structure, similar to other common substances.

UV-Vis Spectra. Solutions (200 ppm) of the coordination polymers were prepared by the addition of 2 M KOH to the aqueous suspensions until all solids were dissolved. KOH solutions were used as blanks.

The UV-Vis spectra of the zinc(II), lead(II), and copper(II) arabinarate coordination polymers had maximum absorbance at $\lambda_{\text{max}} = 217 \text{ nm}$, $\lambda_{\text{max}} = 240 \text{ nm}$, and $\lambda_{\text{max}} = 220 \text{ nm}$, respectively. Further, at the λ_{max} , the absorptivities, ϵ , expressed in $\text{L} \cdot \text{g}^{-1} \cdot \text{cm}^{-1}$, of the zinc(II), lead(II), and copper(II) polymers are 5.045, 14.17, and 14.80, respectively. These absorptions in the ultraviolet region may be due to the charge transfer transitions that arise from the movement of electrons between the carboxyl oxygens in the arabinarate ligand and the metal ions. Only in the spectra of lead(II) arabinarate can a splitting be observed. However, the reason for this behavior was not investigated further. The spectral absorption curves of the complex polymers are shown in Figures 10–12.

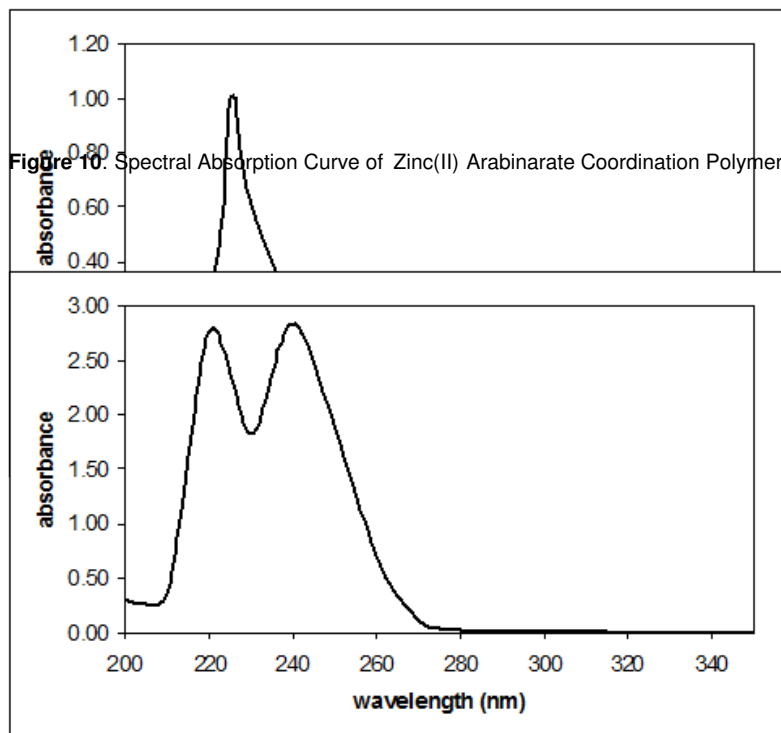


Figure 11. Spectral Absorption Curve of Lead(II) Arabinarate Coordination Polymer

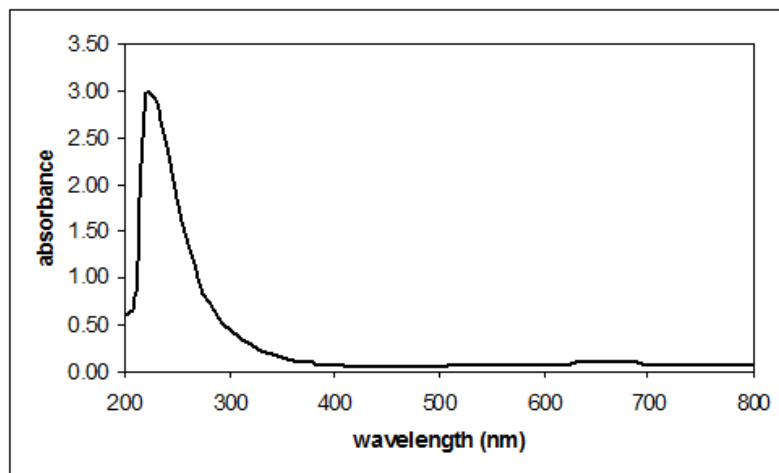


Figure 12. Spectral Absorption Curve of Copper(II) Arabinarate Coordination Polymer

