AMERICAN UNIVERSITY OF BEIRUT

THE QUICK-SILVER PROBLEM: CONQUERING MERCURY POLLUTION USING A GREEN CHEMICAL SOLUTION

by
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A thesis
submitted in partial fulfillment of the requirements
for the degree of Master of Science in Environmental Sciences
to the Interfaculty Graduate Environmental Science Program
(Environmental Technology)
of the Maroun Semaan Faculty of Engineering and Architecture
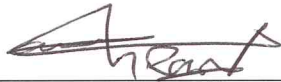at the American University of Beirut

Beirut, Lebanon
April 2019

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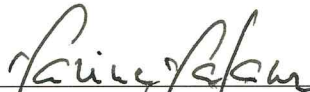
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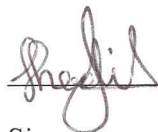☒Master's Thesis   ☐Master's Project   ☐Doctoral Dissertation

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ACKNOWLEDGEMENTS

AN ABSTRACT OF THE THESIS OF

Hadil Ali Borji   for   Master of Environmental Science
                                          Major: Environmental Technology

Title: The Quick-silver problem: conquering mercury pollution using a green chemical
        solution

Pollution of surface and ground water with heavy metals threatens living organisms and their environment. Mitigation techniques are required to reduce the amount of heavy metals to safer levels, complying with the EPA concentrations. One of the established techniques towards the removal of heavy metals is chemical treatment, namely metal chelation, of contaminated water. Building on the knowledge gained from various chemical treatment approaches of water purification, we are reporting a 'green' chemical treatment approach, where minimal chemical waste is generated in the process of water treatment. We are reporting a study that employs commercially available organic compounds (aniline and aldehyde) used to prepare dynamic pyridylimine ligands (receptor) capable of detecting and removing mercury(II) ions from water. The suggested receptor was prepared and its capability in removing mercury ions from water was investigated. It was found out that two receptors bind to one Hg(II) ion tightly (binding affinity K_G =7.8 x 10^7 M^{-1}) in water. It was observed that the used organic ligand can effectively remove 250 mg/L Hg(II) ions from mercury contaminated water, with a complete removal (100% removal efficiency) in 30 mins. The receptor: Hg (II) complex was removed from water and isolated for further characterizations. Formation of the metal-organic complex (2 receptors: 1 Hg (II)) can be reversed under controlled conditions, regenerating the pyridylimine ligand up to four other cycles of water treatment.

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LIST OF ABBREVIATIONS

AAS	Atomic absorption spectrophotometry
AC	Activated carbon
As	Arsenic
BDET	1,3-benzenediamidoethiol dianion
BDP	N,N'-bis-(dithiocarboxy)piperazine
CA	Citric acid
Cd	Cadmium
CDTC	Dithiocarbamate
CNTS	Carbon nanotubes
Cr	Chromium
Cu	Copper
EDTA	Ethylenediamine tetra acetate
EDX	Energy dispersive X-ray spectroscopy
EPA	Environmental protection agency
Hg	Mercury
$Hg(TFA)_2$	Mercury(II) trifluoroacetate
Hg^0	Elemental mercury
HgCl	Mercury Chloride
HTDC	1,3,5-hexahydrotriazinedithiocarbamate
KPF_6	Potassium hexafluorophosphate
MeHg	Methylmercury
MOFs	Metal organic frameworks
Ni	Nickel
OA	Oxalic acid
Pb	Lead
RO	Reverse osmosis
SEM	Scanning electron microscope
STC	potassium/sodium thiocarbonate
UV-vis	Ultraviolet-visible spectrophotometry

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CHAPTER 1
INTRODUCTION

1.1. Introduction

Pollution of fresh water sources has grown to be a major threat worldwide. The vast increase of population size provoked tremendous increase in the demands of life on all aspects, thus typically expanding the process of industries which in return results in organic, inorganic and toxic metallic waste discharges. Moreover, agricultural needs increased to an extent that the normal range doesn't satisfy the demand of increased population, hence the usage of chemical additives has been induced in order to trigger more swift and productive means of harvesting crops to comply with the essentials of the growing population. These put together (industrial discharges, and agricultural wastes) have found their way into polluting fresh water resources in a significant level.

Among the dangerous contaminants to both living organisms and their environment are heavy metals, which are invariably discharged from industrial, agricultural and/or natural sources. These metals are known to be toxic, their continuous release into the environment have caused growing concerns (Nagajyoti *et al.*, 2010; Deng *et al.*, 2013), primarily due to the fact that heavy metals have the ability to dissolve in wastewater and accumulate up in the food chain or discharge in surface waters (Alagappan *et al.*, 2017). Anthropogenic sources of heavy metals and their mode of transportation in the environment is illustrate in Figure 1.
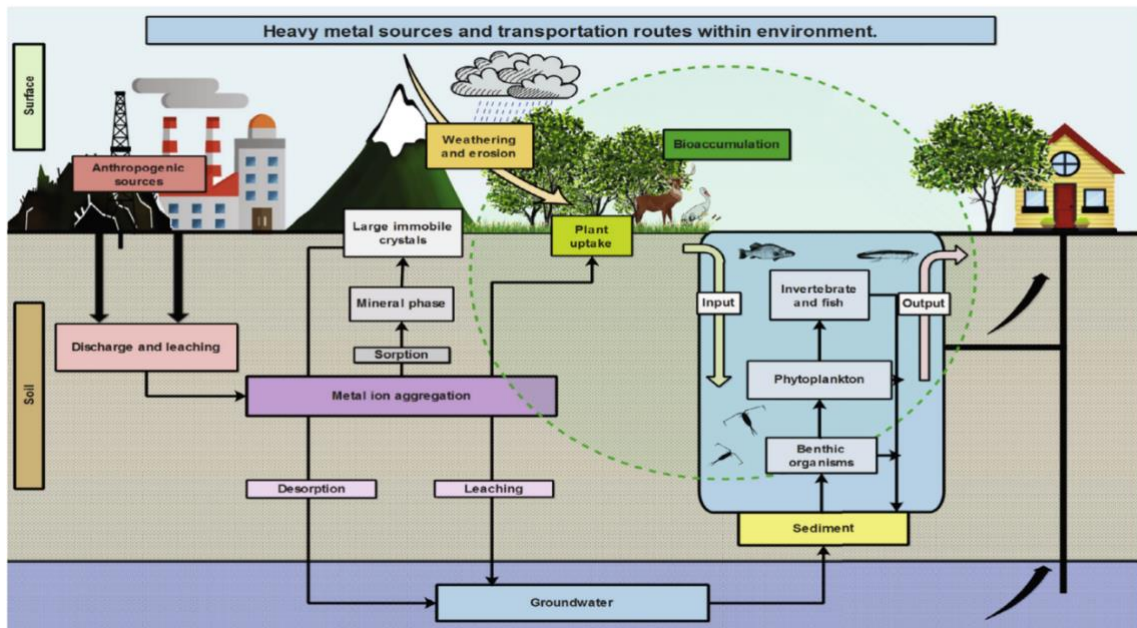
Figure 1 A flowchart showing how soil, fresh-and groundwater system redistribute heavy metals of anthropogenic origin (Kobielska *et al.*, 2018).

Heavy metals are particularly problematic due to their non-biodegradable characteristics, which poses a threat to the well-being of living organisms and to the ecological environment (Lesmana *et al.*, 2009). The most commonly encountered heavy metals include mercury, cadmium, lead, chromium, arsenic, zinc, copper, nickel and cobalt (Abdel Gawad, 2018). These metal ions have the potential to cause toxicities and serious side effects, which can vary from minor to major and severe health problems, might lead to death when exposed to in high concentrations beyond permissible levels (Tang *et al.*, 2012).

Previous studies discussed sources of heavy metals contamination in water sources, where they found that the presence of cadmium, copper, nickel, lead, chromium and mercury (Cd, Cu, Ni, Pb, Cr, and Hg) in aqueous solutions is mainly attributed to industrial activities, pesticides, domestic wastewater, and tannery effluents, whereas the high concentration of arsenic (As) (with its different oxidation states) is mostly due to natural anoxic conditions in the aquifers (Chowdhury *et al.*, 2016).

Heavy metals in waster were found to have diverse effects on human health; As and Ni are classified as human carcinogens, Pb can cause high blood pressure along with kidney problems, circulatory and nervous system problems were attributed to the presence of Hg, and gastrointestinal problems due to the existence of Cu in water (Chowdhury *et al.*, 2016; Azimi *et al.*, 2017). Table1 shows different heavy metals, their toxicity, and their international allowable standards. Consequently, the need for proper removal of such heavy metals from water resources has become mandatory if their concentrations exceeded international allowable levels.

Table 1 International allowable standards for the most hazardous heavy metals (Chikumbusko *et al.*, 2017)

Heavy metals	Toxicity	International allowable standards (mg/l)	Reference (Chikumbusko *et al.*, 2017)
Arsenic	Skin disease, cancer	0.05	EPA/WHO
Cadmium	Kidney problems, cancer	0.003	WHO
Chromium	Headache, diarrhea, nausea, cancer	0.1	EPA
Copper	Liver damage, Wilson disease	2	WHO
Zinc	Neurological problems	Not of a health concern	WHO
Lead	Brain damage, kidney disease	0.015	EPA
Mercury	Circulatory and nervous system problems	0.006	WHO

To date, several methods have been proposed for the efficient removal of heavy metals from water, including: coagulation, chemical precipitation, membrane filtration, ultrafiltration and nanofiltration, reverse osmosis (RO), solvent extraction, flotation, ion exchange by acids or zeolites (Fu and Wang, 2011), and adsorption (Hua *et al.*, 2012). Adsorption (the process of mass transfer, where the suspended solid is accumulated on the surface of solid because of physical or chemical interaction (Babel et al., 2003)) is one of the favored methods due to the regeneration of the adsorbent in some cases, some of the used adsorbents include activated carbon (AC), carbon

nanotubes (CNTS), naturally found adsorbents like kaolinite and montmorillonite (Fu and Wang, 2011), electrocoagulation and MOFs (Kobielska *et al.*, 2018).

Choice of the mode of water treatment method for metal removal depends on many factors, which include: metal concentration, components of wastewater, operation cost, and environmental impact (Fu et al., 2011). Chemical treatment approaches are among the most exploited water treatment methods, extensive research has been invested in using metal chelation techniques for the removal of heavy metals from water and wastewater. (Fu *et al.*, 2006; Fu *et al.*, 2007; Neranon and Ramström, 2016; Kobielska *et al.*, 2018).

1.2. Chemical treatment of heavy metals contaminated water

Treatment methods targeting the removal of heavy metals from water usually have high removal affinity, but also exhibit limitations due to their high operational costs and producing secondary hazardous contaminants (Li, 2014). Hence, extensive research is being conducted to develop effective, cheaper methods for metal ions removal with minimal hazardous side products production. This is where chelating precipitants can be considered an attractive alternative. Metal chelators sometimes referred to as ligands, are organic chemical compounds capable of reacting with metal ion(s) to form a metal-organic complex. The strength of the coordination bonds lying between covalent and non-covalent bonds which differs depending on the used metal and ligand. Moreover, the geometry of the final structure can be controlled by the employed metal, where different metals adopt different geometries resulting in different assemblies.

Metal-organic complexes are held together through coordination interactions (Lehn, 1990; Lehn, 2002), various metal chelators (organic ligands) were designed to

sequester metal ions (by interacting with them, forming a metal-organic complex) from water. Some of these metal chelators will be discussed in this section.

N,N'-bis-dithiocarboxy piperazine (BDP, Figure 2a), is an organic ligand developed to chelate metal ions in water. BDP is not commercially available, it can be obtained through three synthetic steps in the lab. Fu and coworkers studied BDP's capability of removing heavy metals in water and its efficiency to be used in water purification. This metal chelator has shown efficient removal of nickel from industrial wastewater, where results showed that nickel ions decreased sharply far below 0.5 mg/l with the addition of BDP (Fu et al., 2007). Moreover, BDP was found to remove zinc(II) (Thyagarajan et al, 2013), iron(II) (Hirayama et al., 2016), and copper(II) (Blais et al., 2008) from freshwater through chelation.

