Development of polymeric chelating ligands for removal of heavy metals from water

Prince N.A. Amoyaw
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DEVELOPMENT OF POLYMERIC CHELATING LIGANDS FOR REMOVAL 
OF HEAVY METALS FROM WATER

Advisor: Dr. James Bu

Dissertation dated December 2008

Poly[4-(4-vinylbenzyloxy-2-hydroxybenzaldehyde)] and Poly[1-(2-pyridyl)-3-[4-(4-vinylbenzyloxy)phenyl]imidazo(1,5-a)pyridine-co-methacrylate] were synthesized and characterized and have been evaluated to be effective sorbent materials for the removal of heavy metals from aqueous solution. Batch adsorption experiments were performed for several divalent metal ions, namely Pb$^{2+}$, Cd$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Zn$^{2+}$ and Co$^{2+}$. Preliminary batch adsorption screening test revealed that the adsorbents being evaluated had the highest adsorption capacities for Pb and Cd ions, hence they were studied in much greater detail. Upon applying the equilibrium data to the Langmuir and Freundlich isotherm models, the adsorption of the Pb ions on both the polymer and the copolymer fitted well to the Langmuir model. This means that there occurred homogeneous and complete monolayer coverage of the Pb$^{2+}$ ions on the polymer surface as well as on the copolymer surface.
Two kinetic models, pseudo-first-order and pseudo-second-order were also tested to investigate the adsorption mechanisms and the kinetics was found to be second order and equilibrium adsorption occurred within 15 seconds. This suggests that the adsorption sites are either near the adsorbent or on the adsorbent surface therefore the metal ions have easy access to them thereby resulting in a high frequency of collision between the metal ions and the adsorption sites. The metal removal was also found to be strongly dependent on pH and this is reflected in the gradual increase in percent adsorption as pH increases from 1.0 to 5.5.
DEVELOPMENT OF POLYMERIC CHELATING LIGANDS FOR REMOVAL OF HEAVY METALS FROM AQUEOUS MEDIA

A DISSERTATION

SUBMITTED TO THE FACULTY OF CLARK ATLANTA UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

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DEPARTMENT OF CHEMISTRY

ATLANTA, GEORGIA

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CHAPTER 1
INTRODUCTION

A modern high technology society depends on the availability of many metallic elements. This is because the metallic elements are the most numerous of the elements and their chemical properties are central to both industry and contemporary research. Metals have played a major role in the development of civilization because modern societies rely on a large variety of metals for making tools, machines and other items. It is against this background that metals serve many important roles in industry and in biology (1).

Since the advent of the industrial revolution, mining technologies have allowed the extraction of large quantities of metals. Other industrial activities have also transferred them to the environment at rates and concentrations not produced by nature. The consequences impact both human health and ecological systems.

Redistribution of these metals by human industrial activities constitutes a major health hazard (2). Contamination of soil by heavy metals is common at many hazardous waste sites in many developed nations (3). Cadmium, copper, lead, mercury, nickel and zinc are considered the most hazardous heavy metals and are included on the U.S. Environmental Protection Agency’s (EPA’s) list of priority pollutants (4). In technologically developed societies, the widespread use of heavy metals in a diverse number of applications, including pigments, coatings, electronic equipments, etc., has led
to a surfeit of heavy metal-contaminated materials in municipal disposal sites and ground water (5).

The potential source of copper in industrial effluents include metal cleaning and plating baths, pulp, paper and paper board mills, wood pulp production, and the fertilizer industry (6). Copper ions are essential nutrients but when humans are exposed to copper levels above 1.3 mg/L for a short period of time, stomach and intestinal problems occur and long term exposure to copper leads to kidney and liver damage (7-9). Excessive intake of copper results in an accumulation in the liver. It is also toxic to aquatic organisms even at very low concentrations in natural water (6).

Mercury is one of the most dangerous heavy metals. It can be introduced into the natural environment from a variety of sources and it is converted into the more toxic form, methyl mercury, by aquatic living organisms, and accumulated in the tissue of fish (10). What makes mercury even more dangerous is its ability to bioaccumulate in living organisms. For instance, when a fish feeds on a marine or aquatic organism that had consumed methyl mercury contaminated plankton, the methyl mercury is not excreted but instead, it is retained in its tissues. When this fish is preyed upon by another fish or another marine predator, the accumulated methyl mercury in the fish is passed on to the predator and in a similar fashion the methyl mercury is passed on up the food chain until eventually the concentration of the methyl mercury becomes far higher than its initial concentration (10). For this reason therefore, any organism at the top of the food chain i.e. humans, polar bears, etc. faces a serious risk of mercury poisoning upon eating such a
fish (11). Mercury has very high tendency to bind to protein and it mainly affects the renal and nervous system (12).

The disease known as “Minamata” is caused by mercury poisoning as a result of eating mercury contaminated fish (11). In humans, the initial symptoms include numbness of the lips and limbs. As the illness progresses, permanent damage is done to the central nervous system and the victim experiences visual constrictions, loss of motor coordination, and in the final stages prior to death, loss of memory, speech, hearing and taste.

Zinc ions are frequently encountered in industrial wastewaters (e.g., from mining, metal cleaning and electroplating) (13). Although zinc is essential for proper functioning of the brain, excess zinc in the brain is toxic to cells. Therefore, precise control of zinc levels within cells is crucial for health (14).

Chromium occurs in liquid wastes in two forms: trivalent and hexavalent. Chromium(VI) is toxic and known to be carcinogenic (15). It is also known that chromium(VI) is commonly present in wastewater emanating from dye, electroplating, leather and mining industry (16). The limit for liquid wastes discharged into the sea is 1 mg/L. For chromium(III), it is a practice to keep the concentration below 4 mg/L (17). In fact, the presence of chromium in the effluent is a major concern for the tanning industry (18). Basic chromium sulfate (BSC) is a tanning agent, which is employed by 90% of the tanning industry.

Conventional chrome tanning results in wastewater containing as high as 1,500-3,000 ppm (parts per million) of chromium (19). However, present day high exhaust
Chromium tanning methods lead to a wastewater containing 500-1,000 mg/L of chromium. Chromium has low, acute and chronic toxicity to humans at high doses. In its trivalent form, it is an essential trace element when present at the micro level (18) but in excess it is proven to be a potential soil, surface water, groundwater, and air contaminant under specific conditions (20).

Cadmium is highly toxic to humans but less toxic to plants. During the past few years, some attention has been paid to the removal of cadmium and the significance of this element as a potential contributor to environmental damage. According to the action program of the European Community, Cadmium contents of the industrial effluents should be lower than 0.2 (new installations) or 0.3 mg/L (existing installations) (EC, 1991). For this reason, the development of a process for cadmium removal should be given high priority (15).

Lead is the most commonly encountered toxic metal pollutant in the environment because of its current and previous use in, for example, batteries, gasoline, plumbing and paints (21, 22). A considerable effort is being made in the research community in diverse ways to address this environmental problem (23), by way of either continuously reducing its concentration or totally removing it from water and air (24).

There is a considerable need to develop selective ligands for remediation of lead ion (25). Lead interferes with the metabolism and action of essential metals such as calcium, iron and zinc (26-28). The ability of lead(II) to undergo metathesis reactions with zinc(II) and calcium(II) metalloproteins resulting in loss of metabolic function continues to be a primary concern underlying the detrimental effects of lead exposure.
Despite the removal of lead from gasoline and household paint over two decades ago, lead poisoning continues to be the most common environmentally caused illness in children in the United States (31-33). The Centers for Disease Control estimates that in 2001 approximately 454,000 children suffered from elevated blood lead levels (defined as ≥ 10 µg/dL or ≥ 0.5 µM) (34-35). Recent studies have shown that lead has detrimental physiological effects in children at levels less than 5 µg/dL (36). In general, patients with lead poisoning have total blood lead levels that are in the micromolar range (37) and a wide range of symptoms associated with lead poisoning suggests that lead affects multiple targets in vivo (37).

The presence of these heavy metals in the environment as well as their increased discharge, coupled with their toxic nature and other adverse effects (38) on receiving waters has heightened societal concerns so much that many researchers have been prompted to investigate various possible materials which could be used as heavy-metal removal agents (39). Because of the continued increase in the world’s demand for most of these metals, it has become necessary to identify effective and efficient methods for processing waste solutions containing metal ions, even at very low concentrations, so that the water can be recycled. Hydrometallurgical processing (40-43), process-water and waste water detoxification, as well as potable-water production are other applications in which metal removal is required. It is for this reason that the development of chelation materials with specific binding abilities toward heavy metals has received considerably immense attention in recent times (44).
Various methods such as ion exchange, precipitation, adsorption and complexation (45-47) are used for removing heavy metals. Among these, adsorption with reagent impregnated resins, metal-loaded chelating resins, (48-51) and polymer supported chelating agents have become increasingly popular during the last two decades. The objective of this present work is to develop polymer-supported chelating agents and to investigate their adsorption characteristics for heavy metal removal from aqueous solutions.
CHAPTER 2

BACKGROUND

2.1. Heavy Metals

Heavy metals are generally considered to be those metals whose density exceeds 5 grams per cubic centimeter (52). The term “heavy metal” is often used as a group name for metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or ecotoxicity (52, 53). A large number of elements fall into this category, but arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), tin (Sn), vanadium (V) and zinc (Zn) are those of relevance in the environmental context (52, 54).

Heavy metals produce a number of toxic effects: hindering neurological development and function, and interfering with metabolism (53). For this reason, there is a growing demand for the remediation of heavy metal pollution (54-57). Currently, there are a number of ongoing studies focused on the synthesis of different kinds of ligands with potentially greater affinity and selectivity for toxic metal ions.

2.2. Ligands

The term ligands as applied to transition metal receptors is defined as a Lewis base that donates a pair (or pairs) of electrons to the metal via a coordinate covalent bond.
or ions that surround the metal ions in a complex. Ligands are normally either anions or polar molecules. They usually have at least one unshared pair of valence electrons (58-60). Because ligands have unshared pairs of electrons they can function as Lewis bases (electron-pair donors) and because metal ions (particularly transition metal ions) have empty valence orbitals, they can act as Lewis acids (electron-pair acceptors). Hence the bond between a metal ion and a ligand is visualized as the result of their sharing of a pair of electrons that was initially on the ligand (61).

In general, π-donor ligands stabilize high metal oxidation states by donating electron density to the metal and π-acceptor ligands stabilize low oxidation states by delocalizing the metal electron density (62).

2.2.1. Types of Ligands

2.2.1.1. Monodentate Ligands. Monodentate ligands or one-toothed ligands possess a single donor atom and they are able to occupy only one site in a coordination sphere. This is exemplified by NH₃.

2.2.1.2. Bidentate Ligands. These ligands are two-toothed ligands and they occupy two coordination sites (63). Some common bidentate ligands are shown below:
2.2.1.3. **Polydentate Ligands.** Polydentate or many-toothed ligands are those ligands that have two or more donor atoms that can simultaneously coordinate to a metal ion, thereby occupying two or more coordination sites. Polydentate ligands are also known as chelating ligands (63, 64).

2.2.1.4. **Ambidentate Ligands.** An ambidentate ligand is a ligand with different donor atoms. This is exemplified in the thiocyanate ion (NCS⁻) which can attach to a metal atom either by the N atom to give isothiocyanate complex or by the S atom to give thiocyanate complexes. Another example of an ambidentate ligand is NO₂⁻ which can attach to a metal atom either by the N (as in M-NO₂) when the ligand is called nitro or can attach by O (as in M-ONO⁻) when the ligand is called nitrite (62, 64).

The existence of ambidentate ligands give rise to the possibility of linkage isomerism, in which the same ligand may link through different atoms. This type of isomerism accounts for the red and yellow isomers of the compound [Co(NO₂)(NH₃)₅]²⁺.
The red compound has a nitrito Co-O link whereas the yellow compound or isomer has a nitro Co-N link as shown in the structures below (64).