Infrared Spectra. Infrared spectra of all polymers indicate that the arabinarate coordination polymers were formed. Complexation of the metal ion is most likely to occur through the oxygen atoms of the carbonyl and hydroxyl groups of the terminal carboxyl functional groups (Eq. 5). Coordination is expected to cause a shift in the carbonyl band and, in the case of chelation, also the hydroxyl band.

The infrared spectra of the coordination polymers are presented in Figures 13–15. All of the coordination polymers

showed strong broad bands though with different shapes and intensities at 3350 to 3450 cm^{-1} , which indicate the presence of -OH groups common to all carbohydrates and their derivatives. The irregularly and broadly shaped bases of these bands, which extend to 3000 cm^{-1} , also indicate the presence of carboxyl groups or carbonyl groups bonded to hydroxyl groups. The strong bands from 1580 to 1750 cm^{-1} suggest the presence of carbonyl groups (C=O), as expected.

Several sharp peaks at 1280 to 1390 cm^{-1} imply different kinds of C-O bonds present in the polymers. This is expected since arabinaric acid has a number of C-OH groups and two C-O carbonyl groups. Sharp peaks at 700 to 920 cm^{-1} suggest an interaction to a metal ion present in complexes and salts. The results are summarized in Table 1.

Table 1. Infrared Bands with the Respective Functional Groups of Complex Polymers

FREQUENCY (cm^{-1})	FUNCTIONAL GROUP
3350–3450	Hydroxyl groups
1580–1750	Carbonyl group
1280–1390	C-O group
700–920	O-M group