Fu et al., modified the structure of BDP to a new class of dithiocarbamate which chelates to heavy metals by forming supramolecular precipitate, coordination polymerization. The synthesized organic ligand is called 1,3,5-hexahydrotriazinedithiocarbamate (HTDC, Figure 2b) is also not commercially available but can be obtained through a series of different synthetic steps in the lab. HTDC has shown efficiency towards decreasing copper levels in industrial wastewater to 0.5 mg/L which complies with the environmental regulatory limit (FAO, 1998). Thus HTDC was considered a potential candidate for copper removal from wastewater by metal chelation (Fu *et al.*, 2007).

Another class of metal chelating precursor is potassium/sodium thiocarbonate (STC, Figure 2c). This compound is known by the trade name of Thio-Red. STC can be easily prepared by acid-base reaction pathway, with a yield of 67 to 71%. Studies have shown that STC has a high affinity towards the removal of copper, mercury, lead,

and cadmium from water through the formation of metal sulfides, insoluble species in water, thus making them easy to separate from water (Henke,1998).

(a) BDP (Fu et al., 2007)   (b) HTDC (Fu et al., 2007)   (c) STC (Henke,Kevin,1998)
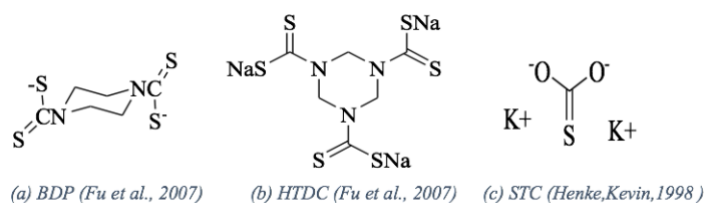
Figure 2 Examples of organic ligands designed to sequester metals from water.

Another metal chelator is 1,3-benzenediamidoethiol dianion (BDET), commercially known as MetX, with a synthesis that requires a one-pot step (Matlock et al., 2002). BDET is used to bind to soft heavy metals such as Al, As, Co, Cr, Cd, Pb, Hg and Cu to ensure their removal from water (Figure 3). Results showed the effectiveness of BDET in the removal of mercury in groundwater to below 0.05 ppb (Blue et al., 2007), and decreasing the concentration of lead (Pb) by 99.4% in an average time of 15 minutes (Matlock, et al., 2002), along with the removal of cadmium Cd(II) from water (Zaman et al., 2007).

(a) M^{2+} = Hg   (b) M^{2+} = Cd or Pb
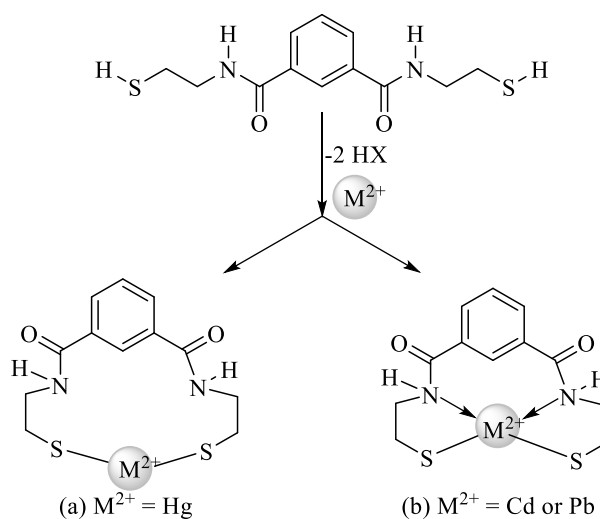
Figure 3 Mode of interaction between BDET and heavy metals (Zaman, et al., 2006).

Furthermore, Li developed carbamide based dithiocarbamate (CDTC), yet another metal chelator for removal of heavy metals from wastewater (Figure 4). CDTC is synthesized through two synthetic steps (Li, 2014) in the lab. Results showed that CDTC had a high binding affinity towards (Zn^{2+}) and (Cu^{2+}) at pH higher than 7 along with the removal of chromium, lead, and cadmium but in lower affinity. The removal amounts were 0.186 mmol/g for Zn^{2+}, 0.206 mmol/g for Cu^{2+} and 0.019 mmol/g for Cd^{2+} (Li, 2014).
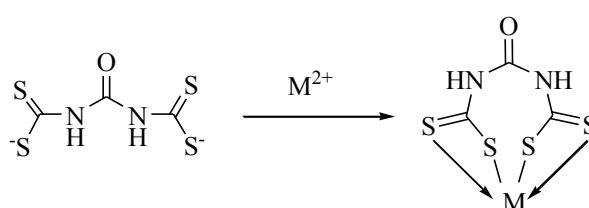
Figure 4 Chelation of metal ion to CDTC (Li,2014).

Al-Quhtani conducted a study where he investigated the effect of three chelating agents ethylenediamine tetra acetate (EDTA, Figure 5a), oxalic acid (OA, Figure 5b), and citric acid (CA, Figure 5c), on heavy metal extraction from polluted water. OA exhibited the highest binding ability towards the extraction of Hg(II) and Cu(II). OA, CA, and EDTA were shown to follow the same behavior in binding towards the selected metal ions, atoms participating in the binding are nitrogen and oxygen- donor atoms with unshared electron pair that can coordinate to the metal ion. Different parameters were examined such as pH, chelating agent concentration and extraction time on the efficiency of metal sequestration from polluted water. Results showed that the optimum pH value is 2-4 for the extraction. Increasing the pH of the extraction led to a decrease in the removal of copper and mercury ions from water. As expected, as the concentration of the chelating agent increased, extraction affinity increased as well. Furthermore, results have shown that it takes about 60 mins for

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extraction to take place, and beyond this time no change was observed (Mohamed Ahmed Al-Qahtani, 2017).

(a) Metal-EDTA structure (Mohamed Ahmed Al-Qahtani,2017)   *(b) Structure of CA (Islam, 2012)*   *(c) Structure of OA (Surov et al., 2017)*
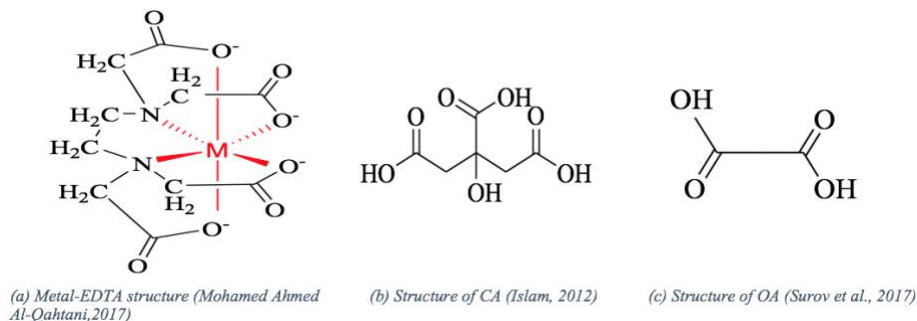
Figure 5 Different metal chelators' structures.

1.3. Mercury and its presence in water as contaminant

Mercury (Hg) is one of the most toxic heavy metal ions in the environment, this is due to its volatility, generating highly toxic vapor, that can cause serious damage to the nervous system, kidneys and liver (Beckers and Rinklebe, 2017; Cheng *et al.*, 2017)

Mercury originates from both natural and anthropogenic activities, which include volcanism, erosion of sediments containing Hg, combustion of fossil fuels, and usage of mercury in industries and agriculture (Figueiredo *et al.*, 2017; Streets *et al.*, 2017).

Mercury is widely used in science, industry, and agriculture. Its importance starts with its services in laboratory products like barometers, thermometers, vacuum pumps, to its unique ability to conduct electricity and its role in dentistry (dental amalgams). In addition to the use of Hg in agriculture as a foliar spray against plant diseases (Beckers and Rinklebe, 2017). Natural and anthropogenic emission of mercury is emphasized in Figure 6.

Hg emissions by natural sources by the year 2010

Hg emissions by anthropogenic sources by the year 2010

Natural sources legend: Oceans, Lakes, Forests, Grassland, Deserts, Agricultural areas, Evasion after Hg depletion events, Biomass burning, Volcanoes

Natural pie values: 2%, 4%, 2%, 13%, 50%, 10%, 10%, 7%, 2%

Anthropogenic sources legend: non-ferrous metal production, Iron and steel production, Cement production, Caustic soda production, Mercury mining, Gold mining, Waste disposal, Coal bed fires, Vinyl chloride monomer production, other

Anthropogenic pie values: 1%, 2%, 5%, 19%, 13%, 26%, 5%, 11%, 15%, 3%

Figure 6 Natural and anthropogenic Hg emissions in the year 2010 (Mahbub *et al.*, 2017).

Presently, almost (5.5-8.9) x 10^6 Kg of mercury is emitted to the atmosphere yearly on a global level, about 10% of which is due to natural resources, 30% due to anthropogenic source, and 60% due to environmental processes which include the re-emission of Hg previously deposited into the surface environment from past natural or anthropogenic resources (Asaduzzaman *et al.*, 2019).

Mercury concentration in uncontaminated natural waters varies by the type of water body and the location. For example, concentrations in the black sea were found to be in the range of 0.36-2.37 ng/L, while the concentration of Hg in the Mediterranean Sea was found to be in the range of 0.05-1.8 ng/L respectively. As for coastal waters, Hg concentration range lies between 0.1 and 35 ng/L. Whereas for natural, pure fresh water system like river waters, Hg concentration seems to be much lower (1.0-5.0 ng/L) as these waterbodies commonly exhibit strong fluctuations and are subject to dilution effect (Beckers and Rinklebe, 2017).

Mercury concentration in contaminated waters is significantly higher than that of uncontaminated natural waters. An extremely high concentration of mercury (280,000 ng/L) was found in drainage water from an abandoned Hg mine in California,

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which caused contamination of the water body due to the reaction of the drainage water with mine tailings (Beckers and Rinklebe, 2017).

Mercury exists in nature mainly as elemental mercury (Hg^0) which has a long lifetime (0.4 – 1.7 years) and can travel long distances through the atmosphere, this is why it is referred to mercury as a "global" pollutant (Gonzalez-Raymat *et al.*, 2017). Moreover, Hg^0 can be oxidized to form (Hg^{2+}) the primary form of mercury existing in aqueous environments. Mercurous ion Hg^+ is present in the environment, however, it is unstable and can rapidly convert to Hg^{2+} or Hg^0. Other forms of mercury consist of Hg^{2+} bound to another compound like mercury chloride ($HgCl^-$) which can be found in seawater, and (HgO^-) which is found in fresh waters. (Asaduzzaman *et al.*, 2019).