2.2.1.5. Chelating Ligands

Polydentate ligands that have two or more donor atoms that can simultaneously coordinate to a metal ion, and occupy two or more coordination sites are referred to as chelating agents because they apparently grasp the metal between two or more donor atoms. Chelating ligands form more stable complexes than do related monodentate ligands since dissociation of the complex involves breaking two bonds rather than one. This is illustrated by the formation constants for \([\text{Ni(NH}_3\text{)}_6]^2+\) and \([\text{Ni(en)}_3]^2+\) as shown below (65):

\[
[Ni(H_2O)_6]^{2+}_{(aq)} + 6H_3N_{(aq)} \rightarrow [Ni(NH_3)_6]^{2+}_{(aq)} + 6H_2O; \quad K_f = 4 \times 10^8
\]

\[
[Ni(H_2O)_6]^{2+}_{(aq)} + 3\text{en(aq)} \rightarrow [Ni(\text{en)}_3]^{2+}_{(aq)} + 6H_2O; \quad K_f = 2 \times 10^{18}
\]

Although the donor atom is nitrogen in both instances, \([\text{Ni(en)}_3]^2+\) has a formation constant of nearly \(10^{10}\) times larger than that of \([\text{Ni(NH}_3\text{)}_6]^2+\). The generally larger formation constants for polydentate ligands as compared with the corresponding
monodentate ligands is known as the chelating effect. Chelate compounds are even more stable when they contain a system of alternative double and single bonds. The electron density is localized and spread over the ring which is stabilized by resonance (62, 65).

Examples of this include acetylacetone and porphyrin complexes with metals.

Scheme 1

Chelating agents may be roughly divided into two classes depending on whether they form water-soluble chelates or whether they form metal chelates which precipitate. The former are called sequestering agents which means to remove or set apart or separate and they are used in aqueous solutions for the effective removal of objectionable metal ions (63, 64, 66).

2.3. Polymer Containing Chelating Ligands or Polymer-supported Reagents

Alexandrados and coworkers highlighted on ligands that have been immobilized on polymers to form polymer-supported reagents which are selective for the complexation of target metal ions from multicomponent solutions. Polystyrene remains the most popular organic polymer support, and its synthesis by suspension polymerization yields beads with a diameter appropriate for large scale applications. Immobilized ligands include amines, pyridines, imidazoles, oximes, hydroxylamines, Schiff bases, thiols, crown ethers and a variety of phosphorus ligands (67).
Two techniques which have found widespread use in both remediation and pollution prevention are solvent extraction and ion exchange. In solvent extraction, a compound capable of interacting with the target ion through ion exchange or other mechanism of complex formation is contacted with an aqueous solution containing the target metal ion. The extractant, which may be dissolved in an organic solvent, brings the metal ion into the organic phase as the interaction occurs. After the organic phase has been loaded with metal ions, the phases are allowed to separate and the metal is recovered by treatment with an appropriate stripping solution. The recovered metals can then be recycled or disposed in a safe manner (68).

A wide variety of compounds have been synthesized and utilized for selective metal ion extractions. Two of the more common extraction agents are bis(2-ethylhexyl) phosphoric acid which has been used for uranium (69) and rare earth recovery (70) and tri-n-butyl phosphate which, in addition to other applications, is used in nuclear plants to separate uranium and plutonium from spent fuel (71).

Solvent extraction is a popular technique due to its versatility, rapid rates of extraction, and the high degree of selectivity which may be attained. However, this method is not economical (72) with dilute solutions due to the large volumes of liquid which must be handled. A more serious problem is that most extractants have a finite solubility in water. Loss of extractant increases the operating cost of the system in addition to the difficulties caused by the introduction of a potentially toxic compound into the aqueous phase. The advantage gained by recovery of a toxic metal can be offset by introducing a toxic organic chemical into the treated stream.
In ion exchange with polymer-supported reagents, the loss of extractant to the aqueous phase is avoided since the ligands are covalently attached to an insoluble organic or inorganic polymer. The aqueous phase is passed through a column containing the polymer (73); an ion exchange resin removes the metal by replacing it with an ion such as H⁺ or Ca²⁺ while a chelating resin removes the metal through complex formation (74). It is worth noting that the recovery of the metal ion and regenerability of the polymer are very important aspects of the overall study and can often be the deciding factors in whether a resin will be used under process conditions. With cation exchange resins, elution with a strongly acidic solution may be all that is needed to recover the metal ion. The more selective the resin, however, the less likely it is that a simple acid will permit regeneration, thus requiring more expensive regenerants such as ethylenediaminetetraacetic acid, EDTA or 1-hydroxyethane-1,1-diphosphonic acid. Unlike solvent extraction systems, ion exchange works well with dilute solutions since the volume of an exchanger does not have to be increased. In general, ion exchange resins can be loaded and regenerated many times without a significant loss of capacity (74). Even though the initial cost of a polymeric reagent can be high, the recyclability of the polymer makes the process economical (75).

2.3.1. Synthesis of Polymer Supported Reagents

A major advance in the production of synthetic ion exchange resins was the production of cross-linked supports via free-radical copolymerization of vinyl monomers with divinyl cross-linking agents (76-80). Helfferich et al. prepared spherical ion exchange particles by suspension copolymerization with these monomers. In suspension
polymerization, a mixture of an organic phase (containing vinyl monomer, divinyl cross-link agent, and free radical initiator) and an aqueous phase containing suspension stabilizers is stirred to produce a suspension of organic droplets in the aqueous layer (73).

Polystyrene beads cross-linked with divinylbenzene prepared by suspension polymerization are most often used to immobilize ligands due to their chemical versatility and the ease with which their physical properties can be varied. The aromatic ring of the styrene unit is easily transformed into a wide variety of chemical structures and the physical properties of the network can be controlled by the amount of cross-linking agent present and the degree of porosity introduced into the network.

2.3.1.1. Ion Exchange Resins

The most widely used cation exchange resin is the polystyrene-supported sulfonic acid resin 1. The sodium salt of this is used in household and industrial water softening systems for the removal of iron, manganese, calcium, and magnesium. The hydrogen form is used in conjunction with an anion exchanger in the hydroxide form 2 to deionize water. While efficient in removing cations, the sulfonic acid resin is nonselective due to a narrow range of reaction free-energy values for the exchange with various metal ions (80). As a result, the sulfonic acid resin cannot be used to separate trace amounts of a given metal ion from high concentrations of others.
The carboxylic acid resin 3 is prepared by suspension polymerization of acrylic or methacrylic acid esters followed by hydrolysis to the carboxylic acid (73). While more selective than the sulfonic acid resin, the carboxylate ligand is less acidic, thus limiting its usefulness in low pH environments.

2.3.1.2. Reactive Ion Exchange. The mechanism by which selectivity can be designed into ion exchange resins was first developed by Helfferich where the concept of ion exchange occurring concurrently with chemical reactions of the metal ion was treated theoretically (81). Neutralization, hydrolysis, and complexation were sited as the reactions which could accompany ion exchange. This process was categorized into four types.

In type I processes, counterions released by the ion exchanger reacted with co-ions in solution. Type II processes had solution counterions reacting with the immobilized exchange sites on the polymer; type III processes started with undissociated polymeric exchange sites which were then ionized by reaction with solution co-ions; and in type IV processes, undissociated polymeric exchange sites were converted from one undissociated form to another by reaction with the solution co-ion. This was later extended by Janauer, who coined the term “reactive ion exchange” (82, 83).

According to Janauer, because of the rather modest free energy changes associated with conventional ion exchange, chemical reactions such as oxidation, reduction, formation of sparingly soluble compounds, neutralization, and others, including traditionally used ion complexing and chelating reactions may be employed to
"drive" ion exchange processes in the direction needed such that the greater ΔG of a chemical reaction imparts its own free energy bias on the overall process (82).

2.3.2. Types of Polymer-Supported Reagents

The production of polymer-supported reagents relies on the bonding of chelation groups to the polymer matrix. Whether a given resin is selective or nonselective depends on the reaction free-energy values (84).

2.3.2.1. Amine Ligands

The use of amine-containing polymers for selective separation was exemplified in the work done by Chanda et al. when they produced a resin 4 by a reaction of poly(ethyleneimine) with poly(vinyl benzaldehyde) .

\[ \text{Resin } 4 \]

This resin has a high selectivity for Fe\(^{3+}\) over Cu\(^{2+}\), Ni\(^{2+}\), Co\(^{2+}\), Zn\(^{2+}\) and Mn\(^{2+}\).

A polymer with amino groups bound directly to the backbone was also obtained by copolymerization of the vinylamine precursor N-vinyl-\textit{tert}-butylcarbamate with styrene, methyl methacrylate, or methacrylic acid and a cross-linking agent. The styrenic resin was selective for copper over lead and cadmium (85-95).
2.3.2.2. Pyridine and Imidazole Ligands

Grinstead et al. obtained polymeric picolylamine 5 which exhibited good selectivity for copper as does supported 8-hydroxyquinoline 6 synthesized by Warshawsky and coworkers (96-98).

Lindsey et al. prepared polymer-bound 2-pyridyl-2-imidazole and 2-aminomethylpyridine which are capable of separating Cu$^{2+}$ from Zn$^{2+}$ (99). An acrylic resin containing both sulfur and an imidazole group 7 was selective for Cu$^{2+}$ over Ni$^{2+}$, Zn$^{2+}$, and Cd$^{2+}$ (100) while a chelating resin containing pyridine units 8 was found to be selective for Fe$^{3+}$ (101).

2.3.2.3. Amine/Carboxylic Acid Ligands

Polymers from N-(4-carboxy-3-hydroxyphenyl)maleimide 9 are selective for Ni$^{2+}$, Fe$^{3+}$, and Pb$^{2+}$ over Ca$^{2+}$, Cr$^{3+}$, Cu$^{2+}$, Zn$^{2+}$, and Cd$^{2+}$ (102).
2.3.2.4. Oxime, Hydroxylamine, and Schiff Base Ligands

Chanda et al. prepared poly(vinylbenzaldoxime) 10 which is selective for Fe$^{3+}$ over Mn$^{2+}$, Cu$^{2+}$, Fe$^{2+}$, Ni$^{2+}$, Co$^{2+}$, and Zn$^{2+}$ (93).

Srivastava and Rao also obtained salicylaldoxime-form-aldehyde resin 11 which showed the affinity series Pb$^{2+}$ ≈ Zn$^{2+}$ ≈ Ni$^{2+}$ > Cu$^{2+}$ > Cd$^{2+}$ > Pd$^{2+}$ > Mn$^{2+}$ > Fe$^{2+}$ > Co$^{2+}$ at pH 8 (103).

2.3.2.5. Sulfur-Based Ligands

In general, sulfur-containing polymers are selective for heavy metal ions. Sahni and Reedijk prepared the thiol resin 12 which was found to be highly selective for
mercury (74). Also the aminophenol resin containing dithiol units 13 had a high selectivity for Ag, Hg, Pt, and Pd (104,105).

2.4. Polymer-Supported Membrane Sorbents

Functionalized membranes have also been used for the sorption of heavy metals from solutions. For instance, one research group (106-108) has performed work in this area by attaching monomeric-to-trimeric chelation groups by plasma-induced radiation grafting. These membrane sorbents have been shown to have a capacity as high as 2.4 mg/g (109) and have better overall mass-transfer characteristics than ion-exchange columns. Bhattacharyya et al. used membrane-based pure cellulose, cellulose acetate, modified polysulfone, and polyethylene-silica composites by taking advantage of the multifunctional ligands for metal capture using a single-point attachment (e.g., amino group) via an aldehyde or an epoxide on the membrane surface. Poly amino acids (PAMs) such as poly(L-glutamic acid) (PLGA), poly(aspartic acids) (PAA), and polyarginine, have also been immobilized on these membranes (110-113) and it was found out that, depending on the molecular weight and loading, metal sorption capacities as high as 27 mg/g can be obtained.

2.5. Surface and Adsorbed Species

When a molecule, for example, a metal ion approaches a surface (adsorbent surface), it encounters a net attractive potential that is similar to the potential between two molecules. The adsorption of a molecule on a solid surface is always an exothermic process. If the adsorbate is represented by A and the adsorption site on the surface is
represented by S, then the process of adsorption can be represented as a chemical reaction (114, 115)

$$A + S \rightarrow AS \quad \Delta_{ads}H < 0$$

where $\Delta_{ads}H$ is the enthalpy of adsorption.

2.5.1. Physisorption and Chemisorption

The forces causing physical adsorption are van der Waals forces. The heat evolved in a physisorption process is of the order of magnitude of the heat evolved in the process of condensing a gas. The extent of physisorption is smaller at higher temperatures. Equilibrium in physical adsorption is generally achieved rapidly and is readily reversible. Physical adsorption is also reversed by raising the temperature of the surface (115).

On the other hand, however, chemisorption involves the formation of chemical bonds and the enthalpy change is much larger than that for physisorption. Physisorption and chemisorption can be distinguished by the rates at which the processes occur. Chemisorption may not occur at an appreciable rate at a low temperature if the chemisorption reaction has activation energy. In this case therefore, the rate of chemisorption increases rapidly with increase in temperature (115, 116).