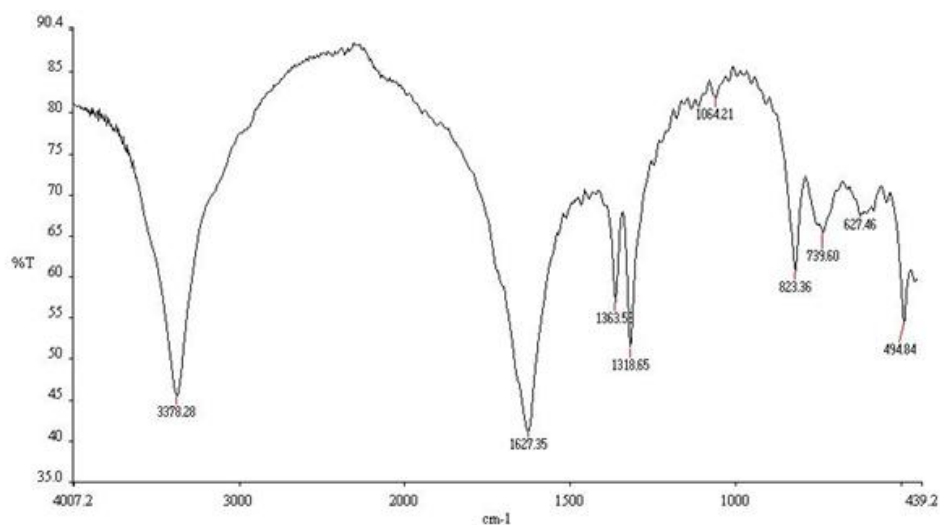


Figure 13. Infrared Spectrum of Zinc(II) Arabinarate Coordination Polymer

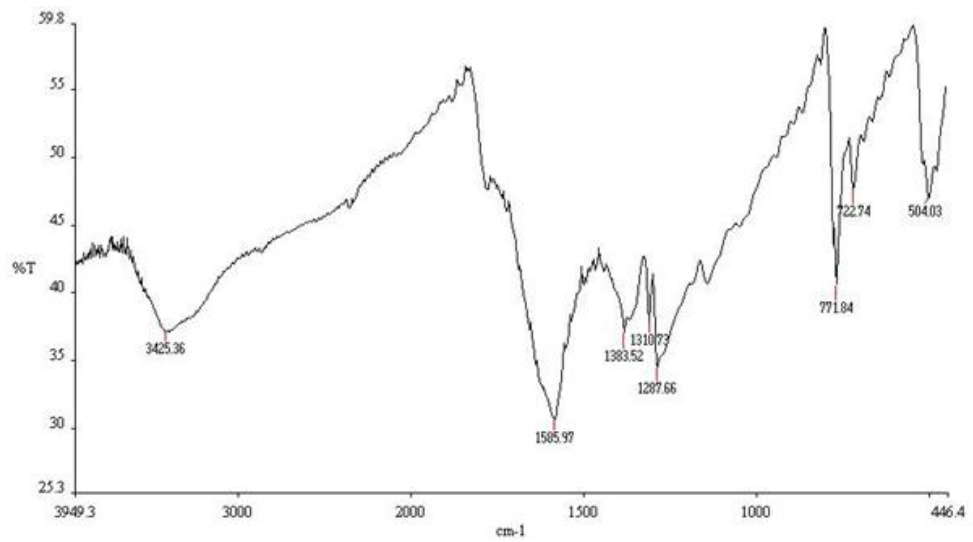


Figure 14. Infrared Spectrum of Lead(II) Arabinarate Coordination Polymer

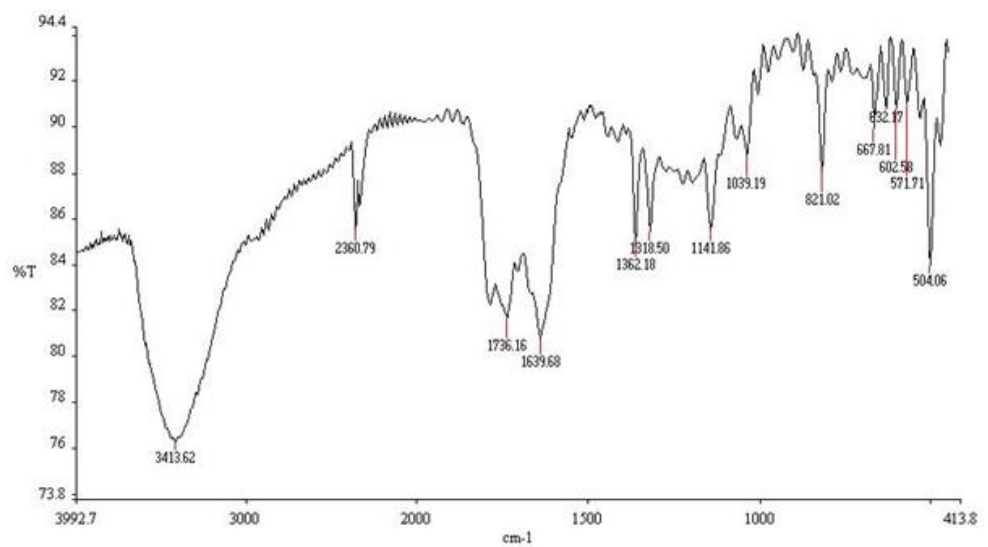


Figure 15. Infrared Spectrum of Copper(II) Arabinarate Coordination Polymer

Azobenzene Inclusion

Since only the zinc(II) and lead(II) coordination polymers produced crystalline solids, these were the only polymers treated with azobenzene. The solid produced using copper(II) was unsuitable for the treatment since there is a great possibility that the powdery precipitate will be washed out. However, there was no danger of washing the polymers of zinc(II) and lead(II) out since they were intact and they were in the form of large crystals.