Mercury (II), Hg^{2+}, exhibit a short atmospheric residence time so it deposits in nearby landscapes, and once deposited it either resides in soils and aqueous environment or reduced back to Hg^0 and re-emitted into the atmosphere as illustrated in Figure 7 (Lehnherr, 2014). Hg(II) can be methylated and change to methylmercury (MeHg) in the aquatic environment by microorganisms (sulfate reducing bacteria, iron reducing bacteria, and methanogenic archea) (Lehnherr, 2014)
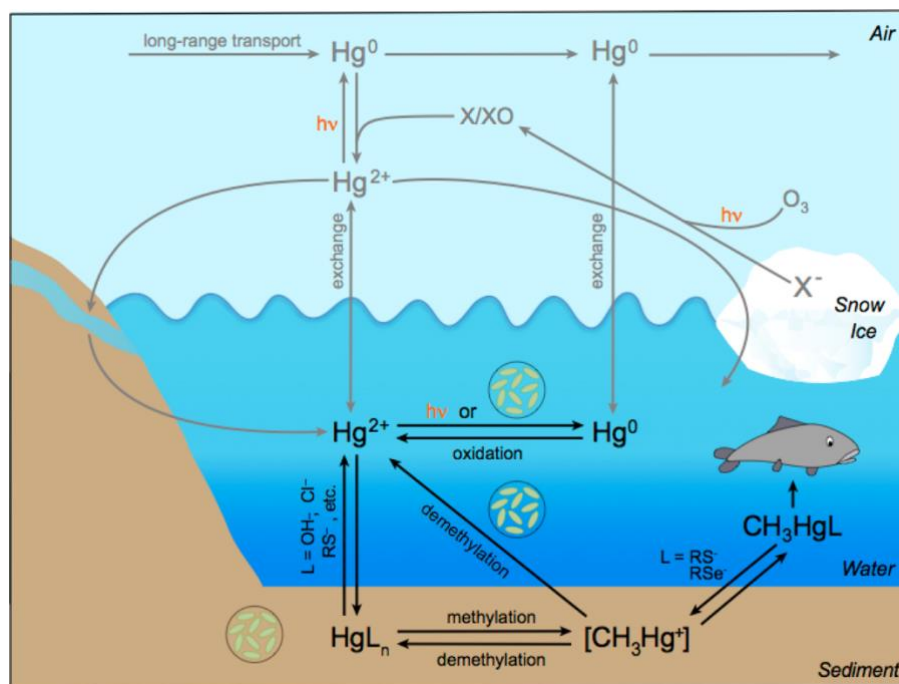
Figure 7 Transport and transformation processes in the global Hg cycle (Asaduzzaman *et al.*, 2019).

Unlike airborne mercury (Hg^0), Hg^{2+} is highly reactive, nephrotoxic, hepatoxic, and immunotoxic (Asaduzzaman *et al.*, 2019). Hg^{2+} is the immediate substrate for the formation of methylmercury (MeHg) which can cross the blood-brain barriers causing neurological problems.

Moreover, most of the mercury in water is found as: (a) the inorganic form, Hg(II), and (b) organic form as methylmercury which is the bio-transformation of the inorganic Hg(II) to methylated organic species in bodies of water (Beckers and Rinklebe, 2017). Methyl mercury (Figure 8) is produced in acidic and neutral aqueous environments and can be transformed into monomethyl mercury (CH_3HgX), in which X is a sulfur containing amino acid, consequently this complex can cross the blood-brain barriers and cause serious damage, making methylmercury the most hazardous form of mercury (Cesario *et al.*, 2017).

$$^+Hg-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}} -H$$
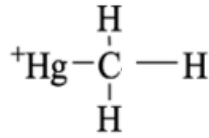
Figure 8 Methylmercury

Most of the mercury present in the human body is in the form of methylmercury. Methylmercury exhibits bioaccumulation properties in fish, where it binds to the sulfhydryl group in proteins distributed in fish, which in turn is consumed by humans. The concern about methylmercury in aquatic environment arises from its toxicity and that fact that Hg species in this form exhibit bioaccumulation and biomagnification properties. The term bioaccumulation, in this setting, alludes to the net accumulation of MeHg within an organism, while the term biomagnification refers to the progressive buildup on MeHg by successive trophic levels. Methylmercury transports in the food chain of the fish species and its predators, hence the larger the fish the higher the concentration of methylmercury it holds (Ritger *et al.*, 2018; Asaduzzaman *et al.*, 2019). Methylmercury exhibits a half-life of 70 days in human bodies due to its lipophilic characteristics (Baird, Cann, 5th edition), where it can accumulate in the human body and cause harmful effects (Juric *et al.*, 2017). According to the world health organization (WHO), the safe limit of methylmercury consumption lies under a threshold of 4 µg/day (Bose-O'Reilly *et al.*, 2010; Ritger *et al.*, 2018). Consequently, the Minamata Convention on mercury resulted in an international treaty to reduce anthropogenic emissions of Hg^{2+}, this treaty entered into force in the year 2003 and took 10 years for all parties to sign. The health impact of mercury exposure to the human body includes damage to the gut and the kidneys, stomach ache, vomiting, loosening of the teeth, blindness, tremor, neurological problems, and many more (Hong *et al.*, 2012).

Efforts to sequester mercury from the environment include different methods such as hydrogel, porous silica, chemical oxidation or reduction, MOFs, ion exchange, electrochemical treatment, filtration, coagulation, adsorption and covalent organic framework all of which showed potential progress in removal of Hg ions from water (Cheng *et al.*, 2017; Awad *et al.*, 2018). Most of these methods have limitations and disadvantages when used for water treatment. For instance, precipitation is inefficient since it produces high secondary hazardous material (sludge), whereas desalination (distillation) and electrochemical treatment require relatively high operational costs. Among the mentioned treatment methods, adsorption is perhaps the most extensively used method, due to its simplicity and high efficiency in large scale applications, but its main disadvantage is the high cost of effective and efficient adsorbents used which increases the cost of water treatment. Traditional adsorbent like silica, metal oxides, zeolites, resin, chitosan, and activated carbon suffer from poor adsorption sites, low selectivity, and poor regeneration which limit their practical application as an efficient adsorbent for mercury removal (Awad *et al.*, 2018). Therefore, it would be valuable to propose a treatment method with fewer limitations than the aforementioned treatment mechanisms.

New methodologies are required to improve economics and decrease the limitations resulting from former techniques to increase the efficiency of the proposed method and enhance environmental protection. Hence, we think we can do much better with more sustainable approaches that fall under the basic principles of "green chemistry sustainable system". Green chemistry by definition is a method devoted to reduce pollution and environmental degradation by utilizing eco-friendly, non-hazardous, reproducible, yet efficient methods for the removal of pollutants from water resources.

1.4. Mercury chelation to organic ligands

Detecting Hg(II) metal ion through chelation mechanism has been investigated in several studies with different techniques. Singhal et al. 2015, detected the presence of Hg^{2+} ion in solution by UV-vis studies, through the synthesis of a probe containing an amine group. Results showed reasonable binding affinity between the synthesized probe and Hg(II) ion forming a metal-ligand complex in methanol/H_2O solution (Singhal *et al.*, 2015). Another study by Cheng and co-workers in 2017, studies the synthesis of a Pillararene- based supramolecular polymer for the removal of Hg ions from water. This supramolecular polymer has two thymine groups, one on each side of the ring that eases the binding with Hg^{2+} ions (Figure 9). Moreover, this polymer has exhibited recycling properties by the addition of Na_2S without any loss of its activity (Cheng *et al.*, 2017).
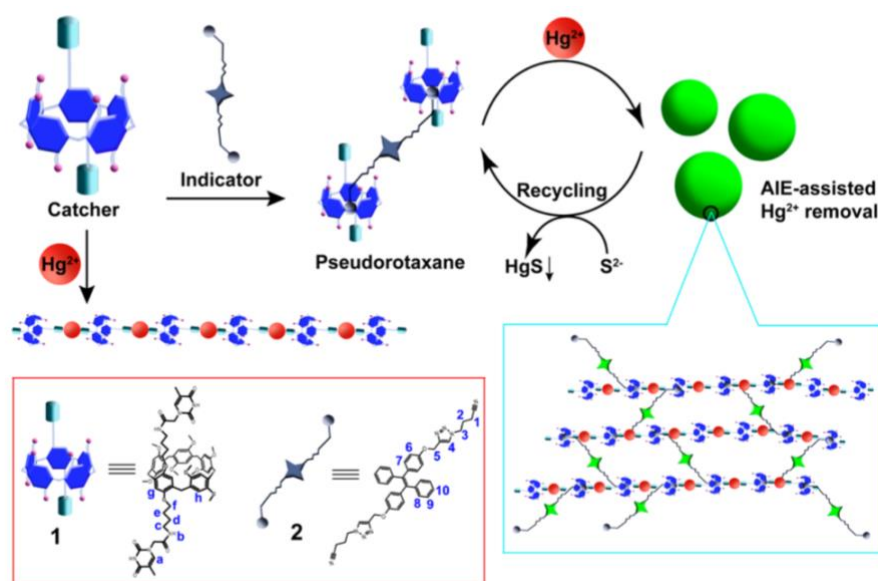
Figure 9 Proposed strategy for the sensing and removal of Hg ions based on the formation of supramolecular polymers. (Cheng *et al.*, 2017)

CHAPTER 2
RESEARCH OBJECTIVES

Despite the extensive work in optimizing water purification methods through chemical treatments/precipitation, hazardous secondary contaminants, separation of the sequestered metal ion and recyclability/ regeneration of the ligand are issues yet to be addressed. This research project aims at the development of a new chemical treatment approach where the organic ligand (metal chelator) used is reversible in nature and its complexation to the metal ion is also dynamic (could be reversed). The reversibility of the formation of the ligand and its complexation to the metal ion will ensure that the sequestered metal ions will be separated from the metal-organic complex. Separating the metal ion from the metal-organic complex leaves behind the organic ligand that could be reused for another round of chemical treatment (metal sequestration). The adopted methodology falls under the title of a green chemistry approach, where a green chemistry concept presents efficient and sustainable systems while eliminating secondary hazardous material and minimizing energy consumption.

The project is designed to target three main objectives: (I) detecting the presence of mercury ions in solution through the formation of the metal-organic complex, (II) removal/ sequestration of the chelated metal from solution, and (III) regeneration of the organic ligand through separating the metal from the organic components.

During the course of this research on detecting, removal, and separation of heavy metal ions, a well-known chemistry of imine-based ligands is discussed (formation of the imine bond is shown in Figure 10) and the capability of the pyridylimine to coordinate reversibly to metal ions in water, forming a metal-organic

complex (Schultz and Nitschke, 2007). Metal-organic complexes are dynamic due to the reversible bonds holding them together. With some exceptions, changing the pH of the metal-organic complex in solution to an acidic media leads to breaking the complex down to its main components.
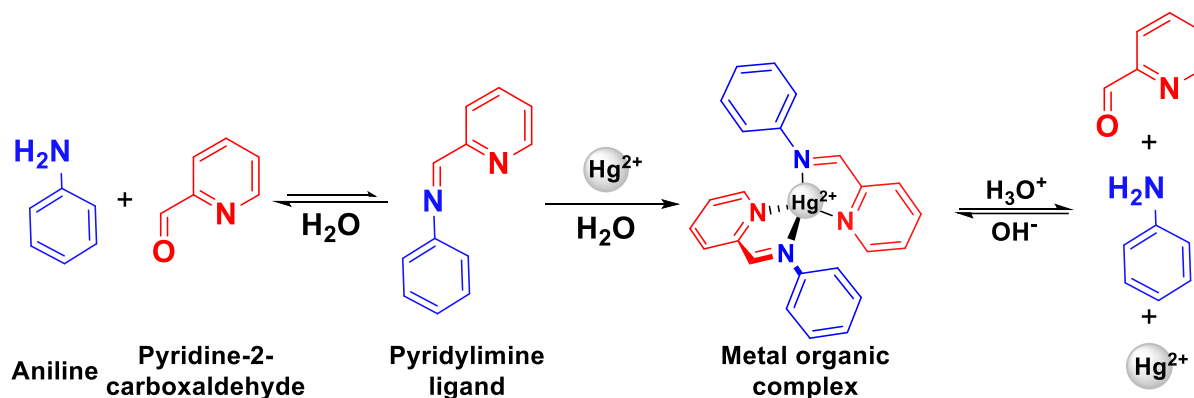
Figure 10 Mechanism of the reaction between Hg2+ ion and the pyridylimine ligand.

Based on the mechanism shown in Figure 10, the ligand will target the sequestration of Hg^{2+} ions from water. Due to the tetrahedral geometry of mercury(II), two sets of ligands will chelate to mercury, satisfying its tetrahedral sphere.

We hypothesize that the three targeted steps (detection, sequestration, and regeneration of the components) will be achieved through employing this dynamic chemistry.

CHAPTER 3

METHODOLOGY

The aim of the project will be represented in the experimental approach which is outlined below.