2.6. Adsorption Isotherm Models

Several approaches have been used to describe the model adsorption reactions. Until, recently, adsorption phenomena were modeled using an adsorption isotherm approach in which the total amount of adsorbed species is modeled as a function of
equilibrium solution concentration of the species. This type of data can be fitted to an adsorption isotherm such as the Langmuir or Freundlich model (117-120). Such approaches give valuable insight into the capacity of surfaces to retain a species but the empirically based fitting parameters have no modeling value beyond the range of experimental conditions in which they were determined (117-120).

The distribution of divalent cations between the liquid phase and the adsorbent is a measure of the equilibrium conditions in the adsorption process and can generally be expressed in terms of the two most popular isotherm models, namely, the Langmuir and the Freundlich isotherms (117-120). Hence, to analyze the experimental data at equilibrium, these models are tested (120).

2.6.1. Langmuir Isotherm Model. The Langmuir isotherm model is based on the assumption of complete monolayer coverage on a surface containing a finite number of adsorption sites of uniform energies of adsorption. The equilibrium data analyzed in accordance with the Langmuir (120) sorption isotherm gives the linear expression of the form

\[ \frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \left(\frac{1}{Q_m}\right)b \]

(1)

2.6.2. Freundlich Isotherm Model. The Freundlich isotherm model which assumes that different sites with different adsorption energies are involved, is tested to explain the sorption equilibrium data using the expression
\[ Q_e = \frac{x}{m} = KC_e^{1/n} \quad (2) \]

or

\[ \log Q_e = \frac{1}{n} \log C_e + \log K \quad (3) \]

where \( x \) is the amount of adsorbate sorbed, \( m \) is the mass of the adsorbent, \( C_e \) is the equilibrium sorbate concentration in aqueous solution and \( Q_e \) is the sorption capacity (119).

### 2.7. Kinetic Models of Adsorption

Kinetics is a very important aspect in the evaluation of sorption as a unit operation. The kinetic constants of metal sorption could be used to optimize the residence time for a column designed to treat industrial wastewater. Functional groups such as aldehydes, ketones, acids and phenolics can be involved in chemical bonding and are therefore responsible for the cation exchange capacity of the adsorbent. Thus the adsorbent-metal reaction may be represented in two ways (121)

\[ 2P^- + M^{2+} \rightarrow MP_2 \quad (4a) \]

and

\[ 2HP + M^{2+} \rightarrow MP_2 + 2H^+ \quad (4b) \]

where \( P^- \) and \( HP \) are polar sites on the adsorbent surface.

To investigate the rate of adsorption of metals onto an adsorbent, two simple kinetic models, namely, the pseudo-first order and the pseudo-second order models were tested (122-123).
2.7.1. Pseudo-First-Order Equation. A simple kinetic analysis of adsorption can be performed with a pseudo-first order equation (122) of the form

\[
d\frac{Q}{dt} = k_1(Q_e - Q_t)
\]

where \(k_1\) (sec\(^{-1}\)) is the rate constant of pseudo first order adsorption, \(Q_e\) (\(\mu g\cdot g\)\(^{-1}\) of dry weight) is the amount of metal ion sorbed at equilibrium, and \(Q_t\) (\(\mu g\cdot g\)\(^{-1}\) of dry weight) is the amount of metal ion sorbed at any time \(t\) (sec). By applying the boundary condition \(Q_t = 0\) at \(t = 0\), equation (1) becomes

\[
\ln(Q_e - Q_t) = \ln Q_e - k_1t
\]

This rate expression is also known as the Lagergren first-order equation and can be expressed as

\[
\log(Q_e - Q_t) = \log Q_e - k_1t/2.303
\]

The value of \(k_1\) can be determined experimentally by the slope of the linear plots of \(\log(Q_e - Q_t)\) versus \(t\).

2.7.2. Pseudo-Second-Order Equation. A kinetic analysis to verify pseudo-second order adsorption can also be performed on the experimental data. For the sorption described by equations (4a) and (4b), the rate expression is (122):

\[
\frac{d(P)_t}{dt} = k[(P)_0 - (P)_t]^2\]

or

\[
\frac{d(HP)_t}{dt} = k[(HP)_0 - (HP)_t]^2\]
where \( (P)_t \) and \( (HP)_t \) are the number of active sites occupied on the adsorbent, \( P \), at time \( t \),

\( (P)_0 \) and \( (HP)_0 \) are the number of equilibrium sites available on the adsorbent.

The kinetic rate equation can also be written as (122, 123).

\[
\frac{dQ_I}{dt} = k(Q_e - Q_t)^2
\]  

(10)

where \( k \) (g/\( \mu \)g.sec) is the rate constant \( (k_2) \) of pseudo-second-order adsorption, \( Q_e \) (mg/g) is the amount of metal ion sorbed at equilibrium, \( Q_t \) (mg/g) is the amount of metal ion on the surface of the sorbent at any time \( t \). Separating the variables in equation (10) gives

\[
\frac{dQ_t}{(Q_e - Q_t)^2} = k dt
\]  

(11)

Integrating this for the boundary conditions \( t = 0 \) to \( t = t \) and \( Q_t = 0 \) to \( Q_t = Q_t \) gives

\[
\frac{1}{(Q_e - Q_t)} = \frac{1}{Q_e} + kt
\]  

(12)

which is the integrated rate law for a pseudo-second order reaction.

Equation (12) can be rearranged to obtain

\[
Q_t = \frac{t}{1/kQ_e^2 + t/Q_e}
\]  

(13)

which is of the form

\[
\frac{t}{Q_t} = \frac{1}{kQ_e^2} + \frac{1}{Q_e} t
\]  

(14)

If the initial sorption rate, \( v_0 \) (\( \mu \)g/g.sec) is

\[
v_0 = kQ_e^2
\]  

(15)
then equation (14) becomes

$$\frac{t}{Q_t} = \frac{1}{v_0} + \frac{1}{Q_e} t$$  \hspace{1cm} (16)

The values of $v_0$ and $Q_e$ can be determined experimentally by the intercept and slope of the linear plots of $t/Q_t$ versus $t$.

2.8. Instrumental Methods of Analysis

Even though flame and graphite furnace Atomic Absorption Spectrometry (AAS) have long been used because of their sensitivity and relatively low cost for the study of several elements, Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) and more recently Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), have proved to be valuable in combining multi-element capability and sensitivity (124). The detection by ICP-MS has been a much better choice for the study of metal speciation in biological samples and for trace metal analysis. For instance, the multi-element capability of ICP-MS for this kind of speciation was demonstrated in work on cadmium, copper, and zinc metalloproteins in biological samples from which metal-binding proteins were extracted from a marine invertebrate (127). The analytes were separated on a reverse-phase column, and the column effluent was directed through the ICP-MS. In addition, the ratios of two cadmium isotopes, $^{109}\text{Cd}$ and $^{114}\text{Cd}$, in the column effluent were studied (125-127).
2.8.1. Atomic Absorption Spectrometry

Although simplicity, rapidity and specificity have made atomic absorption, a standard method in water analysis, often times, solution must be concentrated by means of freezing, evaporation, ion exchange, and solvent extraction prior to measurement (128).

Atomic absorption is routinely used for direct determination of sodium, potassium, calcium, magnesium, and several trace metals such as strontium, lithium, manganese, copper and zinc in natural waters (129). There is ordinarily no need to concentrate these elements since most waters contain detectable amounts. However, certain other trace elements such as cobalt, nickel and lead normally occur in fresh waters at concentrations less than can be detected by atomic absorption directly.

In fact, the concentration of certain metals in many industrial water applications need to be maintained and controlled below the practical limit of detectability by atomic absorption. For instance, in modern high pressure boiler operations, the desired limit for iron, copper and zinc in the boiler feed water cycle is usually less than 5-10 µg/L.

The concentration of lead in drinking water should be less than 50µg/L. Therefore, when the metal or metals of interest are present in the low concentration range, the constituents to be measured in the sample must be concentrated in some manner before analysis by atomic absorption. The solvent extraction technique is usually chosen for investigation because of its simplicity and the definite possibility that several metals could be simultaneously extracted in one operation (129). Preliminary tests
showed that at pH 2-3, the carbamate complexes of ferric iron, zinc, cadmium, copper and lead are extractable from water with methyl isobutyl ketone (130).

2.8.2. Analysis of Water from Selected United States Cities by Atomic Absorption

Table 1 shows the minimum, maximum and median concentrations for lead, cobalt and nickel in the water supplies of the hundred largest cities in the United States (128). Only nine samples contained detectable concentrations of cobalt. The highest concentration was 9.5µg/L, whereas the cobalt found in the other samples was listed as “less-than” values. Ninety-five percent of the water supplies contained less than 10µg/L of both nickel and lead. The detection limits for the lead, cobalt and nickel by atomic absorption are approximately 50, 30 and 20µg/L respectively. A preconcentration procedure was used in determining these elements by atomic absorption (130,131).

Table 1. Concentration of Lead, Cobalt and Nickel in Public Water Supplies of 100 Largest Cities in the United States

<table>
<thead>
<tr>
<th>Metals</th>
<th>Minimum (µg/L)</th>
<th>Maximum (µg/L)</th>
<th>Median (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>ND</td>
<td>62.0</td>
<td>3.7</td>
</tr>
<tr>
<td>Co</td>
<td>ND</td>
<td>9.5</td>
<td>ND</td>
</tr>
<tr>
<td>Ni</td>
<td>ND</td>
<td>34.0</td>
<td>&lt;2.7</td>
</tr>
</tbody>
</table>

ND- not detected

Since the detection limits for cobalt, nickel and lead in aqueous solution by atomic absorption are about 50µg/L but normally these metals occur at lower concentrations in fresh water, thereby making measurements not possible, there is the need to explore other means of direct measurements without having to go through the laborious process of concentrating the samples prior to analysis. It is against this
background that ICP-MS which is a rapid and simple routine method was chosen over atomic absorption in this current work (131).

2.8.3. Inductively Coupled Plasma-Mass Spectrometry

Inductively coupled plasma mass spectrometry (ICP-MS) is probably the most frequently used ion source for inorganic mass spectrometry. It is a plasma-based technique employed in the determination of metals in aqueous solutions, and it is in fact, a very well established and powerful analytical technique for the determination of trace and ultra-trace elements in a variety of environmental and biological samples (132). ICP-MS has been widely accepted as one of the most attractive techniques for trace metal analyses, because of its high sensitivity, low limits of detection (LOD), high dynamic range (133,134) and its high capability of multi-element and isotope ratio measurements (135,136).

In laboratories where environmental and food monitoring analyses are undertaken, ICP-MS systems are usually required in order to analyze large series of samples (134). For routine ICP-MS analysis, Buchman showed the importance of a good choice of calibration procedure (137). A good choice of the dissolution procedure for ICP-MS analysis is more critical than for other techniques of atomic spectroscopy. For example, if vanadium or arsenic is to be determined, then hydrochloric acid must be avoided because of the well-known interferences occurring at the main analytical masses of these analytes. In fact, these problems become less critical with modern ICP-MS instrumentation that now uses the collision cell technology (138,139) or when efficient multivariate correction method can be applied (140).
For ICP-MS routine analysis of complex matrices, dilutions should be then carried out as far as possible to minimize these effects (matrix effects) to the largest extent. For environmental samples, this can in principle be easily achieved because of very low detection limits offered by the ICP-MS technique which has reported detection limit range at ng/L level or lower for most elements usually determined. Actual multi-element capabilities and the high throughput of ICP-based techniques often remain the decisive choice criteria for a routine analysis.

Plasma-based techniques that can be employed in the determination of trace elements are inductively coupled plasma atomic emission spectrometry (ICP-AES), quadruple inductively coupled plasma mass spectrometry (Q-ICP-MS) and the high resolution inductively coupled plasma mass spectrometry (H-ICP-MS). These techniques which can be applied to all possible matrices and analytes (provided that suitable dissolution procedures are followed) are characterized by extended dynamic concentration ranges (several orders of magnitude), are multi-elemental in nature and possess high sensitivity and appropriate detection power.

The risk of interference from polyatomic ions is present for all isotopes of the selected elements. For quadrupole mass spectrometers, interferences from polyatomic ions and even doubly charged ions cause difficulties for the measurements of certain elements (141). A high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) eliminates most polyatomic ion interferences encountered in quadrupole ICP-MS.
2.8.4. Operational Principle of ICP-MS

Multi-element determination of analytes by ICP-MS in aqueous and nitric acid or aqua regia digests is done to detect or analyze trace and ultra-trace elements. The method measures ions produced by a radiofrequency inductively coupled plasma ion source (140). Since the source operates at temperatures of 7000°K, virtually all molecules in a sample will be broken into their component atoms. Analyte species originating in a liquid are nebulized and the resulting aerosol is transported by argon gas into the plasma torch. The ions produced by high temperatures are entrained in the plasma gas and introduced by means of an interface, into a mass spectrometer where they are sorted out according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be assessed and valid corrections applied. Interference correction must include compensation for background ions contributed by the plasma gas, reagents and constituents of the sample matrix (138-141).
CHAPTER 3
RESULTS AND DISCUSSION

3.1. Synthesis of the Sorbent Materials

Two adsorbents, a homopolymer, poly[4-(4-vinylbenzyloxy)-2-hydroxybenzaldehyde] and a copolymer, poly[1-(2-pyridyl)-3-[4-(4-vinylbenzyloxy)phenyl]imidazo(1,5-a)pyridine-co-methacrylate] were synthesized by free radical polymerization.