After suspending the crystalline polymers in molten azobenzene and heating them at 96°C for 4 hours, the both kinds of crystals became dark gray-orange in color. The color remained even after several washings of toluene and pentane. Dry zinc(II) arabinarate crystals increased in mass from 58.6 mg to 63.5 mg. Likewise, the mass of lead(II) arabinarate crystals increased from 60.9 mg to 67.1 mg.

The results suggest that there was a successful inclusion of azobenzene in the crystalline matrix. The azobenzene however, cannot be removed by simple washings using some common solvents.

The infrared spectra of the coordination polymers treated with azobenzene showed changes in the fingerprint region at 600–850 cm^{-1} . For the zinc(II) arabinarate coordination polymer, additional azobenzene-derived bands were observed in the IR spectrum at 771 and 671 cm^{-1} . For the lead(II) arabinarate coordination polymer, additional bands and changes in the shape of the peaks were observed in the IR spectrum at 757, 691, and 478 cm^{-1} , suggesting the incorporation of azobenzene in the crystal structure.

These results are concordant with other coordination polymers synthesized and treated with molten azobenzene. The IR spectrum of zinc saccharate crystals showed azobenzene-derived bands at 776 and 689 cm^{-1} (Abrahams *et al.*, 2003).

The infrared spectra of the coordination polymers treated with azobenzene are presented in Figures 16 and 17.