Figure 11 Experimental Scheme.
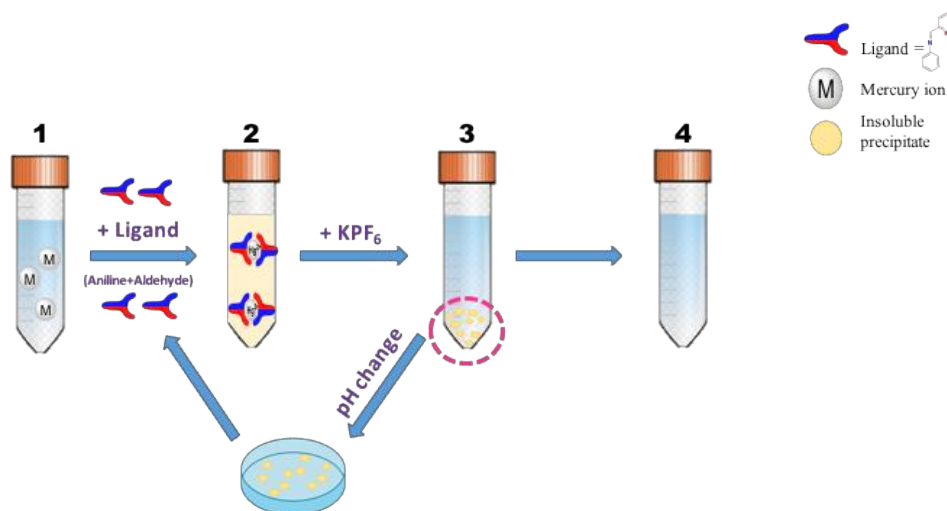
3.1. Sensing and sequestering of Hg^{2+} ions by UV spectroscopy:

The experimental setup designed to validate the hypothesis is depicted in Figure 11, where the organic components (aniline and 2-pyridinecarboxaldehyde) are added to the synthetic water, to form a covalently reversible imine bond in solution, the organic ligand that will chelate to mercury.

Water enriched with mercury(II)ions (mercury(II)triflate) will be prepared to mimic polluted water (Figure 11, tube 1), and the organic ligand components (aniline and 2-pyridinecarboxaldehyde compounds) will be added to the water, for sequestering the Hg^{2+} ions (Figure 11, tube 2).

For over 150 years, extensive research has been conducted on the reaction of amines with aldehyde to produce Schiff bases, most popular classes of compounds in organic and coordination chemistry (Ahmed *et al.*, 2017). Schiff base reactions have

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been shown to be promising candidates for the design of metal chelators (Al Zoubi, 2013).

In this study, the proposed ligand exhibited excellent solubility in water. Once the ligand is added to mercury spiked water this reversible bond will be further stabilized through its coordination with Hg^{2+} ions (W. Steed *et al.*, 2007). Coordination of such ligand to the metal ion is due to an unshared pair of electrons in the ligand, which donates it to the metal to form a coordinate bond with the latter.

The experiment will be carried out at room temperature, thus no temperature change will affect the formation of the ligand or the metal-organic complex. Moreover, a titration was carried out, where different concentrations of the metal will be added sequentially to the aqueous solution of ligand (the concentration of the ligand will be kept constant throughout the experiment as shown in table.3-appendix.) in the cuvette to be analyzed by ultraviolet spectroscopy (UV-vis). Different initial concentrations of the organic ligand will be selected to identify the optimum concentration for the complex formation, and to check for saturation of the ligand (the point at which the ligand can bind no more to the metal). Detecting the metal-organic ligand complex is achieved by UV spectroscopy, where the absorption of visible or ultraviolet light by the complex will produce a distinct spectrum (different from the ligand on its own).

3.2. Removal of Hg^{2+} ions from water by adding a counter salt:

Once the metal-organic complex is formed, sensed (detected by UV) the next step is to separate this soluble complex from water. The proposed approach is to treat the solution with a salt (KPF_6) to change its counter ion and consequently change its solubility forming a precipitate (Figure 11, tube 3). This precipitate will be removed from solution through filtration, leaving a clear treated solution which presents the

treated water sample (Figure 11, tube 4). Finally, the change in the solution pH of the filtered precipitate will break the coordination of the complex releasing the organic ligand that could be recycled and leaving behind the heavy metal as suspended in the precipitate.

The proposed method is investigated by UV-vis and its efficiency is verified by atomic absorption spectroscopy. The concentration of the metal in the synthesized contaminated water will be measured by atomic absorption, before and after treating the water with the organic ligand to check for decrease in the concentration of the metal ion. Atomic Absorption spectroscopy (AAS) is a technique in which gaseous atoms are absorbed by free absorbing atoms (Hg(II) in our case) to produce a measurable signal (Assubaie, 2015). The measurable signal is proportional to the concentration of the free absorbing atoms in the optical signal path that will be compared to a reference (of the same atoms) tested using the same setup. The chemistry in this proposal relies on dynamic bonds (imine bond and the coordination bond) between the aniline and 2-pyridinecarboxaldehyde, which will ensure the regeneration of the ligand after sequestering the metal and the ability for reusing it for future work.

3.3. Analysis of the method's efficiency by different techniques:

For further analysis of the bond between the pyridylimine ligand and Hg(II) ion, the binding constant (K) is investigated. Binding constant (K) reflects the association of the binding reaction of the ligand (L), to the metal (M), which is formalized by:

$$M+L \longleftrightarrow ML$$
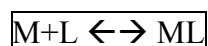
The binding constant indicates how tightly the ligand and the metal are bound together.

The detection of the metal-organic complex by UV-vis, and the use of atomic absorption to measure the concentration of the metal before and after treatment with metal chelation, reflects the structure of the complex, and confirms the efficiency of removal. In the last section of our proposed research, we will check for the recyclability of the proposed ligand using the same techniques mentioned above (UV-vis spectroscopy and AAS).

CHAPTER 4

OPTIMIZATION OF THE DETECTION OF METAL-ORGANIC COMPLEX BY UV-VIS SPECTROSCOPY

4.1. Introduction

Due to mercury's highly toxic nature, its exposure causes serious health issues for human beings, hence, standards have been established. The Environmental Protection Agency (EPA) set a standard level of 0.002 ppm of mercury in drinking water (EPA, 2018). As for the Lebanese government, the allowable limits of mercury in drinking water is 0.006 ppm (Libnor, 2016). Thus, comes the need to detect and determine the concentration of Hg(II) ions in water, followed by its removal in cases where its concentration exceeds the allowed limits. Detection of mercury and other metal ions can be efficiently achieved through spectrophotometric techniques.

In analytical chemistry, spectroscopy is widely used as an instrumental tool for the determination of chemical structures of neutral and charged compounds (chemical complexes) in aqueous solutions. Ultraviolet-visible (UV-vis) spectrophotometry is the classical method used to determine light absorption of a sample at different wavelengths. When light passes through a solution, a certain fraction of this light will be absorbed depending on the composition of the solution, and the rest will be transmitted; where the transmitted light (I) is of a lower intensity than that of the incident light (I_0) as shown in Figure 12. The absorption and transmission of the light passing through a sample can then be recorded in a spectral form providing qualitative (identity) and quantitative (concentration) information on the analyzed sample (Yadav, 2005).
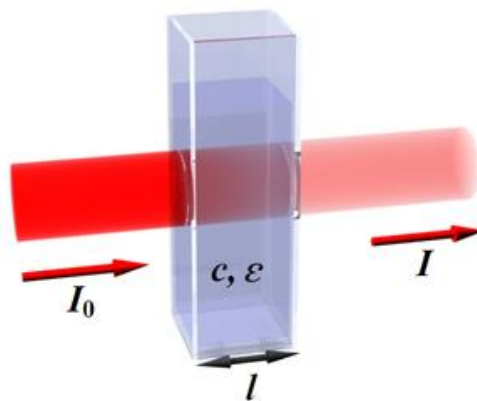
Figure 12 Behavior of light emitted from UV-vis towards the sample.

Light absorption is directly related to the concentration of the compound in the sample, as the concentration of the sample increases, light absorption increases, while transmitted light decreases. UV-vis spectrophotometry complies with Beer Lambert's law, which states that the concentration of a substance is directly proportional to the amount of light absorbed or inversely proportional to the logarithm of transmitted light:

$$A = \varepsilon bc$$

Beer Lambert's Law is presented in the equation above, where (A) is the absorbance, (ε) proportionality constant defined as wavelength dependent molar absorptivity ($M^{-1}cm^{-1}$), (b) is the light path in (cm), and (c) is the concentration in (M). According to Beer Lambert's law, acceptable spectral data lies in the absorbance range of $0.5 < A < 2.7$ range, otherwise, the data is dismissible (Hardesty and Attili; Swineharf, 1962).

Changes in the chemical structure of the analyzed sample can also be detected by UV-vis, where spectral changes (shifts in the wavelength and/or changes in the absorption intensity) take place relative to the initial chemical compound. Changes in UV-vis spectra reflect changes in the chemical structure of the analyzed sample. These changes are presented by either a shift towards a smaller wavelength, often called a hypsochromic shift (blue shift), or a shift towards a larger wavelength, often called

bathochromic shift (red shift). UV-vis spectral data display other behavior, such as a hyperchromic shift that describes the enhancement of a certain absorption peak, versus hypochromic shift which describes the quenching of the absorption peak as shown in Figure 13 (NEPTEL, 2013).
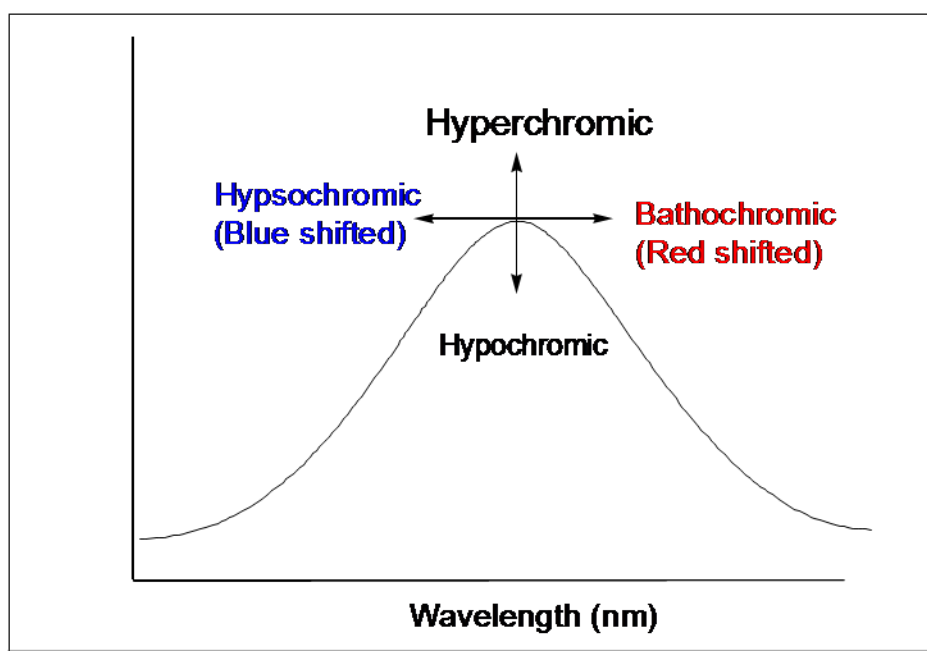
Figure 13 Different spectral shifts in response to a change in the chemical structure of the analyzed sample.

Many studies adopt the use of UV-vis spectrophotometry for detecting the formation of metal-organic complexes in solution. This is due to the simplicity in operating it, accuracy of detecting changes in the analyzed compound's structure (undergoing a chemical reaction) or concentration(Waranyoupalin *et al.*, 2009; Ncube *et al.*, 2014; Singhal *et al.*, 2015; Sunil *et al.*, 2018).