3.1.1. Synthesis of Homopolymer

The homopolymer, I, was synthesized by free radical polymerization using a precursor, 4-(4-vinylbenzyloxy)-2-hydroxybenzaldehyde and azobis-(isobutyronitrile), (AIBN), as initiator in a ratio of 130 to 1 in dry THF at 60°C (142).

\[
\text{I} \quad \text{Figure 1. Structure of homopolymer I.}
\]
$^1$H-NMR showed that the vinyl proton signals at δ 5.31 ppm, δ 5.80 ppm and δ 6.80 ppm in the precursor had disappeared and the peaks being broader, suggesting that the vinyl double bond has been converted to carbon-carbon single bonds. The hydroxyl and formyl groups appeared at δ 11.48 ppm and δ 10.38 ppm respectively indicating that the chelating groups are on the polymer backbone. Molecular weight of I was determined to be $M_w$ = 252,200 using THF with polystyrene standard.

### 3.1.2. Synthesis of Copolymer

The copolymer, II, on the other hand was synthesized by copolymerizing 1-(2-pyridyl)-3-[4-(4-vinylbenzyl oxy)phenyl]imidazo[1,5-a]pyridine with methyl methacrylate and initiated by AIBN in a ratio of 1:7:0.025 in DMAc at 100°C for 72 h (143,144).

![Structure of copolymer II](image)

Figure 2. Structure of copolymer II.
Both $^1$H-NMR and $^{13}$C-NMR spectra showed that the vinyl protons and the aliphatic carbon-carbon double bonds in the starting materials had disappeared and a number of broad peaks had appeared at the aliphatic region of the spectra. The molecular weight of II was determined as $M_w=39,600$ by GPC in THF against polystyrene standard and the glass transition temperature, $T_g$, of the copolymer determined by DSC is 150°C.

By varying the molar equivalent ratio of the monomer and methyl methacrylate while keeping the amount of the initiator constant, series of reactions were also carried out under the same condition to verify the effect of equivalent ratio on the chelation portion of the resulting copolymers.

Table 2. Effect of Methyl Methacrylate on Ratio of Chelate Group to Non-chelate Group in Copolymer

<table>
<thead>
<tr>
<th>run</th>
<th>copolymer</th>
<th>ratio of monomer to methyl methacrylate (MMA)</th>
<th>ratio of chelate to nonchelate part of copolymer</th>
<th>$M_w$</th>
<th>$M_n$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>IIa</td>
<td>1:5</td>
<td>1:1.96</td>
<td>27,800</td>
<td>19,900</td>
<td>1.4</td>
</tr>
<tr>
<td>2</td>
<td>II</td>
<td>1:7</td>
<td>1:2.5</td>
<td>39,600</td>
<td>27,600</td>
<td>1.4</td>
</tr>
<tr>
<td>3</td>
<td>IIb</td>
<td>1:14</td>
<td>1:11</td>
<td>62,200</td>
<td>58,000</td>
<td>1.1</td>
</tr>
</tbody>
</table>

As shown in table 2, the $M_w/M_n$ value which is a measure of the poly dispersity index of the copolymer is higher for IIb. This suggests that the normal distribution of the molecular weight is narrower for IIb than IIa and II. It is also obvious that as the equivalent ratio of the monomer to the MMA changes from 1:14 to 1:5, the amount of the chelating moiety of the copolymer increases.
3.2. Adsorption screening test of metal ions on adsorbents

The polymer and copolymer were found to be insoluble in weakly acidic and alkaline medium as well as in de-ionized water so they can easily be suspended in water and they will not hydrolyzed within the experimental pH range for the batch tests. Tables 3 and 4 show the percent removal and the amounts of the metal ions adsorbed onto the polymer, poly[4-(4-vinylbenzyloxy)-2-hydrobenzaldehyde] and the copolymer, poly[1-(2-pyridoyl)-3-[4-(4-vinylbenzyloxy)phenyl]imidazo(1,5-a)pyridine-co-methacrylate] during batch equilibrium studies at pH 5.5. Under the same experimental conditions used, the amounts adsorbed by the adsorbents are different for the various heavy metals as shown in Tables 3 and 4 below. This revealed that the Pb and Cd are best adsorbed.

Table 3. Adsorption of Heavy Metals from Solution on Poly(4-vinylbenzyloxy-2-hydrobenzaldehyde)

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Percent Removal (%)</th>
<th>Amount Adsorbed (µg/g polymer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>63.6</td>
<td>278.7</td>
</tr>
<tr>
<td>Zn</td>
<td>66.2</td>
<td>357.3</td>
</tr>
<tr>
<td>Co</td>
<td>70.1</td>
<td>423.2</td>
</tr>
<tr>
<td>Pb</td>
<td>80.9</td>
<td>430.1</td>
</tr>
<tr>
<td>Cd</td>
<td>75.3</td>
<td>374.0</td>
</tr>
<tr>
<td>Ni</td>
<td>65.6</td>
<td>312.5</td>
</tr>
<tr>
<td>Cr</td>
<td>71.5</td>
<td>393.3</td>
</tr>
</tbody>
</table>

Initial metal ion concentration: 1000 ppb, temperature: 25°C, contact time: 2 h, and pH=5.5, mass of adsorbent: 0.025g, volume of solution: 12.5mL.
Table 4. Adsorption of Heavy Metals from Solution on Copolymer

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Percent Removal (%)</th>
<th>Amount Adsorbed (µg/g copolymer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>71.2</td>
<td>333.5</td>
</tr>
<tr>
<td>Zn</td>
<td>48.1</td>
<td>236.4</td>
</tr>
<tr>
<td>Co</td>
<td>58.6</td>
<td>327.8</td>
</tr>
<tr>
<td>Pb</td>
<td>85.8</td>
<td>470.1</td>
</tr>
<tr>
<td>Cd</td>
<td>64.6</td>
<td>317.3</td>
</tr>
<tr>
<td>Ni</td>
<td>53.4</td>
<td>290.7</td>
</tr>
<tr>
<td>Cr</td>
<td>60.6</td>
<td>317.7</td>
</tr>
</tbody>
</table>

Initial metal ion concentration: 1000 ppb, temperature: 25°C, contact time: 2 h, and pH=5.5, mass of adsorbent: 0.025g, volume of solution: 12.5 mL

3.3. Adsorption Tests

3.3.1. Effect of pH on Lead Uptake

The pH effect was performed in the pH range of 1.0 to 5.5 with initial lead ion solution concentrations between 53.961 µg/L (for pH 1) and 48.011 µg/L (for pH 5.5) using 25 mg of the adsorbent. The experiments led to the conclusion that the removal of lead ion by the adsorbent (polymer) increases with increasing pH; from its minimum of pH 1.0 to its maximum at a pH of 5.5.

The adsorption results for the removal of lead ion onto 25 mg of the polymer for pH values between 1.0 and 5.5 are given in Figure 3. The removal of the Pb ions is highly dependent on pH. The effectiveness of removal for lead ion is reflected in the percentage adsorption obtained at any given pH. For instance, at pH 1.0 only 5% (1.0 µg/g) was removed but at pH 5.5 as much as 99% (23.8 µg/g) of the adsorbent was removed.

The decrease in adsorption capacity as pH decreases could be explained on the basis that, at low pH the carbonyl groups of the aldehyde on the surface of the polymer
are easily protonated thereby inducing an electrostatic repulsion between them and the lead ions. Consequently, competition is created between the protons and lead ions for the adsorption sites, hence the low adsorption capacity.

On the other hand, the increase in lead ion removal at higher pH can be attributed to a decrease in competition between the protons and lead ions in solution for the same functional groups or by a decrease in positive surface charge, which results in a decreased electrostatic repulsion between the surface and the lead ions thereby increasing the adsorption capacity. This observation gives us an insight into the mechanism of the binding involved within the adsorbent and also suggests that within the chosen pH range of study, lead does not precipitate out of the solution.

![Figure 3. Effect of pH on lead adsorption from solution on poly[4-(4-vinylbenzyloxy)-2-hydroxybenzaldehyde].](image)
3.4. Metal Adsorption Isotherms

3.4.1. Effect of Lead Concentration on Adsorption by Polymer

Equilibrium sorption studies were performed to obtain the maximum metal adsorption capacity of the polymer. For all the initial lead concentrations studied, the pH value was 5.5. The adsorbed metal ion onto the polymer was found to be a function of the initial concentration of the ions in solution and therefore the extent of sorption increased with increase in initial concentration of the metal ion (145, 146). Figure 4 shows that the saturation point of the adsorption sites of the polymer has been reached within the concentration range of studies. This means that upon increasing the initial lead ion concentrations, the adsorption capacities gradually increased until higher equilibrium concentrations were reached, and then a leveling effect occurred indicating that the adsorption capacity of the polymer has been reached.

The gradual increase in the uptake of lead ion with increase in initial concentration indicates that all the adsorption sites on the adsorbent are not occupied simultaneously. Instead, the sites are occupied gradually until all the adsorption sites are occupied. The equilibrium data was analyzed in accordance with the Langmuir sorption isotherms as (146)

\[ Q_e = \frac{Q_m b C_e}{1 + b C_e} \]  

(17)

where \( C_e \) is the equilibrium or final concentration of lead, \( Q_e \) is the amount of lead ions adsorbed per unit weight of the polymer at equilibrium concentration, \( Q_{\text{max}} \) is the maximum adsorption at monolayer coverage and \( b \) is the Langmuir adsorption equilibrium constant and it is the measure of the energy of adsorption (147, 148).
Figure 4. Effect of concentration on lead ion adsorption onto polymer, I.

The adsorption behavior can be described with the Langmuir equation (44)

\[
\frac{C_e}{Q_e} = \frac{1}{bQ_{\text{max}}} + \frac{1}{Q_{\text{max}}} C_e \quad (18)
\]

A plot of \( \frac{C_e}{Q_e} \) versus \( C_e \) gave a straight line of slope \( \frac{1}{Q_{\text{max}}} \) and an intercept of \( \frac{1}{bQ_{\text{max}}} \) and the values of \( Q_{\text{max}} \) and \( b \) are deduced from the graph as shown in Figure 5.
The linearized Langmuir equation is of the form $Y = A + BX$, where the intercept on the ordinate axis, $A$, and the slope of the curve, $B$, as well as the regression coefficient, $r$, are determined to be:

$$A = 0.039, \quad B = \text{slope} = 0.0031 \quad r^2 = 0.9991$$

From the curve, the values of $Q_{\max}$ and $b$ are deduced.

$$B = \frac{1}{Q_{\max}} = 0.003 \quad ; \quad Q_{\max} = 333.3 \ \mu g/g$$

$$A = \frac{1}{b \ Q_{\max}} = 0.039 \quad ; \quad b = \frac{1}{Q_{\max} A} = \frac{1}{(333.3)(0.039)} = 0.0769$$
The maximum adsorption capacity is when all adsorption sites are occupied. The Langmuir plot obtained shows a good agreement with the experimental data and suggests that the Pb ions adsorbed cover the adsorbent surface in a monolayer fashion.