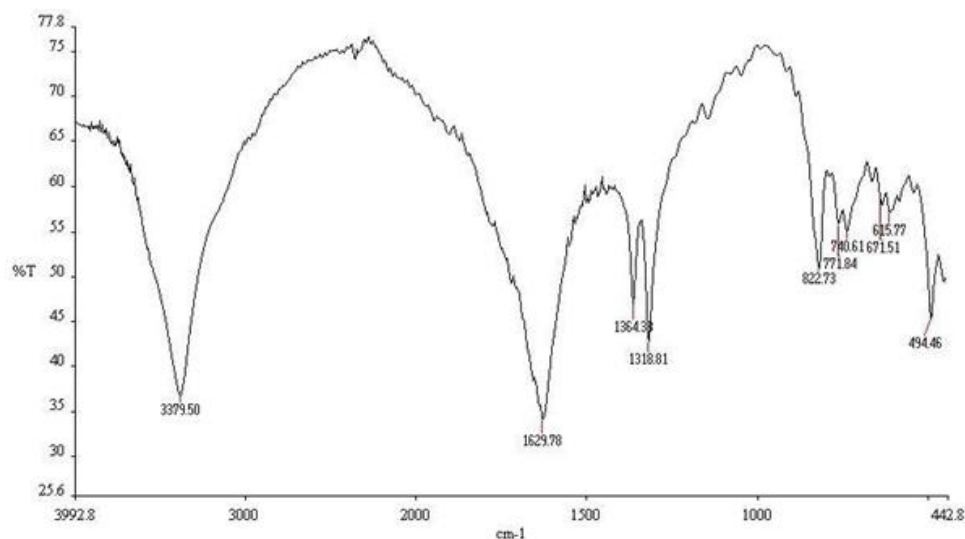


Figure 16. Infrared Spectrum of Zinc(II) Arabinarate with Azobenzene

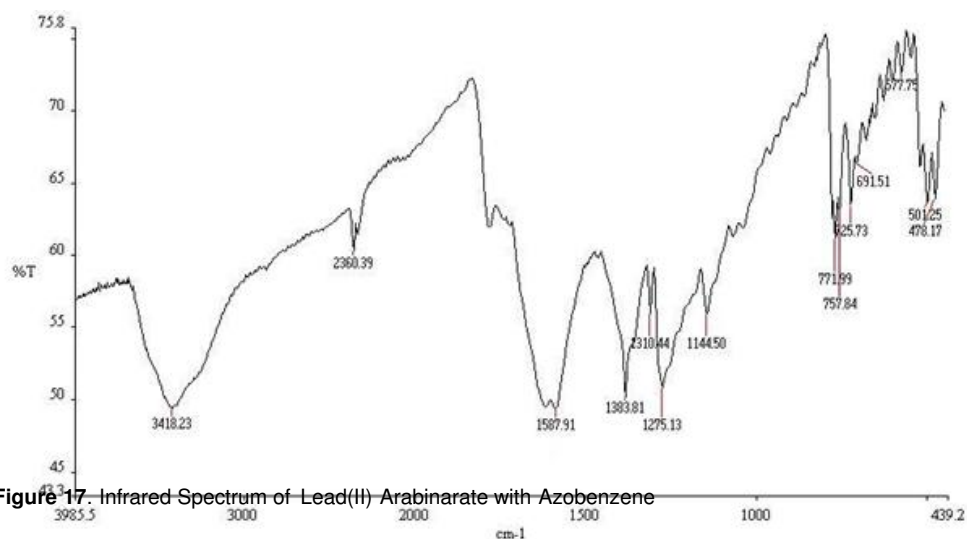


Figure 17. Infrared Spectrum of Lead(II) Arabinarate with Azobenzene

Iodine Inclusion

The solids obtained using zinc(II), lead(II), and copper(II) were all used in the treatment of iodine.

After exposing the complex polymers with iodine vapor in a sealed jar for 140 hours, the crystals become reddish in color. All kinds of polymers increased significantly in mass. The total iodine content of the polymers was determined using the titration of standard Na₂S₂O₃ solution using starch as the indicator. All titrations yielded clear end points.

The experimental data indicated that iodine is absorbed by the complex polymers and possibly incorporated in the crystal lattices. An average of 2.232×10^{-5} mole of I₂ or 5.664×10^{-3} grams of I₂ was incorporated per gram of zinc(II) arabinarate complex polymer. A gram of lead(II) arabinarate absorbs about 2.863×10^{-5} mole of I₂ or 7.267×10^{-3} grams of I₂. Copper(II) arabinarate traps significantly higher amounts of I₂. It yields 8.243×10^{-5} mole or 0.02092 grams of I₂ per gram. This is possible since copper(II) arabinarate is in powdered form and generally has larger surface area for adsorption. The result is summarized in Table 2.

Table 2. Amount of Iodine Absorbed by the Coordination Polymers

Samples	I ₂ Absorbed*
Zn polymer	2.232×10^{-5}
Pb polymer	2.863×10^{-5}
Cu polymer	8.243×10^{-5}

*values are expressed as mole I₂ per gram of complex polymer

Several hours after the titration of the suspensions containing the polymers, the blue color, which indicates the presence of iodine in the solution, reappeared. This observation suggests that iodine was not merely adsorbed at the surface of the polymers; rather, the iodine was absorbed or incorporated in the crystalline structure. The polymers continued to release iodine to the solution even after the completion of the titration.

Lead Inclusion through Column Elution

Since only the zinc(II) and lead(II) arabinarate coordination polymers produced crystalline products suitable for column elution, only these two coordination polymers were used in the lead ion inclusion experiments.

Atomic absorption spectrometric (AAS) analysis through external calibration method (ECM) of the lead(II) solutions after being eluted from the packed column of the coordination polymers indicated significant decrease in all of the three lead(II) concentrations, which implies significant incorporation of lead(II) ions by the coordination polymers. All analyzed samples yielded instrumental absorbances and hence, lead concentrations below the detection limit of the SpectrAA AAS instrument, which is 0.20 ppm Pb.

Based on the blank concentrations and the maximum amount of lead concentration in the eluted samples, which is 0.20 ppm Pb, the experimental data are also expressed in terms of unabsorbed lead, percent lead reduction, and lead uptake by the coordination polymers as shown in Tables 3 and 4.