In this project, UV-vis spectrophotometry was chosen to be the most relevant instrumental technique to detect the formation of the metal-organic complex, chelation of the pyridylimine ligand to Hg(II) in water.

4.2. Objective

In this study, we introduce a pyridylimine organic ligand capable of binding Hg^{2+} ions in water to form a metal-organic complex as part of a mercury sequestration

process. The strong spectrochemical characteristics of this complex allow us to study the interaction between the ligand and mercury by UV-vis spectrophotometry. Spectral shifts resulting from the formation of the metal-organic complex relative to the organic ligand alone will reflect on interactions between the ligand and the metal as shown in Scheme 1.
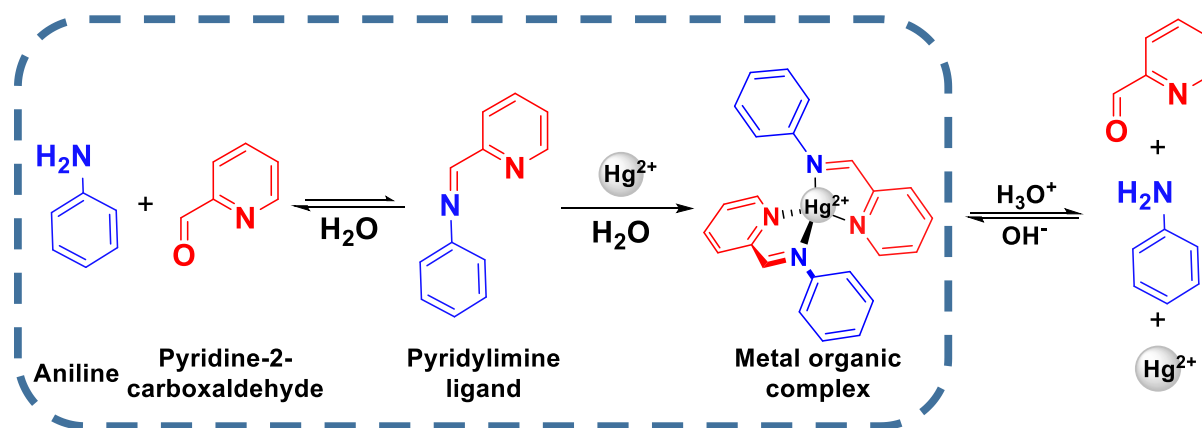
Scheme 1 Formation of the pyridylimine ligand and the metal-organic complex in solution.

The objectives of this study are to employ UV-vis spectrophotometric techniques to detect different stages of formation of the metal-organic complex (chelation of the ligand to Hg(II)) in water. UV-vis spectrophotometry will be used to detect the formation of the (i) pyridylimine organic ligand from its components (aniline and 2-pyridine carboxaldehyde) and (ii) metal-organic complex (chelation of the ligand to Hg(II)). Furthermore, the binding process will be further analyzed by UV-vis spectrophotometry to determining the stoichiometry (metal to ligand ratio) and affinity (association constant Ka) of the binding process.

4.3. Instruments and reagents

Agilent 8453 UV-Vis spectrophotometer using a 1 cm path length (Figure 14), in a standard quartz cell (cuvette) was used to detect the absorption spectra of the samples with a wavelength range of 200 to 1100 nm was used to detect the complexes

in this study. A diagram of UV-vis spectrophotometer and the mechanism by which it separates light absorbed from the sample is presented in Figure 15. The radiation source of this system is both deuterium and tungsten lamps. Both light sources are optically combined to utilize a common axis to the source lens, which forms a single light beam. This beam passes through a shutter light filter, then through the sample and finally reaches the spectrograph lens and slit. The lens disperses light onto the diode array by a holographic grating, access to all wavelength data (Figure 15).

All chemicals used in this work were of analytical reagent grade and were used without further purification. Aniline, 2-pyridine carboxaldehyde, and mercury salts (counter ions: chloride, sulfate, nitrate, and trifluoroacetate) were purchased from Sigma Aldrich (USA).
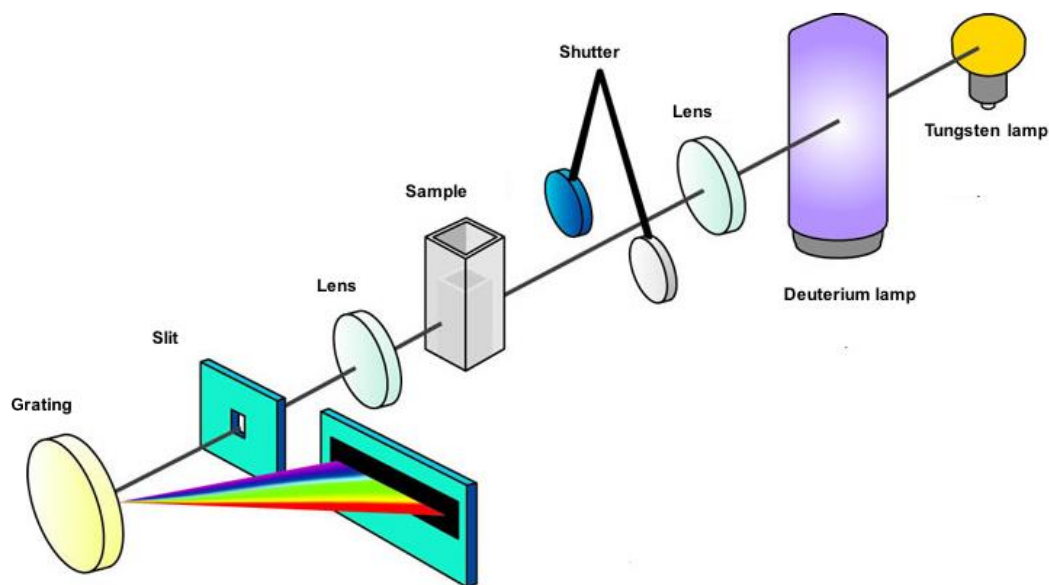
Figure 14 A Components of a UV-vis absorption spectrometer.

4.4. Experimental

4.4.1. Preparation of stock solutions

Solubility of different mercury(II)salts in water were assessed (mercury chloride, mercury sulfate, mercury nitrate and mercury trifluoroacetate), but none of the

mentioned salts exhibited solubility in water except for mercury(II) trifluoroacetate (Kočovský and Luxenburger, 2018) which showed high solubility (100g/100 ml) in water at neutral pH. Therefore, experiments conducted in this project employ mercury(II) trifluoroacetate, Hg(TFA)$_2$ as a mercury source.

Stock solutions of (44 mM) aniline, and (44 mM) aldehyde, were freshly prepared in distilled water at room temperature and neutral pH (pH 7). A stock solution of Hg(II) ion (14.6 mM) was also prepared under ambient conditions. All stock solutions showed high solubility in water at neutral pH, with no need for sonication, changing the medium pH or temperature.

4.5. UV-Vis analysis – Results and discussion

4.5.1. Optimization of the detectable ligand concentration by UV-vis

In determining the optimum ligand concertation to be carried throughout the experiments, different initial concentrations of the organic ligand (1:1 molar ratio of the aldehyde: aniline) were selected and mixed with the metal ion and detected by UV-vis spectrophotometer. Complex formation at each one of the concentrations was evaluated in solution, consequently the point by which the ligand gets saturated with the metal (chelation process is complete and ligand can bind no more to the metal) was determined.

Based on that, the assessment of the optimum detectable ligand concentration was studied. Several trials, of mixing aniline: aldehyde in a 1:1 stoichiometric equivalence, resulting with different concentrations of the pyridylimine based ligand ranging from (1×10^{-4} to 2×10^{-6}) were evaluated to optimize one universal concentration for both the selected aniline and aldehyde in solution. This range was selected to comply with the absorbance limit according to Beer Lambert's law. Accordingly, a

concentration of 1.1 x 10^{-5} M of pyridylimine ligand was found to be the optimum

detectable concentration by UV-vis (according to Beer Lambert's law) and for the

formation of the metal-organic complex with Hg (II) ions in mercury induced water.

Furthermore, to investigate the presence of the metal-organic complex, UV-vis

studies were carried out in distilled water infused with Hg^{2+} ion. Absorption peaks of

the reaction components are presented in Figure 14 where UV-spectra of aniline and

aldehyde (B and C) are being compared to that of their mixture leading to the

pyridylimine ligand formation (spectrum D). The spectrum of the ligand shows an

enhancement of the aniline and aldehyde peak at 232 nm due to the formation of the

imine bond. The mercury salt did not exhibit absorption peaks (E) in the range of 200 –

1100 nm, while its chelation to the pyridylimine ligand resulted in the formation of

spectrum (A). Detection of the metal-organic complex by UV-vis (A), results in a

distinct spectrum, different from that of the ligand on its own (spectrum D), hence, we

can sense the presence of the complex by comparing its spectrum to the ligand's

spectrum as a reference.
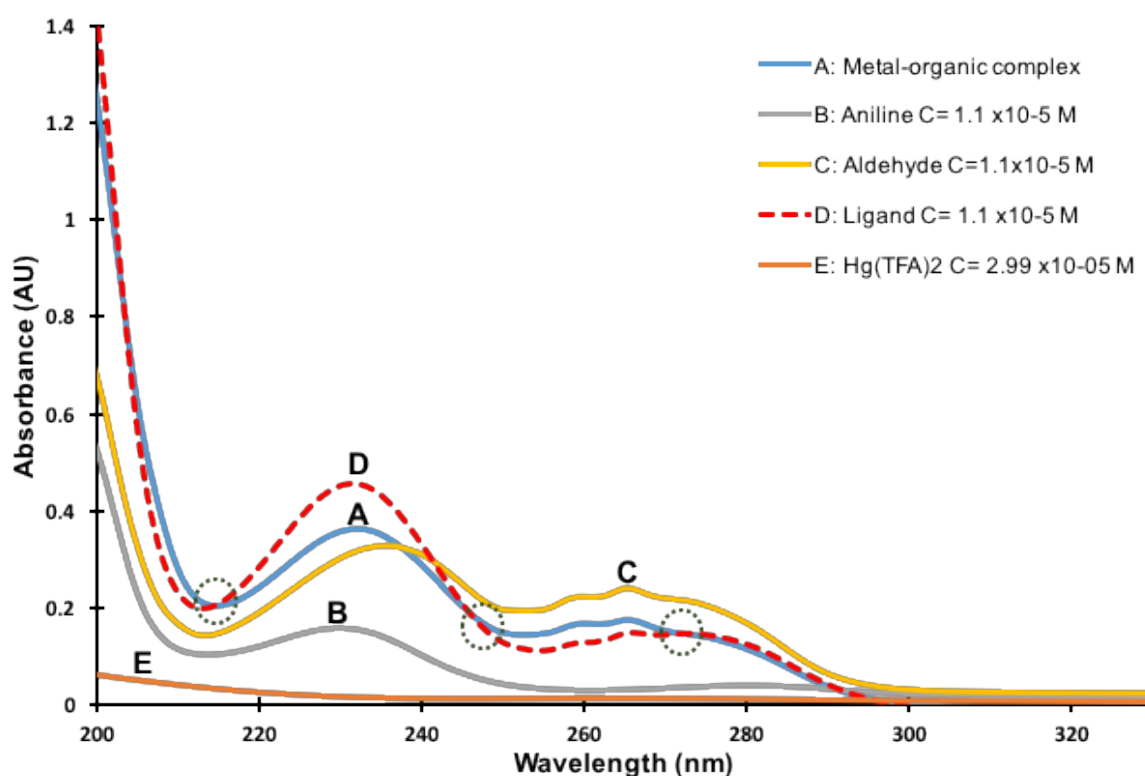
Figure 15 UV-visible absorption spectra of the (a) metal-organic complex and its components: (b) aniline, (c) pyridine-2- carboxaldehyde, (d) iminopyridine-based ligand and the (e) mercury(II) Trifluoroacetate in water.