It has been reported that the effect of isotherm shape can be used to predict if an adsorption system is "favorable" or "unfavorable" (149). Table 5 shows how the parameter indicates the isotherm shape. The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor or equilibrium parameter, $R_L$, which is defined by

$$R_L = \frac{1}{1 + b C_e}$$  \hspace{1cm} (19)

<table>
<thead>
<tr>
<th>$R_L$ value</th>
<th>Type of isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_L &gt; 1$</td>
<td>Unfavorable</td>
</tr>
<tr>
<td>$R_L = 1$</td>
<td>Linear</td>
</tr>
<tr>
<td>$0 &lt; R_L &lt; 1$</td>
<td>Favorable</td>
</tr>
<tr>
<td>$R_L = 0$</td>
<td>Irreversible</td>
</tr>
</tbody>
</table>
Table 6. Equilibrium Parameter Values for Polymer

<table>
<thead>
<tr>
<th>Initial concentrations of lead ions (µg/L)</th>
<th>Equilibrium</th>
<th>Amount Adsorbed (µg/g)</th>
<th>R_L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration of lead ions (µg/L)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>44.37</td>
<td>1.49</td>
<td>21.39</td>
<td>0.23</td>
</tr>
<tr>
<td>112.91</td>
<td>4.87</td>
<td>54.02</td>
<td>0.10</td>
</tr>
<tr>
<td>219.47</td>
<td>5.29</td>
<td>107.08</td>
<td>0.06</td>
</tr>
<tr>
<td>329.28</td>
<td>9.51</td>
<td>159.88</td>
<td>0.04</td>
</tr>
<tr>
<td>391.72</td>
<td>15.38</td>
<td>187.56</td>
<td>0.03</td>
</tr>
<tr>
<td>494.99</td>
<td>26.14</td>
<td>234.39</td>
<td>0.02</td>
</tr>
<tr>
<td>672.52</td>
<td>80.64</td>
<td>295.36</td>
<td>0.02</td>
</tr>
<tr>
<td>734.84</td>
<td>134.65</td>
<td>300.19</td>
<td>0.02</td>
</tr>
<tr>
<td>797.48</td>
<td>165.05</td>
<td>315.21</td>
<td>0.02</td>
</tr>
<tr>
<td>879.45</td>
<td>235.01</td>
<td>321.72</td>
<td>0.01</td>
</tr>
<tr>
<td>993.07</td>
<td>340.00</td>
<td>326.17</td>
<td>0.01</td>
</tr>
<tr>
<td>1097.05</td>
<td>443.56</td>
<td>326.41</td>
<td>0.01</td>
</tr>
<tr>
<td>1151.13</td>
<td>498.05</td>
<td>326.54</td>
<td>0.01</td>
</tr>
</tbody>
</table>

The R_L values calculated for different initial lead concentrations in table 6 shows that favorable adsorption of lead has indeed taken place suggesting that the chelating polymer is a good adsorbent. The sorption data of the lead ions sorption onto the polymer was also fitted to the Freundlich isotherm (150) in the following linear form

\[ \log Q_e = \frac{1}{n} \log C_e + \log K \]  

(20)

where K and 1/n are Freundlich constants, indicating the sorption capacity and sorption intensity, respectively. Figure 6 shows the Freundlich plot obtained by plotting log Q_e against log C_e, and this indicates that sorption of the Pb ions obey Freundlich isotherm as well.
3.4.2. Effect of lead ion concentration on adsorption by copolymer

The effect of lead ion concentration on the uptake behavior of the copolymer was studied in the concentration range of 100-2000 μg/L of the lead solution.

The adsorption isotherm of the lead ions on the copolymer is shown on Figure 7. Increasing the initial concentration of the lead solution resulted in a corresponding increase in the amount of lead ions adsorbed onto the copolymer suggesting that the adsorption sites on the copolymer are gradually occupied as the initial lead concentration is increased. At about an equilibrium concentration of 400 μg/L a plateau was reached indicating that all the adsorption sites are occupied.
Figure 7. Effect of initial concentration on lead adsorption onto copolymer.

A good agreement of the experimental data with the Langmuir plot in Figure 8 suggests that the lead ions sorbed covered the adsorbent surface in a monolayer fashion. The equilibrium data was also well described with the Freundlich model as shown in Figure 9.
Figure 8. Langmuir isotherm for the adsorption of lead onto copolymer.

Figure 9. Freundlich isotherm for the adsorption of lead onto copolymer.
3.4.3. Effect of cadmium ion concentration on adsorption by polymer

Figure 10 presents the Langmuir adsorption isotherm of cadmium ions on polymer to determine the concentration at which all the available chelating sites on the polymer will be chelated. Within the initial concentration range of the studies (100-2000µg/L), cadmium adsorption onto the polymer increased first with increase in equilibrium concentration of cadmium ion and then leveled at about an equilibrium concentration of 500 µg/g indicating saturation of the adsorption sites on the adsorbent. Figures 11 and 12 show the Langmuir and Freundlich plots obtained upon analyzing the experimental data.

![Figure 10. Effect of initial concentration on cadmium adsorption onto polymer, I.](image-url)
Figure 11. Langmuir isotherm for the adsorption of cadmium ions on polymer, I.

Figure 12. Freundlich isotherm for the adsorption of cadmium ions on polymer, I.
3.4.4. Effect of cadmium ion concentration on adsorption by copolymer

In Figure 13 is shown the effect of cadmium ion concentration on the uptake behavior of the copolymer studied within the concentration range of 100-2000 μg/L of cadmium solution. By increasing the Cd ions in solution, the amount of Cd ions adsorbed also increased until the graph leveled up at higher concentrations of the solution. This is because at higher concentrations saturation of the available adsorption sites occurs. Figures 14 and 15 represent the Langmuir and Freundlich plots obtained when the experimental data was analyzed and the correlation coefficients $R^2$ and the adsorption parameters were also deduced.

Figure 13. Effect of initial concentration of cadmium adsorption onto copolymer, II.
Figure 14. Langmuir isotherm for the adsorption of cadmium ions onto copolymer, II.

Figure 15. Freundlich isotherm for the adsorption of cadmium ions onto copolymer.
Table 8. Langmuir and Freundlich Parameters for Metal Adsorption onto Copolymer

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>Freundlich model</th>
<th>Langmuir model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K</td>
<td>Q_m(µg/g)</td>
</tr>
<tr>
<td>Pb</td>
<td>51.59</td>
<td>625.0</td>
</tr>
<tr>
<td>Cd</td>
<td>34.11</td>
<td>277.8</td>
</tr>
</tbody>
</table>

The experimental data were analyzed by a regression analysis to test for the Freundlich and Langmuir isotherm models in order to determine the best fit. Tables 7 and 8 show the respective correlation coefficients, R^2, as well as the computed Langmuir parameters Q_m and b and the Freundlich parameters K and 1/n.

The Langmuir model much better described the adsorption process for both the polymer and the copolymer. The sorption of the lead ions onto the polymer and the copolymer reflects the maximum capacity values in Tables 7 and 8.

In the studies, the values of 1/n are all less than 1, which is an indication of favorable sorption. Smaller values of 1/n indicate better sorption mechanism and formation of relatively stronger bond between adsorbate and adsorbent (148).

3.5. Adsorption Kinetics of Removal of Metal Ions

In order to compare the performance of the polymer and the copolymer in kinetic terms, the adsorption of each of the metals onto the adsorbents was studied with respect to time.
3.5.1. Effect of time on cadmium adsorption onto polymer and copolymer

Figure 16 shows the comparison of the performance of the polymer and the copolymer in kinetic studies of adsorption of cadmium ions onto the adsorbents. For both of the adsorbents, equilibrium was reached within 30 seconds and virtually the same amount of cadmium ions were adsorbed onto the polymer and the copolymer. This suggests that it was easier for the cadmium ions to reach all of the available adsorption sites regardless of the adsorbent used and 45.1 ug/L of the cadmium ions remains in solution at equilibrium.

The fast adsorption time suggests that the adsorbents have most of their chelating groups on or near the surface of the adsorbents and each of the adsorbents have short ion diffusion path which facilitates the kinetics of the adsorption.
3.5.2. Effect of Time on Lead Adsorption onto Polymer and Copolymer

The kinetic result in Figure 17 shows that equilibrium was reached in 30 seconds and nearly the same amount of lead ions were adsorbed on both the polymer and the copolymer suggesting that the affinity of the two adsorbents towards the adsorption of lead is the same. Furthermore, the fast equilibrium also indicates that both adsorbents have short ion diffusion paths and also shows that the chelating groups are on the surface or near the surface of the adsorbents (150-152).

![Figure 17. Effect of contact time on adsorption of lead onto polymer and copolymer at pH 5.5 and 25°C. Mass of each adsorbent: 0.25 g; volume of lead solution: 12.5 mL.](image-url)
3.5.3. Effect of Concentration on Rates of Adsorption of Metal Ions onto Polymer and Copolymer

Figures 18-21 show the kinetic behavior of lead and cadmium uptake by the polymer and copolymer. The plots are representations of the amount of metal adsorbed, $Q_t$, onto the adsorbent versus time for varying initial concentrations. For all the plots, it is evident that the sorptions were extremely fast because equilibrium was attained within 1 min. Over 95% of the metal ions were removed within 5-30 sec of contact time. For both lead ions and cadmium ions, the bulk of the uptake occurred within the same period of time onto the adsorbents.

Increasing the concentration of the metal solution increases the concentration of the reacting species and therefore frequency of collision increases, hence the reaction rate increases. This is consistent with the gradual increase of the initial rate, $v_0$ in Tables 9 and 10. Figures 18-21 also show that, as the initial metal concentration increases, the percent adsorption decreases although the amount of metal uptake per unit weight of the adsorbent, $Q$(mg/g) increases. This suggests that at higher initial concentrations, the ratio of the metal ions in solution to the available adsorption surface area is high.
Figure 18. Plot of sorbed amounts of lead ions at varying initial concentrations with time on polymer, I.

Figure 19. Plot of sorbed amounts of cadmium ion at varying initial concentrations with time on polymer, I.
3.5.4. Modeling of the Kinetics

The adsorption rate or mechanism was tested by subjecting the experimental data to two simple kinetic models, namely the pseudo-first-order and the pseudo-second-order...
equations (122,123). As described in sections 2.7.1. and 2.7.2., the pseudo first order kinetic was verified by plotting $\log(Q_e-Q_t)$ versus $t$ to obtain linear graphs from which the slopes and the intercepts were determined and hence the values of $K_1$. The correlation coefficients of the straight lines obtained were not high.

Pseudo-second-order model was also tested by a plot of $t/Q_t$ versus $t$ which gave a straight line from which the slopes and the intercepts were deduced and used to determine the initial sorption rate $v_0$. Figures 22 and 23 show the fits obtained with the pseudo-second-order model for the adsorption of cadmium and lead onto copolymer.

![Figure 22. Second-order kinetic plot for the sorption of cadmium on copolymer, II.](image)
Figures 24 and 25 show the fits obtained with the pseudo-second-order model for the adsorption of cadmium and lead on polymer. The plots show that for both adsorbents, as the initial concentration of the metal solution is increased, the slopes of the lines for the solutions of higher concentrations correspondingly decrease. This observation is coincidental to the fact that equilibrium is reached more slowly at increasing metal ion concentration \((146, 147)\). Thus rate of removal of metal ions from solution onto the adsorbents become restricted at increasing metal ion concentration. The fast reaction rate indicates that the activation energy is small and that a larger fraction of the metal ions in solution have an average kinetic energy higher than the activation energy, hence resulting in high collision frequency \((148, 149-153)\).
Figure 24. Second-order kinetic plot for the sorption of cadmium on polymer, I.

Figure 25. Second-order kinetic plot for the sorption of lead ions on polymer, I.
Table 9. Kinetic Parameters for Metal Adsorption onto the Polymer

<table>
<thead>
<tr>
<th>metal ions</th>
<th>$C_0$ (µg/L)</th>
<th>$K_1$ (sec$^{-1}$)</th>
<th>$R^2$</th>
<th>$v_0$ (µg/g sec)</th>
<th>$K_2$ (g/sec µg)</th>
<th>$Q_e$ (µg/g)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>89.7</td>
<td>0.0721</td>
<td>0.772</td>
<td>4.12 x 10$^4$</td>
<td>2.20 x 10$^2$</td>
<td>43.29</td>
<td>0.999</td>
</tr>
<tr>
<td>Pb</td>
<td>261.8</td>
<td>0.0958</td>
<td>0.841</td>
<td>1.82 x 10$^2$</td>
<td>1.22 x 10$^2$</td>
<td>121.95</td>
<td>0.999</td>
</tr>
<tr>
<td>Pb</td>
<td>437.0</td>
<td>0.0677</td>
<td>0.863</td>
<td>1.85 x 10$^2$</td>
<td>5.00 x 10$^3$</td>
<td>192.31</td>
<td>0.999</td>
</tr>
<tr>
<td>Cd</td>
<td>86.9</td>
<td>0.0700</td>
<td>0.857</td>
<td>2.60 x 10$^1$</td>
<td>1.26 x 10$^2$</td>
<td>45.45</td>
<td>0.998</td>
</tr>
<tr>
<td>Cd</td>
<td>248.5</td>
<td>0.1011</td>
<td>0.947</td>
<td>7.19 x 10$^1$</td>
<td>4.84 x 10$^3$</td>
<td>121.95</td>
<td>0.999</td>
</tr>
<tr>
<td>Cd</td>
<td>505.4</td>
<td>0.0887</td>
<td>0.955</td>
<td>9.90 x 10$^1$</td>
<td>2.58 x 10$^3$</td>
<td>196.08</td>
<td>0.998</td>
</tr>
</tbody>
</table>

As shown in tables 9 and 10, very high initial sorption values were obtained for the pseudo-second-order equations indicating that the adsorption is in compliance with the pseudo-second-order model. The initial sorption rate ($v_0$) increase with increasing metal ion concentration and this is consistent with the rapid occurrence of the adsorption process. The generally fast kinetics of the adsorption process reflects the substantially large initial sorption rate values of the pseudo-second-order model which is consistent with the fast attainment of equilibrium (150, 151).