Table 3. Mean Maximum Values of Unabsorbed Lead using the Coordination Polymers

Factor Levels	Unabsorbed Lead (ppm) ¹	Unabsorbed Lead (ppm) ²
Coordination Polymers (A)		
A1 (zinc arabinarate)		
A2 (lead arabinarate)		
Blank Lead Concentrations (B)		
B1	1.614	20.18
B2	3.228	40.35
B3	6.456	80.70
A x B Combinations		
A1B1	< 0.20	< 2.50
A1B2	< 0.20	< 2.50
A1B3	< 0.20	< 2.50
A2B1	< 0.20	< 2.50
A2B2	< 0.20	< 2.50
A2B3	< 0.20	< 2.50

1 these concentrations are based on the diluted solutions used in the analysis

2 corrected concentrations based on the original volume and concentrations

Table 4. Mean Minimum Values³ of Percent Reduction and Lead Uptake using the Coordination Polymers

Factor Levels	Percent Reduction (%)	Lead Uptake (mg Pb/g)*
Coordination Polymers (A)		
A1 (zinc arabinarate)		
A2 (lead arabinarate)		

Blank Lead Concentrations (B)

B1 (20.18 ppm)

B2 (40.35 ppm)

B3 (80.70 ppm)

A x B Combinations²

A1B1	> 87.6 ^c	> 1.04 ^d
A1B2	> 93.8 ^b	> 2.29 ^b
A1B3	> 96.9 ^a	> 4.74 ^a
A2B1	> 87.6 ^c	> 0.35 ^f
A2B2	> 93.8 ^b	> 0.75 ^e
A2B3	> 96.9 ^a	> 1.53 ^c
Grand Mean	> 92.77	> 1.783

¹ these concentrations are based on the diluted solutions used in the analysis

² corrected concentrations based on the original volume and concentrations

³ Means with each factor or factor combination followed by a common letter are not significantly different at alpha = 5% based on DMRT

* milligrams Pb per gram of coordination polymer

All samples showed relatively high minimum percent reduction of lead even after several volume and concentration corrections. Among the six treatment combinations, A1B3 and A2B3 had the highest minimum percent lead reduction (96.9 %) since all of the above data are based only on the minimum percent lead reduction. The actual reduction cannot be obtained since all concentrations are below the instrumental detection limit. Since A1B3 and A2B3 had the highest initial lead concentrations, naturally they would produce the highest lead reduction.

Metal uptakes (mg Pb²⁺/g polymer) as influenced by the initial lead concentration and mass of the coordination polymer were significantly different from each other at 5% level using the Duncan's Multiple Range Test (DMRT) (Table 4). Statistical analysis of the interactions between the two factors showed that the highest uptake of lead was exhibited by treatment A1B3 (Table 4, Figure 18), the treatment using zinc(II) arabinarate coordination polymer. Obviously, zinc(II) polymers will have higher lead uptake than lead(II) polymers because zinc (65.39 g/mol) is much lighter compared to lead (207.2 g/mol). For a given mass of a compound, zinc compounds will contain more particles than that of lead compounds.

Results imply that zinc(II) and lead(II) arabinarate coordination polymers are especially useful in incorporating lead ions in aqueous solutions.

The bidentate arabinarate anion, the conjugate base of arabinaric acid, which is derived from L-arabinose, can chelate and bind with metal ions such as zinc(II) and lead(II) to form coordination polymers containing channels in the crystal lattices. The channels that are possibly formed can indeed trap and include heavy metal lead ions and can be used in bioremediation treatments. The removal of lead ions in the aqueous solutions can also be enhanced by adsorption effects by the solid polymers.