Absorption intensity at 232 nm of the metal-organic complex spectrum (A) was quenched relative to that of the organic ligand (D), as demonstrated by Figure 15. This change is an indication of the chelation of the ligand to Hg(II) ion in solution. While no bathochromic or hypsochromic shifts at 232 nm were observed, the shoulder peak of spectrum (A) at 270 nm undergoes a hypsochromic shift from 270 nm to 260 nm along with a hyperchromic shift (enhancement of the peak's absorbance at 260 nm) relative to spectrum (D) upon forming the metal-organic complex. These changes in the ligand's spectrum are a result of its complexation to Hg (II) ion, hence, the formation of the L: Hg (II) complex. These collective changes result in the formation of three isosbestic points at wavelengths: 218 nm, 247 nm, and 269 nm, as pointed out with the dashed circles in figure 4. An isosbestic point is a specific wavelength at which the total absorbance of a sample does not change during a chemical reaction or a physical

change of the sample. In this case, the three isosbestic points indicate the formation of at least two complexes in solution. Formation of the isosbestic points confirms the change in state (from uncomplexed organic ligand species to complexed metal-organic species in solution). (Deblonde *et al.*, 2013).

Moreover, the absorption peak of the organic ligand (D) presented remained as the constant reference for the presence of the metal-organic complex. The proposed organic ligand exhibited stability with respect to time (after 24 hours), the ligand didn't break nor its absorbance had changed

Furthermore, this ligand's concentration (1.1×10^{-5} M) was also shown to work for chelating to different transition metals, in water: Cd^{2+}, Zn^{2+}, and Fe^{2+} which were investigated under the mentioned conditions (optimized ligand concentration, room temperature, and neutral pH) and results exhibited by UV-vis spectra showed the presence of the metal-organic complex in each case.

4.5.2. *Monitoring the formation of the metal-organic complexes in water*

Titration experiment of the ligand with Hg^{2+} ion was carried out in order to investigate the formation of the metal-organic complex. The experiment was conducted through the sequential addition of different concentrations of the metal to an aqueous solution of the organic ligand in the cuvette to be analyzed by UV-vis spectrophotometry (the concentration of the ligand was kept constant throughout the experiment as shown in table 1, in the appendix). All samples were subjected to the same physical and chemical conditions throughout the titration process.

In a cuvette, 4 ml of water was added, followed by the addition of 1μl in volume of the pyridylimine-based ligand (concentration=1.1×10^{-5} M). Incremental amounts in the range between 2μl to 16μl of aqueous Hg(TFA)$_2$ (concentration of 0 to

5.84 x 10^{-5} M) were added to the pyridylimine ligand solution at room temperature. The UV-vis spectrum was recorded after each addition, with a time frame of 1 hour between each addition. Furthermore, the pH of the prepared samples in the cuvette were measured using a pH meter (Starter 300), indicating a neutral medium throughout the experiment.

The correlation between different metal concentrations and the ligand was constructed using Microsoft excel. The experimental spectra of mercury in the solution of pyridylimine organic ligand show that the absorbance lies between 0.5<Abs<2.7, complying with Beer Lambert's law, which enables us to proceed with the work.
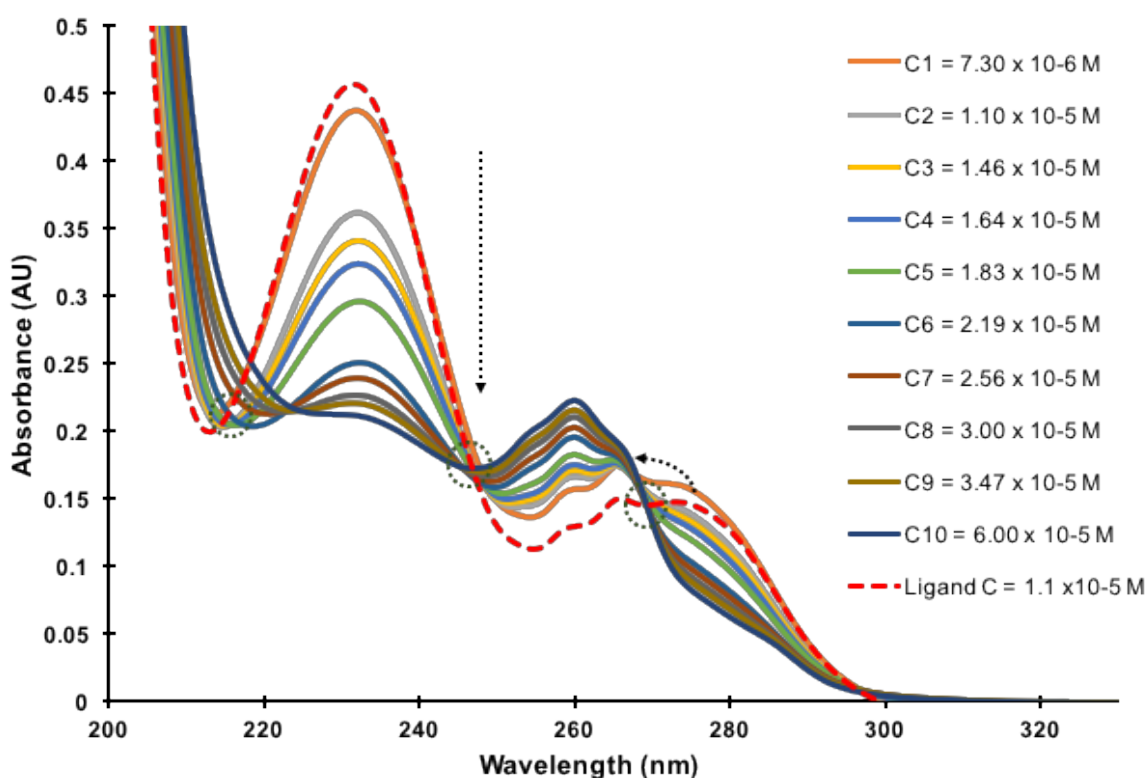
Figure 16 UV-visible absorption spectrometric titration of the pyridylimine -based ligand (concentration) with an aqueous solution of Hg(TFA)2 (concertation range).

The titration experiment, where a gradual increase in the concentration of Hg(II) were added to the ligand in solution is presented in Figure 5. The UV-vis spectra for each addition were compared to the organic ligand's spectrum (spectrum dashed

red). The metal-organic ligand in solution shows a broad characteristics absorption peak around 200-300 nm, with a maximum peak at 232 nm along with a new shoulder peak at about 260 nm and a decrease in absorbance level (0.4 au vs 0.2 au) as shown in Figure 16. The decrease and eventual disappearance of metal adsorption peak (clean region around 310 nm) indicates that the system is free of pyridylimine ligand species upon the addition of excess Hg^{2+} ions.

The maximum absorption of the organic ligand at 232 nm decreases in intensity as the concentration of Hg(II) ion increases in solution, a new peak appeared at 260 nm and increased in intensity with increasing Hg(II)'s concentration as well (Figure 16). Furthermore, an isosbestic point was detected at wavelengths 247 nm and 267 nm. The presence of an isosbestic point indicates that two species were present in solution in equilibrium with each other at this wavelength, and found in two spectrally distinct forms: free and bound. The formation of the two isosbestic points confirmed the change from uncomplexed species (organic ligand) to complex species (metal-organic complex).

Subsequently, to check for the reproducibility of the system, and to confirm the presented data, the titration was repeated again, giving almost identical results as the one presented, which assures the reproducibility of the system.

4.5.3. Evaluating metal to ligand affinity

Another titration experiment was conducted where the metal sample was titrated with an aqueous solution of the ligand. This titration was implemented to investigate: (i) the binding process and binding affinity of the complex at a certain concentration, (ii) determining the stoichiometry (ratio of ligand: metal) of the reaction through fitting the spectral data into different stoichiometric equations.

For this titration, 4 ml of water were added into a cuvette, followed by the addition of 8.2 μl of Hg^{2+} ions of fixed concentration (2.99×10^{-5} M) throughout the titration process. Gradual additions (1μl – 88μl) of the ligand were added to the mercury solution in the cuvette. UV-vis spectra were recorded after each addition, with a time frame of 1 hour between each addition and the recording. The added volumes corresponded to ligand concentrations in the range of 5.98×10^{-6} to 4.78×10^{-4} M as shown in table 2 in the appendix. Moreover, the pH of the prepared samples was measured and a neutral pH maintained throughout the experiment. The aim behind this titration experiment was to use the spectrophotometric data in the calculation of the binding constant (K). Results of the experiment are shown in Figure 17. For a fixed Hg(II) ion concentration and increased the ligand concentration, an enhancement of the peak at 230 nm escorted by another increase of its shoulder peak at 270 nm were recorded.
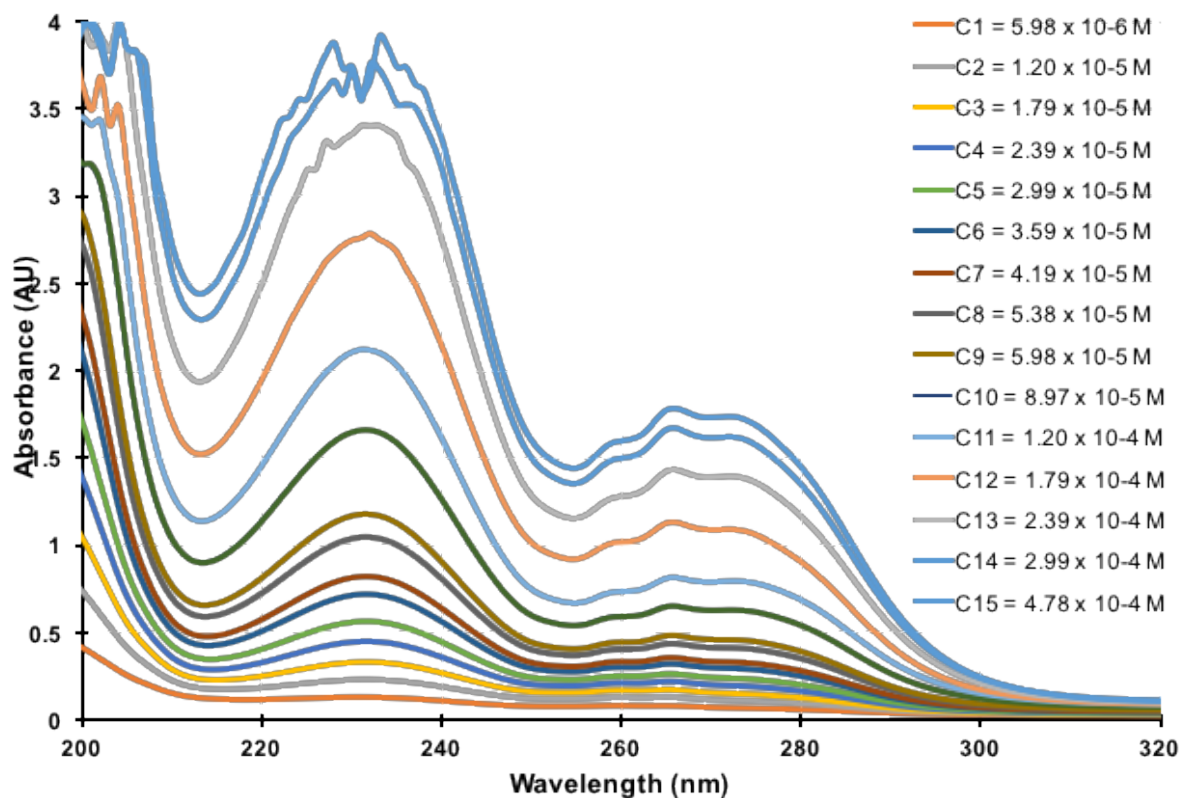
Figure 17 UV-visible absorption spectrometric titration of the Hg(TFA)2 (concertation in water) with an aqueous solution of the pyridylimine-based ligand (concertation range).