Apart from the very high correlation coefficient values in tables 9 and 10 suggesting a pseudo-second-order model for the adsorption process, the large sorption rate values also indicate that collision frequency is high and this reflects a small activation energy which is consistent with increase in initial rate when initial concentration increases.
Table 10. Kinetic Parameters for Metal Adsorption onto the Copolymer

<table>
<thead>
<tr>
<th>metal ions</th>
<th>C_0 (μg/L)</th>
<th>K_1 (sec^{-1})</th>
<th>R^2</th>
<th>v_0 (μg/g/sec)</th>
<th>K_2 (g/sec μg)</th>
<th>Q_e (μg/g)</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>90.1</td>
<td>0.1117</td>
<td>0.842</td>
<td>4.27 x 10^4</td>
<td>2.07 x 10^{-2}</td>
<td>45.45</td>
<td>0.998</td>
</tr>
<tr>
<td>Pb</td>
<td>287.8</td>
<td>0.0539</td>
<td>0.766</td>
<td>8.33 x 10^1</td>
<td>4.20 x 10^{-3}</td>
<td>140.85</td>
<td>0.998</td>
</tr>
<tr>
<td>Pb</td>
<td>604.8</td>
<td>0.0893</td>
<td>0.942</td>
<td>1.13 x 10^2</td>
<td>1.39 x 10^{-3}</td>
<td>285.71</td>
<td>0.989</td>
</tr>
<tr>
<td>Cd</td>
<td>90.2</td>
<td>0.0783</td>
<td>0.918</td>
<td>1.47 x 10^1</td>
<td>6.57 x 10^{-3}</td>
<td>47.39</td>
<td>0.994</td>
</tr>
<tr>
<td>Cd</td>
<td>285.4</td>
<td>0.0555</td>
<td>0.897</td>
<td>5.13 x 10^1</td>
<td>2.81 x 10^{-3}</td>
<td>135.14</td>
<td>0.996</td>
</tr>
<tr>
<td>Cd</td>
<td>587.7</td>
<td>0.0829</td>
<td>0.972</td>
<td>9.62 x 10^1</td>
<td>1.46 x 10^{-3}</td>
<td>256.41</td>
<td>0.996</td>
</tr>
</tbody>
</table>

3.6. Column Adsorption

Figure 26 shows the column sorption and elution profile of lead using a solution of concentration 91.5 μg/L at pH 5.5. The column tests the chelating polymer's potential for lead ion uptake from aqueous solution. The polymeric chelating ligand was used not only as batchwise adsorbent but also as a stationary phase of column separation. The lead concentration of series of eluents collected successively as 10 ml fractions were examined by ICP-MS analysis for a total elution of 1000 mL of the lead solution upon passing through the micro-column of internal diameter 0.5 cm which was packed with 0.25 g of the chelating polymer. The flow rate was 1 mL/min.

Figure 26 also shows that most of the chelating sites were occupied after 200 mL of the lead solution was passed through the column suggesting that there occurs fast adsorption of lead ions at the initial stage. Further passing of additional 200 mL lead
solution through the column resulted in lesser adsorption of the lead ions onto the adsorbent. After 400 mL of the lead solution was passed through the column, the lead concentration in the effluent steadily increased and eventually became equal to the influent concentration after about 900 mL of the lead solution was passed through the column. This indicates that the lead solution simply passed through the column with little adsorption taking place inside the column. The S-shape curve obtained showed that the breakpoint is at about 900 mL (156, 157).

The polymer exhibited a strong adsorption capacity for lead ions from solution at the pH value of 5.5 studied, suggesting that the polymer is efficient for lead ions removal from solution under static conditions. In comparison to the adsorption capacity of lead ions (333.3 µg/g) onto the polymer under batch conditions, the amount of lead ions adsorbed onto the polymer under static conditions is 177.5 µg/g before the breakthrough point and this is about 53% of the adsorption capacity of batch experiment. This shows that the polymer has a potential for lead ions removal from industrial effluent.
Figure 26. Column adsorption for a solution of lead in column operation at 25°C at pH of 5.5.
CHAPTER 4
EXPERIMENTAL SECTION

4.1. General Aspects

Melting points were obtained in open capillary tubes with Mel-temp II Laboratory devices, Inc. melting point apparatus and are uncorrected. Infrared (IR) spectra were run on an Impart FT-IR spectrometer in KBr pellets. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker ARX 400 MHz spectrometer in CDCl$_3$ or DMSO-$d_6$ with TMS as an internal standard. Chemical shifts are reported in parts per million (ppm). Gas Chromatography-Mass Spectrometry (GC-MS) analyses were performed on a Hewlett Parker GC-MS instrument. Elemental analyses were performed by the Atlantic Microlab, Inc. in Norcross, Georgia.

Silica gel 63-200 micron was used for column chromatography. The elution solvent for purification was determined by thin layer chromatography (TLC). Analytical thin-layer chromatography (TLC) was carried out using precoated silica gel plates and the TLC plates were visualized with UV light.

All chemicals and solvents were purchased from Aldrich. Solvents used for air or moisture sensitive reactions were degassed and distilled under nitrogen atmosphere using the following methods: tetrahydrofuran (THF) was dried from sodium/benzophenone ketyl; methylene chloride was distilled from calcium hydride; N,N-Dimethylformamide (DMF) was distilled from calcium chloride dried over 4Å molecular sieves and initiator
2,2'-azobis(isobutyronitrile) (AIBN) was purified by recrystallization from methanol. All reactions were carried out under nitrogen.

4.2. Syntheses of Monomers

4.2.1. Synthesis of 1-(2-pyridyl)-3-(3-hydroxyphenyl)imidazo[1,5-a]pyridine:

Scheme 1

To a 100 mL three-necked round-bottom flask was added a mixture consisting of di-2-pyridyl ketone (10.001 g, 0.054 mol), 4-hydroxybenzaldehyde (13.259 g, 0.109 mol) and ammonium acetate (20.923 g, 0.271 mol) in 200 mL of glacial acetic acid. The reaction was stirred at 110 °C under N₂ and was monitored by TLC (EtOAc:hex:MeOH=2:1:0.5). After 5 hr the reaction was cooled to room temperature. The reaction mixture was poured into 500 mL ice water and was neutralized by 10% solution of NaHCO₃ to pH 8 (143). The yellow solid formed was filtered, dried and then recrystallized from ethyl alcohol to obtain an analytically pure yellow compound. (yield: 93 %), mp: 217-219 °C; ¹H NMR (400 MHz, DMSO-d₆, ppm) 9.92 (1H, s), 8.52-8.46 (2H, m), 8.15 (1H, d, J=7.0 Hz), 8.04 (1H, d, J=8.0 Hz), 7.61 (1H, t, J=7.0 Hz), 7.52 (2H, d, J=8.0 Hz), 6.99 (1H, t, J=6.5 Hz), 6.86 (1H, d, J=8.5 Hz), 6.81 (1H, t, J=8.0 Hz), 6.59 (1H, t, J=6.5 Hz). GC-MS m/z: 287 (M⁺). Anal. Calc'd for C₁₈H₁₃N₃O: C, 75.25; H, 4.56; N, 14.63. Found: C, 75.11; H, 4.62; N, 14.49.
4.2.2. Synthesis of 1-(2-pyridyl)-3-[4-(4-vinylbenzyloxy)phenyl]imidazo[1,5-a]pyridine:

Scheme 2

In a three-necked round bottom flask equipped with a magnetic stirrer and a thermometer is added potassium carbonate (8.659g, 0.063mol) and the solvent, 1-methyl-2-pyrrolidinone (100 mL) and the mixture was stirred at room temperature for 30 minutes. To the mixture was added compound 1-(2-pyridyl)-3-(3-hydroxyphenyl)imidazo[1,5a]pyridine (6.012g, 0.021mol) and the reaction mixture was stirred for 30 minutes whilst still at room temperature until it dissolved. 4-vinylbenzylchloride (4.414mL, 4.781g, 0.031mol) is then added dropwise over a period of 5-10 minutes at a temperature of 0°C. The reaction mixture was kept at 0°C for another 10 minutes and then the temperature was raised to room temperature and was stirred under nitrogen. The reaction mixture was monitored by TLC (CH$_2$Cl$_2$:EtOAc = 2:2:0.5). After 64 hrs all the starting materials were consumed. The reaction mixture was poured into 500mL of ice water and the solid yellow precipitate formed was collected, washed with cold water and dried in air overnight. The crude product was recrystallized from methylene chloride to get a pure yellow solid product which was dried under reduced pressure (143,144).
Yield: 65%; pale yellow solid; mp: 227-229°C; $^1$H NMR (400 MHz, CDCl$_3$, ppm) 8.66 (2H, d, J = 24.4Hz), 8.22 (2H, d, J = 18.2Hz), 7.73 (3H, d, J = 11.4Hz), 7.44 (4H, t, J = 18.8Hz), 7.11 (3H, d, J = 23Hz), 6.91 (1H, d, J = 3.2Hz), 6.74 (1H, m), 6.63 (1H, t, J = 6Hz), 5.8 (1H, d, J = 17.6Hz), 5.27 (1H, d, J = 10.8Hz), 5.15 (2H, s). $^{13}$C NMR (CDCl$_3$, ppm) δ 149.59, 137.21, 136.75, 136.40, 131.27, 130.52, 129.75, 128.11, 126.90, 125.68, 123.77, 122.56, 121.48, 121.13, 115.99, 115.42, 115.07, 114.71, 70.31.

Anal. Calcd for C$_{27}$H$_{21}$N$_3$O: C, 80.37; H, 5.25; N, 10.41. Found: C, 79.94; H, 5.23; N, 10.43.

4.2.3. Synthesis of 1-(2-Pyridyl)-3-(4-hydroxyphenyl)imidazo[1,5-a]pyridine

**Scheme 3**

In a three-necked round bottom flask equipped with a magnetic stirrer and a thermometer is added a mixture of α-pyridoin (2.012g, 0.901mmol), 4-hydroxybenzaldehyde (0.571g, 4.670mmol), and ammonium acetate (0.539g, 7.001mmol) and glacial acetic acid (40 mL). The reaction mixture is heated at 110°C under nitrogen and was monitored by TLC. After 3 hrs the reaction mixture was cooled to room temperature and added to 100mL ice water while stirring and the pH adjusted to 7 using 5N Na$_2$CO$_3$. The crude product was extracted with methylene chloride and the extract was dried under Na$_2$SO$_4$ overnight. The solvent was removed and column
chromatography was performed to isolate a yellow compound. The yellow solid was recrystallized from MeOH/DMSO to obtain the pure dark yellow compound which was dried under reduced pressure (143, 144).

Yield; 18-24%; yellow solid; mp: 286-288°C; $^1$H NMR (400 MHz, DMSO-d6, ppm) 10.12 (1H, s), 8.84 (1H, d, J = 4.0 Hz), 8.69 (1H, d, J = 6.0 Hz), 8.43 (1H, d, J = 8.4 Hz), 8.19 (1H, d, J = 8Hz), 8.09 (1H, t, J = 7.4Hz), 7.76 (2H, d, J = 8.0Hz), 7.67 (1H, t, J = 5.2), 7.58 (1H, t, J = 7.4Hz), 7.21 (1H, t, J = 6.2Hz), 7.08 (2H, d, J = 8.0Hz). $^{13}$C NMR (DMSO-d6, ppm) δ 187.34, 159.49, 157.20, 149.94, 139.99, 137.18, 137.03, 31.49, 131.10, 128.89, 128.23, 126.47, 126.07, 125.53, 124.85, 120.11, 116.67.