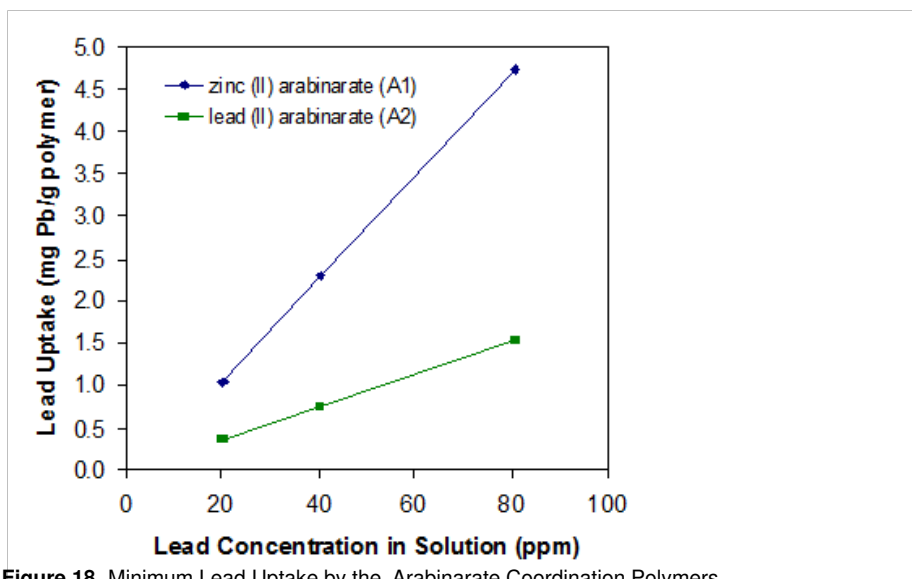


Figure 18. Minimum Lead Uptake by the Arabinarate Coordination Polymers

SUMMARY

L-Arabinose was oxidized using warm HNO₃ to form arabinaric acid. The arabinaric acid was made to react, chelate, and polymerize with several metal ions. Among the metal ions, only zinc(II), lead(II), and copper(II) ions produced insoluble coordination compounds with arabinaric acid. Zinc(II) and lead(II) ions produced crystalline coordination polymers while copper(II) yielded gummy precipitates.

Preliminary characterization of the coordination polymers based on their solubility, melting points, UV-Visible spectra, and infrared spectra was investigated. The coordination polymers seemed to be insoluble in some common organic solvents and in acidic aqueous solutions. However, they are soluble in basic solutions particularly at pH 12. The melting points of the zinc(II) and lead(II) arabinarate coordination polymers were above 300°C while that of copper(II) was in range of 218–225°C. The determination of the UV-Visible spectra using basic 200 ppm aqueous solutions of the three coordination polymers showed that the maximum wavelengths were in the ultraviolet region. Zinc(II), lead(II), and copper(II) arabinarate coordination polymers had maximum absorbance at $\lambda_{\text{max}} = 217 \text{ nm}$, $\lambda_{\text{max}} = 240 \text{ nm}$, and $\lambda_{\text{max}} = 220 \text{ nm}$, respectively. The determination of the infrared spectra of the three coordination polymers showed strong bands at 3350–3450 cm^{-1} , 1600–1750 cm^{-1} , 1290–1390 cm^{-1} and 820–920 cm^{-1} , which indicate the presence of O–H, C=O, C–O, and the interaction with metal ions, O–M groups, respectively.

The potential of the coordination polymers to incorporate azobenzene and molecular iodine was also investigated. The coordination polymers showed the possibility of the inclusion of organic compounds in the crystalline structure. The inclusion results manifested the successful incorporation of the organic compounds and the possibility of having channels in the polymeric structure. The change in the infrared bands below 1000 cm^{-1} of the infrared spectra of the coordination polymers treated with molten azobenzene, the discoloration and increase in mass of the polymers, and the continuous and gradual discharge of I₂ in aqueous suspensions seemed to confirm the possibilities.

Crystalline zinc(II) and lead(II) arabinarate coordination polymers were found to absorb significant amounts of lead present in aqueous solutions. Considerable lead concentration reduction of up to 80.70 ppm of lead(II) was observed on the different lead solutions eluted from the coordination polymers packed in a column using the blank samples and AAS analysis.

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