This increase in absorbance as the concentration of the ligand increases led to the calculation of the binding constant of the metal-organic complex in water. The binding constant was determined through fitting the experimental spectrophotometric data to a 2:1 equilibrium, (Benesi-Hilderband plot equation (Thordarson, 2011). The model used to fit the UV-vis data is based on ligand/metal ratio of 1:1 and 2:1. Attempts to fit spectral analysis to a single 1:1 species failed. The data (Figure 17) were fitted according to the method of Taylor and Anderson, using the equation $((a*b*x+(2*c)*d*x^2)/(1+b*x+d*x^2))$ to fit the data as illustrated in Figure 18. The constants obtained were found to be in good agreement (R-squared of 0.994) with 2:1 (2 ligands: 1 Hg(II)) fitting model. The first (K_1) and second (K_2) association constants (which can be considered to be binding constants) were calculated and found to be $5.8(0.08) \times 10^3$ M^{-1} and $1.3(0.3) \times 10^4$ M^{-1} (Figure 18), respectively, with a global

binding constants, K_β of $7.8 \times 10^7 \pm 0.4$ in water. Interestingly, the **2L:Hg** complex is significantly more stable than the **1L:Hg** complex, suggesting that the binding of two ligands is a cooperative process. The calculated binding constants ratio (K_2/K_1) is approximately 2.2, indicating positive cooperativity. This also suggests that binding of the first ligand results in facilitating the binding of the second ligand.
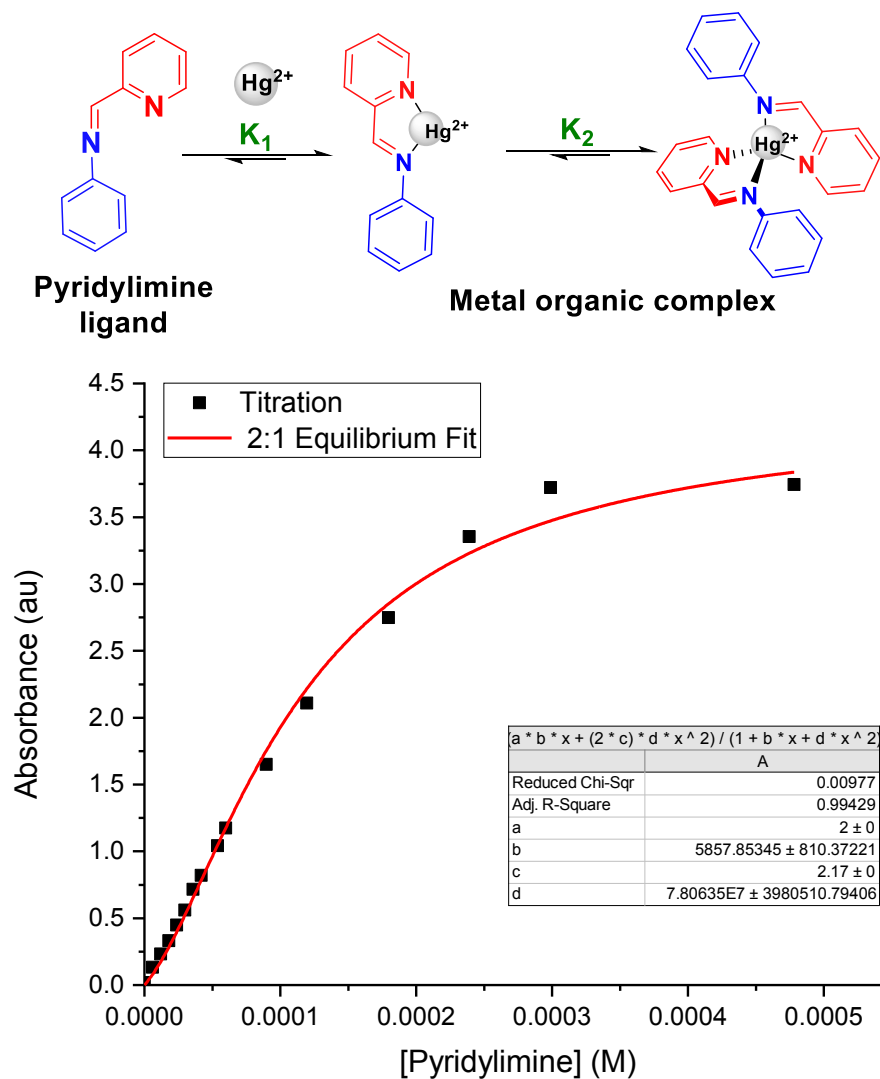
Figure 18 Change in the UV-vis absorbance (black squares) at 230 nm and calculated binding isotherm (red curve) obtained by titrating a solution of the pyridylimine ligand in water (0.022 M) with an aqueous solution of Hg(TFA)$_2$ (0.015M).

CHAPTER 5

ANALYSIS OF HG(II) REMOVAL FROM WATER BY ATOMIC ABSORPTION SPECTROSCOPY

5.1. Introduction

Atomic Absorption Spectrophotometry (AAS) is a technique used for measuring quantities of a certain element present in samples (typically environmental samples) through measuring the absorbed radiation of its free atoms in the gaseous state. AAS is based on the absorption of light by free metallic ions. This technology relies on the principle that each element absorbs and emit light with wavelengths that are atom specific. In other words, atoms absorb electromagnetic radiation resulting in electronic excitation state, the excited atoms with then emit electromagnetic radiation restoring their ground state. This process can be monitored spectroscopically (absorption or emission spectroscopy) leading to the determination of the tested element's concentration (Robinson,1996).

The common light source for exciting atoms is a hollow cathode lamp, which is filled with an inert gas (argon or neon) and a cathode layer of the metal to be analyzed. A light source with a wavelength specific for the analyzed element is directed through the sample introduced to the flame, and a measurement of the intensity is made without the sample and another one with the sample introduced into the flame. The decrease in intensity observed is a reflection of the concentration of the sample. The radiation that passes from the flame then passes through a monochromator to separate the element specific radiation from any other emitted radiation, and finally, the measured concentration is determined by the detector as shown in Figure 19. (Harris, 2007; HK, 2016).
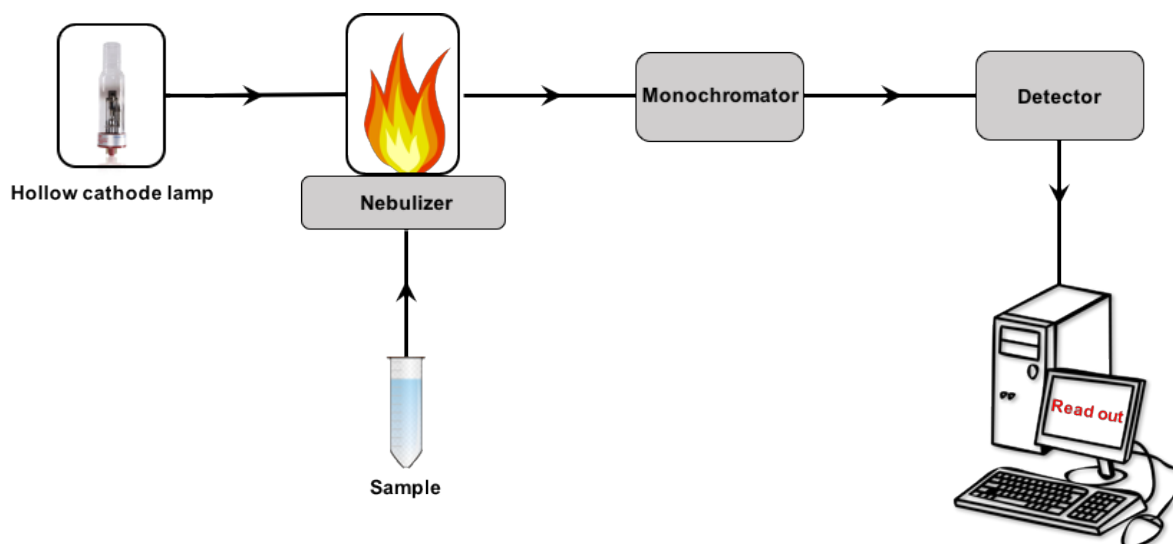
Figure 19 Components of a typical atomic absorption spectrometer.

Several studies have been conducted for the determination of heavy metals' concentration in water by atomic absorption spectrometry (AAS). This is mostly due to the reliability of the technique in detecting metals and metalloids in water samples, owing to its high sensitivity due to the use of selective irradiation sources, and good accuracy towards the detection of heavy metals. AAS is widely used as a routine technique for elemental analysis in water samples. (Chen and ChuanTeo, 2001; Assubaie, 2015; Hk, 2016; Ipeaiyeda and Ayoade, 2017).

Atomic absorption is a crucial technique for our project. As it is the most relevant analytical method for the determination of mercury (II) ion concentration in water samples before and after treatment using the proposed green chemical treatment method.

5.2. Objective

The objective of this chapter is to illustrate the effect of various factors on the removal of Hg(II) ions from mercury infused water using the proposed pyridylimine organic ligand (formed from aniline and aldehyde). In the present work, we will be comparing the amount of Hg(II) of known concentration, in mercury spiked water, before and after chemical treatment. In addition, to investigating different parameters

affecting the removal of Hg(II) from water. The studied parameters include: (a) effect of KPF$_6$ on the metal-organic complex and its components; (b) stoichiometric ratio of the ligand to Hg^{2+}ion in solution; (c) contact time between the ligand and the metal - a kinetic study; (d) removal of mercury(II) from water in the presence of other metal ions.

5.3. Experimental

5.3.1. Instruments

An iCE 3000 series atomic absorption spectrometer with deuterium background corrector equipped with single element hollow cathode lamp was used in the study. All measurements were carried out in an air/acetylene flame. The operating conditions are presented in Table 2, also the adjustments in the spectrometer were carried out according to the standard guidelines of the manufactures. The instrumental detection limit for flame AAS was 700 mg/L for mercury.

Table 2 Conditions for flame atomic absorption spectrometric determinations

Element	Wavelength (nm)	Slit (nm)	Lamp current (A)	Flow rate of oxidant and fuel	
				Air (L/min)	Acetylene (L/min)
Hg	253.7	0.5	0.4		

5.3.2. Reagents

All chemicals used in this work are of analytical reagent grade and were used without further purification. All plastic and glassware were rinsed with deionized water prior to use.

Aniline, 2-pyridine carboxaldehyde, and mercury(II)trifluoroacetate were purchased from Sigma Aldrich and were used throughout the analysis. Potassium

hexafluorophosphate was purchased from ACROS. All chemicals were used without further purification.

5.3.3. Preparation of standard solution for mercury

Before starting the AAS analysis, the element standard solutions used for calibration were prepared by diluting a stock of 5 M (1000 ppm) of Hg(II) ions in deionized water generating seven different standards solutions of 20, 50, 65, 100, 150, 200, and 300 ppm respectively.