4.2.4. Synthesis of 1-(2-Pyridoyl)-3-[4-(4-vinylbenzyloxy)phenyl]imidazo[1,5-a]pyridine

**Scheme 4**

In a three-necked round bottom flask equipped with a magnetic stirrer and a thermometer was added potassium carbonate (1.301g, 9.402mol) and the solvent, 1-methyl-2-pyrrolidinone (30 mL) and the mixture was stirred at room temperature for 30 minutes. To the mixture was added 1-(2-pyridoyl)-3-(4-hydroxyphenyl)imidazo[1,5-
a]pyridine (1.011g, 3.202mol) and the reaction mixture was stirred for 30 minutes whilst
still at room temperature until it dissolved. 4-vinylbenzylchloric (1.141 mL, 1.241g,
0.031mol) was then added dropwise over a period of 5-10 minutes at a temperature of
0°C. The reaction mixture was kept at 0°C for another 10 minutes and then the
temperature was raised to room temperature and was stirred under nitrogen. The reaction
mixture was monitored by TLC (CH$_2$Cl$_2$ : EtOAc = 2: 2: 0.2). After 64 hrs all the starting
materials were consumed. The reaction mixture was poured into 100 mL of ice water and
the solid yellow precipitate formed was collected, washed with cold water and dried in air
overnight (143,144). The crude product was recrystallized from ethanol to get a pure
yellow solid product which was dried under reduced pressure. Yield: 72%; pale yellow
solid; mp: 195-196 °C; $^1$H NMR(400 MHz, CDCl$_3$, ppm) 8.82 (1H, d, J = 4.4Hz) , 8.55
(1H, d, J = 9.2Hz), 8.35 (2H, t, J = 12Hz), 7.86 (2 H, t, J = 7.6 Hz), 7.74 (2 H, d, J =
8.8Hz), 7.47-7.41 (4 H, m), 7.27 (1H, t , J = 15Hz), 7.13 ( 2 H, d, J =8.4Hz), 6.89 (1 H, t,
J = 6.2Hz), 6.780-6.709 ( 1H, m, J = 10.8Hz), 5.78 ( 1 H, d, J =17.8Hz), 5.28 (1 H, d, J =
10.8Hz) , 5.14 (2 H, s, J =10Hz). $^{13}$C NMR (CDCl$_3$, ppm) δ 186.99, 160.09, 160.09,
156.43,150.23, 149.84, 139.56, 137.88, 137.54, 136.72, 136.35, 130.70, 129.74, 128.06,
127.27, 126.87, 126.46, 125.95, 125.71, 123.05, 122.13, 121.48, 116.26, 115.86, 115.67,
114.68, 70.46. Anal. Calcd for C$_{28}$H$_{21}$N$_3$O: C, 77.94; H, 4.91; N, 9.74. Found: C, 77.79;
H, 4.87; N, 9.63.
4.2.5. Synthesis of 4-(4-vinylbenzyl oxy)-2-hydroxybenzaldehyde

Scheme 5

\[
\text{HO-} \overset{\text{CHO}}{\text{CH}_2\text{OH}} + \overset{\text{CH}_2\text{Cl}}{\text{C}_6\text{H}_4\text{CH}_2\overset{\text{CHO}}{\text{OH}}} + \text{NaHCO}_3 \xrightarrow{\text{DMF} \quad 100^\circ\text{C}} \text{H}_2\text{C:} \overset{\text{OH}}{\text{C}_6\text{H}_4\text{CH}_2\text{O}} \overset{\text{CHO}}{\text{OH}}
\]

Into a 250 ml three-necked round bottomed flask equipped with a stirrer, an argon gas inlet, a condenser and a thermometer, 2,4-dihydroxybenzaldehyde (5.002g, 0.036mol) was dissolved in 100 ml of dry DMF and the mixture was stirred at room temperature until the solid completely dissolved and then sodium bicarbonate (3.041g, 0.036mol) was added. To the mixture was then added 4-vinylbenzyl chloride (5.1ml, 0.036mol) at 0°C drop-wise over a period of 5 minutes and afterward the temperature was raised to 100°C and the mixture heated for 3 hrs. After cooling, the reaction mixture was poured into 500ml ice-water followed by extraction with 100ml of ether. The organic layer was then extracted with (1N NaOH) 100 ml to separate the insoluble disubstitution and unreacted 4-vinylbenzyl chloride. The extract was neutralized with 1N HCl and extracted with 200ml ethyl acetate and dried in anhydrous sodium sulfate overnight. The solvent was removed and the viscous crude product obtained quickly solidified and was recrystallized from ethanol to give the pure product.

Yield: 72; pale brown solid; mp. 95-96°C. \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm) 11.47 (1H, s), 10.38 (1H, s), 7.40 (1H, d, J = 8Hz), 7.37 (1H, d, J = 6.8Hz), 6.76-6.69 (1H, m, J=10.8Hz), 6.63 (1H, d, J =8.8Hz). 6.58 (1H, d, J = 11.2Hz), 6.51 (1H, s), 5.78 (1H, d, J =17.6Hz), 5.28 (1H, d, J =10.8Hz), 5.10 (2H, s). GC-MS m/z: 254(M\(^+\)). Ana. Calcd for C\(_{16}\)H\(_{14}\)O\(_3\): C, 75.57; H, 5.55; Found; C, 76.14; H, 5.58.
4.3. Preparation of Poly[1-(2-pyridyl)-3-[4-(4-vinylbenzyl)oxy]phenyl]imidazo[1,5-a]pyridine-co-methacrylate]

Scheme 6

In a one-neck pear-shaped round bottom flask equipped with a stirrer, N₂-gas inlet, a condenser and an air-tight adapter with a rubber septum to let in samples, was dissolved the monomer (0.501g, 0.002mol) in anhydrous DMAc (8 ml). Nitrogen gas was bubbled through the monomer solution for 20 minutes and four cycles of freeze-pump thaw was carried out. Since the monomer is insoluble in DMAc at room temperature (or lower temperature) the reaction flask was occasionally heated to dissolve the monomer during the freeze thaw process. After four freeze-pump thaw cycles, the initiator, AIBN (0.005g, 0.039mol) which was dissolved in 2 ml of DMAc in a small air-tight vial with N₂ bubbled through it for 10 minutes, was added to the air-free monomer solution. One more freeze-pump thaw cycle was carried out and lastly, freshly distilled methyl
methacrylate (1.749g, 1.855 ml, 0.018mol) was added. One more freeze-pump thaw cycle was carried out and the reaction mixture was immersed in a pre-heated oil bath at 100°C and kept at this temperature for 72 hrs. The reaction flask was cooled to room temperature and upon cooling the reaction mixture was transferred drop-wise into 500 ml stirring methanol. The yellow precipitate formed was filtered under vacuum and re-dissolved in 10-15 ml of CH₂Cl₂ and then again precipitated in another 500 ml stirring methanol (3 times). The brownish yellow solid obtained was dried to constant weight within 24 hours. Proton NMR showed that the vinyl protons have disappeared and new methylene peaks appeared in the aliphatic region of the spectrum. The copolymer is soluble in halogenated solvents (CH₂Cl₂, CHCl₃) and in THF but it is insoluble in water. The relative molecular weight, Mₙ, and number average molecular weight, Mᵥ, were determined as Mₙ=39,600, Mn=27,600 respectively and Mₙ/Mᵥ = 1.43 as measured by GPC calibrated with polystyrene standard. ¹H NMR (400 MHz, CDCl₃, ppm) 8.655 (2H, d), 8.21 (2H, d), 7.72-6.62 (8H, m), 5.12 (2H, s), 3.59 (3H, s), 3.03-2.90 (3H, m), 2.49-1.80 (2H, s), 1.19-0.65 (3H, s).

4.4. Preparation of poly[4-(4-vinylbenzyloxy)-2-hydroxybenzaldehyde]

Scheme 7
10.001 g (0.039 mol) of the monomer and 0.051 g (0.304 mmol) of AIBN was dissolved in 70 ml of dry THF. The solution was put in a 100 ml-size pear shaped flask which was pre-evacuated and argon gas bubbled through it for 15 minutes. The mixture was subjected to the standard freeze thaw technique and stirred at a temperature of 60°C for 48 hours. The resulting viscous solution was added to 100 ml of CHCl₃. The mixture formed was then transferred drop-wise into 800 ml of methanol forming a white solid which was filtered under vacuum. The crude product was dissolved in 100 ml of CHCl₃ and re-precipitated in 1000 ml methanol (2 times). The pale white solid formed was filtered and dried. The resulting polymer is soluble in THF.

H-NMR was done on the samples of the products and the characteristic broad peaks of polymer was obtained and the vinyllic proton signals at δ5.31 ppm and δ5.80 ppm had disappeared, but there was still some traces of residual protons at δ6.80 ppm suggesting that there has not been a 100% conversion of the monomer to the polymer.

Gel permeation chromatography (GPC) done on the sample in THF gave a good normal distribution curve of the molecular weight distribution (MWD) suggesting that there is high polydispersity of the polymers formed. The relative molecular weights and the number average molecular weights for the polymer are $M_w = 252,200$, $M_n = 162,600$, polydispersity index = 1.55. ¹H NMR (400 MHz, CDCl₃, ppm) 11.48 (1H, s), 10.38 (2H, d), 9.65 (1H, s), 7.77 (2H, d), 7.36-7.07 (3H, m), 6.53 (s, CH₂-CH), 4.93 (2H, s)
4.5. ICP-MS Analysis

4.5.1. Instrumentation

All measurements were carried out with an ICP-MS spectrometer ELAN DR-e (Perkin Elmer) equipped with an AS-90 autosampler, a cross flow nebulizer and a 4-channel peristaltic pump (pump 1). Pump 1 was used for both introduction of carrier solution (0.65% nitric acid) as well as spray chamber draining. Platinum sampler and skimmer cones were used throughout the experiments. The typical operating parameters and conditions are summarized in Table 8.

Table 8. Operating conditions of the ICP-MS spectrometer

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<td>Argon nebulizer gas flow rate</td>
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<td>Sampler cone</td>
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<td>Lens voltage (Autolens On)</td>
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<td>Data acquisition parameters</td>
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</tr>
</tbody>
</table>
4.5.2. Reagents and standards

All reagents used were of analytical grade. Trace metal grade nitric acid and hydrochloric acid (Fisher Scientific, Pittsburgh, PA) were used for cleaning laboratory ware. All solutions were prepared with distilled de-ionize water (18MΩcm⁻¹) from a Milli-Q analytical reagent-grade water purification system (Millipore, Bedford, MA). Calibration standard solutions and internal standards were prepared from commercial metal standard solutions (Spex Plasma, Edison, NJ). Optimal grade nitric acid (Fisher) was used for the preparation of all calibration standards solutions and analytical solutions.

Standard working solutions of lead and cadmium were prepared by 1000 mg/L standard solution (Titrisol, Merck), and internal standard was added (10 µg/L) to all of the working standard solutions to ensure sensitivity and accuracy and most importantly to eliminate interferences. The pH measurements were made on digital Beckman (Φ350 pH/Temp/mV meter) pH meter equipped with a combined pH electrode. Before measurements the pH meter was calibrated with the buffers of 4, 7 and 10. A Burrell Wrist Action shaker model 75 was used as the shaking device for the batch experiments.

4.5.3. Preparation of stock solution

Stock solutions of cadmium and lead were prepared using analytical-grade nitrate or chloride salts (99.99% purity) of the respective heavy metals being studied. Solutions of varying initial concentrations were prepared for the experimental work by serial dilution using all metal ions in their nitrate or chloride forms using distilled de-ionized
water in 2% nitric acid. For each metal, a 1000 mL stock solution of 1000 mg/L in 2% nitric acid was prepared.

4.5.4. Batch Adsorption Tests on poly[4-(4-vinylbenzyloxy)-2-hydroxybenzaldehyde] and copolymer

Various batch experiments to determine adsorption capacities of metal ions were performed using two adsorbents; poly(4-vinylbenzyloxy-2-hydroxybenzaldehyde) and poly[1-(2-pyridoyl)-3-(4-benzyloxystyrene)imidazo[1,5-a]pyridine-co-methacrylate]

For all adsorption tests, blank experiments were carried out with the same experimental procedure to check the extent of adsorption by the reaction containers. Each experiment was duplicated under identical conditions. The amount of metal ion retained in the sorbent phase or the adsorption capacity \( Q_e \) at equilibrium is determined by

\[
Q_e = \frac{ (C_i - C_e) \times V }{ m }
\]

where \( C_i \) and \( C_e \) are the initial and equilibrium concentrations of metal ion in solution (\( \mu g/L \)), \( m \) is the mass of the adsorbent (g), and \( V(L) \) is the volume of the sample solution.

4.5.5. Metal Screening Experiment.

The batch screening studies was performed to study the extent of uptake of metals by the polymer, I and copolymer II. The stock solutions (1000mg/L) of selected metals; Cu, Ni, Co, Cd, Pb, Zn, and Cr were each diluted to obtain their respective 50 \( \mu g/L \) solutions and the pH’s were measured to be 5.0-5.2 for all the solutions.

Sixteen ultra clean polyethylene vials were obtained. To the first vial labeled blank was added 25ml of de-ionize water and to the second, third, fourth, fifth, sixth,
seventh, and eighth vials respectively was added 25 mL of 50μg/L different metal solution to be used as blank or neat solutions of the metals being investigated in order to check the extent of adsorption by the polymer (or copolymer). To another set of eight clean vials, 50 mg of the polymer (or the copolymer) was added to each. To the first of this set was added only distilled de-ionized water and to the second, third, fourth, fifth, sixth, seventh and eighth was added separately 25mL of 50 μg/L of the metal solutions.

All 16 water-tight vials were closed and placed on a mechanical shaker and agitated for two hours at room temperature and then the suspensions in each of the vials were filtered into separate set of clean vials and the pH's were recorded and then set aside to be analyzed by ICP/MS. The percent uptake was calculated by the equation

\[
\text{Uptake} \, (\%) = \left( \frac{C_i - C_e}{C_i} \right) \times 100
\]

where \(C_i\) and \(C_e\) are the initial and equilibrium concentrations of the metal ions.

4.6. Batch Kinetic Adsorption Experiment for Lead

The kinetic adsorption test was done to determine the equilibrium time. Based on the result of the kinetic studies, the contact time was fixed at 30 minutes. The sorption experiments were carried out in 50 mL polypropylene vials. To the first of twenty ultra clean polypropylene plastic vials was added only de-ionized water (25 mL), to the second was added 50 mg of polymer and 25 mL of de-ionized water and to the third was added only lead solution (25mL) to be used as blank to check the extent of adsorption. To each of the remaining vials was added 50 mg polymer and 25 mL of lead solutions.

Subsequently, the vials were agitated on a mechanical shaker and at varying time intervals of between 0.5 and 30 minutes, the samples were removed at the appropriate
times and the resulting suspension were filtered into different separate clean vials. The pH of all the samples were around 5.5 and the equilibrium concentrations of the lead solution in each filtrate was determined by ICP-MS. The percent uptake of was calculated by

\[
\text{Uptake (\%)} = \left( \frac{(C_i - C_e)}{C_i} \right) \times 100
\]

where \( C_i \) and \( C_e \) are the initial and equilibrium concentrations of the P ions.

4.6.1. Modeling of the Kinetics for Lead

To investigate the adsorption mechanism, two simple kinetic models, namely the pseudo-first and pseudo-second-order were tested by studying the kinetics of different initial concentrations of lead solution. Three different concentrations (100, 300 and 500 \( \mu \)g/L) were chosen and for each, kinetic experiments were carried out in different batches. In each case, 0.025g of the adsorbent (polymer or copolymer) was equilibrated separately with 12.5mL aliquots at different time intervals between 5 sec and 75 sec for a given concentration. The suspensions were filtered and the pH's of the filtrates were measured and then analyzed by ICP-MS. The percent uptake was calculated by the equation

\[
\text{Uptake (\%)} = \left( \frac{(C_i - C_e)}{C_i} \right) \times 100
\]

where \( C_i \) and \( C_e \) are the initial and equilibrium concentrations of the metal ions.

4.6.2. Batch Equilibrium Adsorption Experiment for Lead

Equilibrium sorption studies were performed to determine the maximum lead adsorption capacities of the adsorbent in the concentration ranges of 50-2000 \( \mu \)g/L for
lead. 50 (or 25) mg of the adsorbent was equilibrated separately with 25 (or 12.5) mL aliquots of lead solutions of different concentrations between 50 and 2000 μg/L. The suspensions together with blank lead solutions of concentrations between 50 and 2000 μg/L to check the extent of adsorption were also shaken on a mechanical shaker at 25°C for 2 hrs. The suspensions were filtered through whatman filter paper (no.42) and the pH’s of the filtrates recorded. The filtrates were then analyzed for lead ion concentration using ICP-MS spectrophotometer. The percent uptake was calculated by the equation

\[
\text{Uptake (\%) = } \left( \frac{C_i - C_e}{C_i} \right) \times 100
\]

where \( C_i \) and \( C_e \) are the initial and equilibrium concentrations of the metal ions.

4.6.3. Batch Adsorption Experiment to Determine Optimum Amount of Adsorbent for Loading

To the first of twelve ultra clean polyethylene plastic vials was added only de-ionized water (25 mL), to the second was added 50 mg of polymer and 25 mL of de-ionized water and to the third was added only lead solution (25 mL) to be used as blank to check the extent of adsorption. Varying masses between 50 and 1000mg of the polymer were added to ten separate vials and to each was added 25 mL of 50 mg of lead solutions. pH of all samples were kept at 5.5. Subsequently, the vials were agitated on a mechanical for 2 hours. The resulting suspensions were filtered into different separate clean vials and the equilibrium concentration of the lead solution in each filtrate was determined by ICP-MS.
4.7. Kinetics of Cadmium Adsorption

Batch kinetic adsorption experiments were carried with 100μg/L of cadmium aqueous solution using the adsorbent (polymer or copolymer). 25mg of the adsorbent was equilibrated separately with 12.5mL aliquots of cadmium solutions at different time intervals and the resulting suspensions were each filtered and analyzed by ICP-MS. The percent uptake was calculated by the equation

\[ \text{Uptake} (\%) = \left( \frac{C_i - C_e}{C_i} \right) \times 100 \]

where \( C_i \) and \( C_e \) are the initial and equilibrium concentrations of the metal ions.

4.7.1. Modeling of the Kinetics for cadmium

For each of 3 different cadmium solution of concentration 100, 300 and 600μg/L, 25mg of the adsorbent was equilibrated separately with 12.5mL aliquots of cadmium solutions at different time intervals and each of the resulting suspensions was filtered and analyzed by ICP-MS. The percent uptake was calculated by the equation

\[ \text{Uptake} (\%) = \left( \frac{C_i - C_e}{C_i} \right) \times 100 \]

where \( C_i \) and \( C_e \) are the initial and equilibrium concentrations of the metal ions.

4.7.2. Batch Equilibrium Adsorption Experiment for cadmium

25 mg of adsorbent was equilibrated separately with 12.5mL aliquots of cadmium solutions of different concentrations (100, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1200, 1400, 1600, 1800 and 2000 μg/L) and the resulting suspensions were filtered and analyzed by ICP-MS. The percent uptake was calculated by the equation
Uptake (%) = \left( \frac{(C_i - C_e)}{C_i} \right) \times 100

where $C_i$ and $C_e$ are the initial and equilibrium concentrations of the metal ions.

4.8. Column adsorption Experiment

Column adsorption experiment was performed using a 0.5x10 cm glass column packed with 0.25 g of the polymer. A solution containing 91.5 μg/L of pH 5.5 was passed through the column of inner diameter of 0.5 cm at a flow rate of 1.0 mL per minute. The solution which was passed through the column was fractionated in 10 mL portions at regular intervals, and the concentration of lead was determined by ICP-MS.
Imidazole or its derivatives, salicylaldehyde and 2,2'-dipyridyl ligands were functionalized by successfully incorporating organic functional groups such as vinyl groups into them and subsequently developing them into polymeric chelating ligands via free radical polymerization. Characterization techniques such as GC-MS, elemental analysis, $^1$H and $^{13}$C-NMR as well as GPC and DSC confirmed the successful synthesis of the monomers and the incorporation of the functional groups as well as the synthesis of the polymer and the copolymer. Poly[4-(4-vinylbenzyloxy)-2-hydroxybenzaldehyde] and poly[1-(2-pyridyl)-3-[4-(4-vinylbenzyloxy)phenyl]imidazo[1,5-a]pyridine-co-methacrylate] which were successfully synthesized as a result of the free radical polymerization were then investigated for toxic heavy metals removal from aqueous solution.

The polymer and the copolymer were subjected to batch adsorption tests and they were found to be excellent sorbent materials for heavy metal removal from water. Both adsorbents were found to be very effective in removing copper, nickel, cobalt, cadmium, zinc, and lead but the highest uptakes occurred for cadmium and lead. The adsorption capacity of the polymer when treated with lead solution is 333.3 µg/g within the concentration range of study. Upon treating the copolymer with lead solution, adsorption capacity was found to be 625 µg/g within the concentration range of study.
Both adsorption capacities are consistent with the Langmuir adsorption isotherm. The kinetics of sorption was found to be very fast and a time of 30 second was sufficient for equilibrium to be attained. The kinetics of sorption also followed a second order rate equation suggesting that the frequency of collision on the adsorption sites is very high. For both the polymer and the copolymer, the Langmuir model best described the adsorption mechanism suggesting that the sorbed metal ions formed a monolayer at homogeneous sites on the adsorbent surface.

The advantages of these adsorbents include fast metal removal, large binding energy, stability of the adsorbents in both acidic and basic media, mechanical stability, high thermal stability and good reproducibility. From literature review, so far, no other adsorbents have metal removal time as small as the 15 seconds determined for these two adsorbents.
Appendix

A

1-(2-pyridyl)-3-(3-hydroxyphenyl)imidazo[1,5-a]pyridine

$^1$H NMR
Appendix

B

1-(2-pyridyl)-3-(4-benzyloxystyrene)imidazo[1,5-a]pyridine

$^1$H NMR
$^{13}$C NMR
Current Data Parameters
NAME  13C-P725ynd
EXPNO  1
PROCNO  1

FE - Acquisition Parameters
Date_  20070210
Time  0.27
INSTRUM  spect
PROCNO  1
PULPROG  J009
TD  0.0536
SOLVENT  DMSO
VE  12000

SP  2
DM  23231.2982 Hz
FIDNCE  0.276855 s
AE  0.276855 s
CS  15.0369 s
SE  2.4313 s
TE  10.0412 s
J2  0.20000004 s
D18  15.0000 kHz
D11  30010000 s
CPTRANS  0 s
FT1  100.087471 sec
D11  0.0000000 s
D15  25.0000 sec
P1  7.9000 sec
SFO1  100.087471 MHz
AXXLES  15C

FE - Processing parameters
SI  3.1799
SF  10.00000000 MHz
SCN  50
SB  0
JE  5.644 MHz
JS  0
PC  1.40

1D NMR Data Parameters
CH  20.00000000
CF  109.990 ppm
CI  109.990 ppm
CIF  -11.100 ppm
CF  -1100.94 Hz
FWHM  9.73501 ppm/cm
Hzcm  925.3290 Hz/cm
Appendix

C

1-(2-Pyridoyl)-3-(4-hydroxyphenyl)imidazo[1,5-a]pyridine

\[ ^{1}H \text{ NMR} \]
\[ ^{13}C \text{ NMR} \]
Appendix

D

1-(2-Pyridoyl)-3-(4-benzylloxystyrene)imidazo[1,5-a]pyridine

$^1$H NMR
$^{13}$C NMR
Appendix

E

4-vinylbenzyloxy-2-hydrobenzaldehyde

\[
\begin{align*}
\text{H}_2\text{C}=:\text{C} & \quad \text{CH}_2\text{O} \quad \text{C} & \quad \text{OH} \\
\text{H} & \quad \text{H} & \quad \text{CHO}
\end{align*}
\]

\textsuperscript{1}H NMR
Appendix

poly(4-vinylbenzyloxy-2-hydrobenzaldehyde)
Appendix

G

Poly[1-(2-pyridoyl)-3-(4-benzyloxystyrene)imidazo[1,5-a]pyridine-co-methacrylate]

$^1$H NMR
$^{13}$C NMR
Current Data Parameters
NAME C13Cp84syn3
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Data.  200668203
T1m 20.44
INSTRUM spect
PROBE 5 mm H2O
MTRPSP 2902
TD 65556
SOLVENT CDCl3
NS 12000
DS 2
SMR 33333.333 Hz
FTIGES 0.598626 Hz
AG 0.9809090 sec
RG 32768
DM 15.000 ussec
EE 21.43 ussec
TE 300.0 K
D10 0.0000000 sec
D16 25.000 dB
D1 3.0000000 sec
CPDPSPG wait15
F3i 105.000 ussec
D11 0.0300000 sec
D15 25.00 dB
P1 7.50 ussec
SEOG 100.0254258 MHz
NUCLEUS 13C
F2 - Processing parameters
SI 32768
SF 100.0127250 MHz
XHP EM
S5B 0
LB 5.00 Hz
SB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
FP 190.040 ppm
F1 2005.0 Hz
FP 11.040 ppm
F2 -1001.63 Hz
PPCH 10.5362 ppm/cm
HZCH 1059.39001 Hz/cm
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