5.4. Experimental approach

In this section, the AAS will be used to compare the concentration of Hg^{2+} in water before and after it was subjected to treatment by the pyridylimine ligand. The schematic presentation of the experimental procedure (with visual monitoring of the process) carried out is demonstrated in Figure 20; where the first tube demonstrates a clear solution of mercury infused water, undergoing a color change to yellow (tube 2) upon the addition of the pyridylimine ligand. The yellow color rushes down with the precipitate containing the metal-organic complex upon the addition of KPF_6 (tube 3), the precipitate is filtered out to reach a colorless supernatant solution (tube 4) for analysis by AAS, as for the precipitate it's taken for further analysis by EDX.
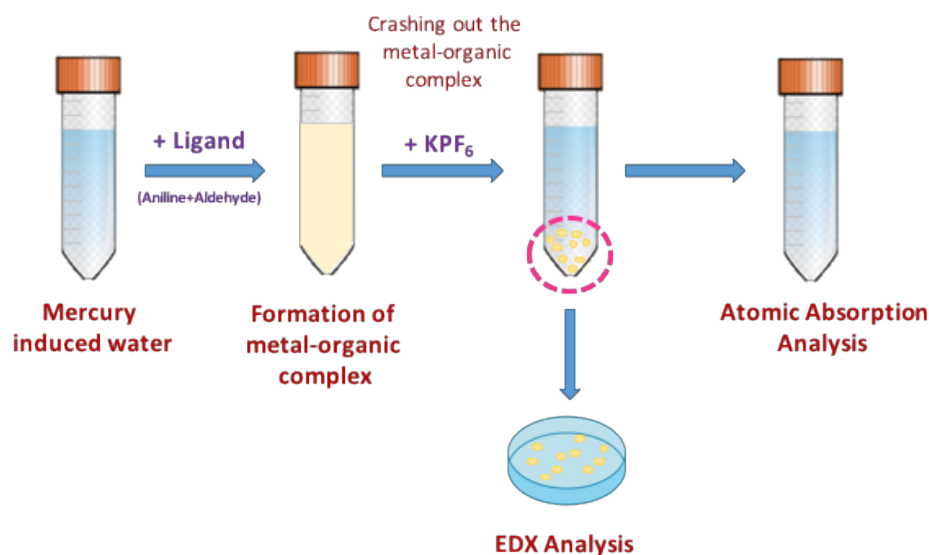
Figure 20 Illustration of the experimental procedure carried out to determine the percentage removal of Hg(II) ion in water after it's been subjected to the chemical treatment.

5.4.1. Preparation of samples for AAS

A stock solution of 250 ppm of mercury in water was prepared and divided into two tubes; one tube was treated with 500 ppm of the pyridylimine ligand (tube B, Figure 21) and the other tube was left untreated (no ligand was added – tube A, Figure 21). Upon the addition of the ligand, the clear aqueous solution turned yellow (tube B, Figure 21) indicating the formation of the metal-organic complex The metal-organic complex formed in solution was salted out by adding potassium hexafluorophosphate (KPF_6) immediately after the addition of the ligand, which instantly formed a yellow suspension and turned the solution turbid (tube C, Figure 21). Then, the sample was centrifuged at 1000 rpm/10 min and the precipitate was isolated through filtration. The supernatant (with a neutral pH) was transferred to another tube for determining the concentration of mercury after treatment by AAS analysis.

A= Hg²⁺ induced water
B= Hg²⁺ + ligand
C= Hg²⁺ + Ligand + KPF₆
D= Tube C + centrifugation
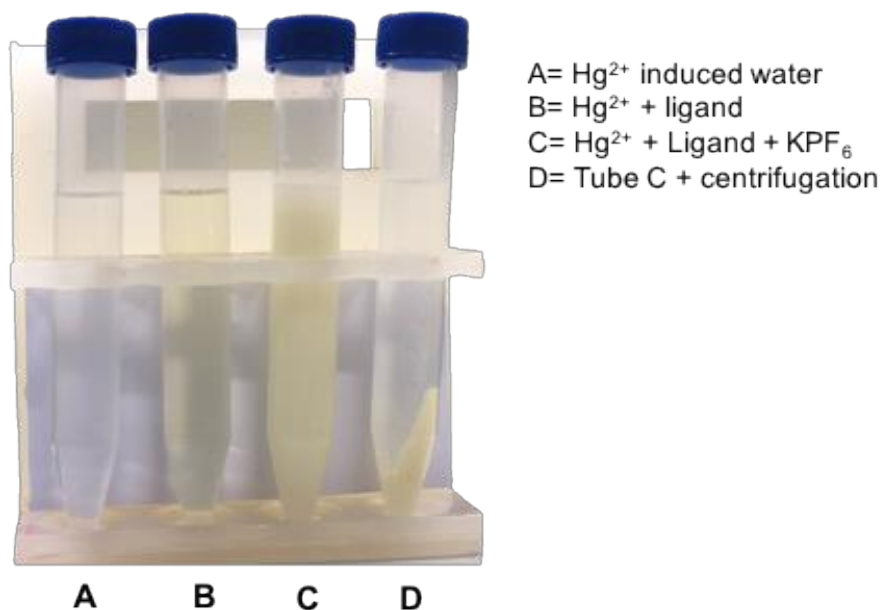
Figure 21 Mercury induced sample before and after it was subjected to treatment with the pyridylimine ligand.

5.5. AAS analysis – Results and discussion

Atomic absorption analyses were carried out at room temperature. A method was designed relative to the number of samples of the element used and the prepared standard solutions to start the analysis. This preliminary step of building up a method in AAS program was conducted before every AAS measurement

The instrument builds up a calibration curve using the calibration standards prepared (0, 20, 50, 65, 150, 200, and 300 ppm), with R= 0.998 (Figure 22).
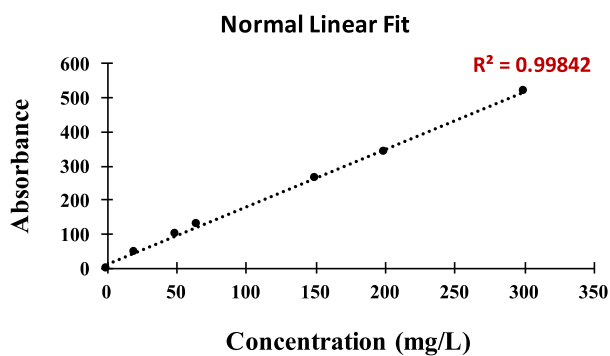
Figure 22 Calibration curve generated for AAS analysis

The initial concentration of the prepared sample (C_i =250 mg/L) was detected using AAS as an actual concentration of 273.94 mg/L. This concentration decreased after the addition of the organic ligand to C_f=17.25 mg/L measured by AAS (supernatant solution from tube D, Figure 21), thus removal of 93.7% was achieved (

Table 3). This decrease in concentration indicates that 93.7 % of mercury(II) present in water was chelated to the pyridylimine ligand, forming a metal-organic complex that precipitated upon the addition of KPF_6. The formed precipitate was collected for further analysis by EDX (to confirm the presence of mercury in the precipitate). This method was applied to determine the percentage removal of different mercury spiked samples before and after it was subjected to the treatment. Concentrations before and after treatment with the percentage removal are reported in Table 3.

Table 3 AAS analysis of different Hg2+ concentrations before and after treatment

Sample	C_i of Hg^{2+} (mg/L)	C_f of Hg^{2+} (mg/L)	% Removal
Negative control	273.94	273.94	0
Sample 1	273.94	17.25	93.7
Sample 2	311.55	2.43	99.2
Sample 3	678.2	20.3	97

5.5.1. Effect of KPF_6 on the metal-organic complex and its components

Separation of the metal-organic complex from solution was achieved through changing the solubility of the metal-organic complex in water. This was executed through the addition of KPF_6 salt to the water sample containing the metal-organic complex. Control experiments were carried out to ensure that only the complex will crash out of solution; four different samples were prepared in deionized water each of a fixed concentration of 250 mg/L of mercury at room temperature and neutral pH. No

reagents were added to the first sample, only aniline was added to the second sample, only aldehyde was added to the third sample, and both aniline and aldehyde (to form the pyridylimine ligand) were added to the fourth sample. A fifth sample deprived of mercury and containing only the pyridylimine ligand was also prepared. Equal amounts of KPF$_6$ were added to each of the five samples to investigate the crashing out of the complex from solution as shown in Table 4. Precipitate formation was observed only in the fourth sample containing the organic ligand with the mercury (II) ion in solution as shown in Figure 21. This indicates that the crashing out of the complex will take place merely in the presence of the organic ligand which is chelated to the metal forming a metal-organic complex.
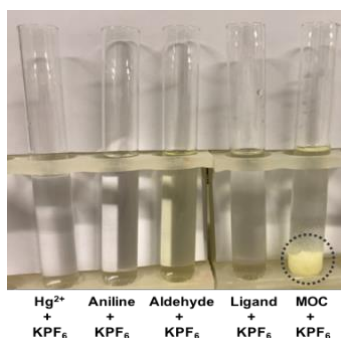
Figure 23 Behavior of reagents upon the addition of KPF6.

Table 4 Effect of behavior of reagents in the presence of KPF6

	Metal	Ligand		Salt	
Sample	[Hg^{2+}]	[Aldehyde]	[Aniline]	KPF$_6$	Precipitate
	mg/L	mg/L	mg/L	mg	
S1	+	-	-	+	-
S2	+	-	+	+	-
S3	+	+	-	+	-
S4	+	+	+	+	+
S5	-	+	+	+	-

5.5.2. Stoichiometric ratio of the ligand to Hg^{2+}ion in solution

For the removal of mercury from water as it chelates to the pyridylimine ligand, different concentrations of the ligand relative to the metal were evaluated to assess the optimal stoichiometry of the reaction. The effect of chelation of the metal to the ligand was investigated in different stoichiometry of ligand to metal ratios; 1 : 1, 2 : 1, and 3 : 1 (ligand : metal). Three different samples were prepared of fixed

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concentration (250 mg/L) of mercury, the pyridylimine ligand was added in different stoichiometry (as shown in Table 5) to the three prepared samples under fixed conditions, that was followed by the addition of KPF_6 in equal amounts to the three samples. The heterogeneous solution was filtered out and the supernatant was analyzed by AAS to determine the percentage removal of Hg(II) in each sample.

Results showed that the removal efficiency of mercury (II) ion in the first sample with 1:1 (ligand: metal) stoichiometry was 78%, while that of the second and third samples, with 2:1 stoichiometry and the third with 3:1 stoichiometry, were 99% and 99.2% respectively. The percentage removal of mercury increased upon increasing the concentration of the added ligand increased, but the 0.2% difference between the 2:1 and 3:1 ligand-metal stoichiometry is incomparable/negligible, which suggests that each Hg (II) metal ion requires 2 ligands to obtain efficient removal. The results from AAS comply with the results presented previously by UV-vis analysis confirming the 2:1 ligand to metal stoichiometric ratio as being the optimal stoichiometry for mercury removal.

Table 5 Effect of the stoichiometric ratio of the ligand on the % removal of Hg^{2+}

| Samples | Ratio | | KPF_6 mg | % Removal |
	Hg^{2+}	Ligand (aniline+aldehyde)		
S1	1	1	80	78
S2	1	2	80	99
S3	1	3	80	99.2

5.5.3. Effect of contact time between the ligand and the metal: a kinetic study

The reversible nature of the pyridylimine ligand used and its dynamic complexation to the metal establishes an equilibrium between the metal-organic complex and its components. A kinetic study was carried out to determine the

maximum removal efficiency of Hg(II) ion, through the formation of the metal-organic complex, from water with respect to time. In this experiment, metal ion uptake capacities were determined as a function of time to determine an optimum contact time for the chelation of Hg^{2+} ion to the organic ligand.

Five different samples of mercury infused water (250 mg/L) were prepared under the same ambient conditions. Sample 1 was treated with the ligand and instantly salted out and filtered, sample 2 was treated with the ligand and left in solution for 30 mins before salting and filtering it out, whereas sample 3, 4 and 5 were treated with the ligand and left in contact in the solution for 2, 4, and 24 hrs respectively, then salted out and filtered. The effect of contact time (between the ligand and Hg^{2+} ion) reflected on the percentage removal of Hg^{2+} from water. The five samples were analyzed by AAS to compare the concentration of mercury before and after the treatment with respect to the contact time between the ligand and the metal. Atomic absorption results showed 98, 100, 100, 100, and 99% removal efficiency for samples 1, 2, 3, 4, and 5 respectively. The variation of percentage removal of mercury (II) ion with respect to time is shown in Table 6. This indicates that the chelation between mercury and the organic ligand needs 30 mins to obtain 100% removal of Hg^{2+} ion from mercury infused water of concentration 250 mg/L, and removal efficiency slightly decreases after 24 hrs possible due to the dynamic structure of the complex and the presence of a reversible immine bond.

Table 6 Effect of contact time between the ligand and the metal: a kinetic study
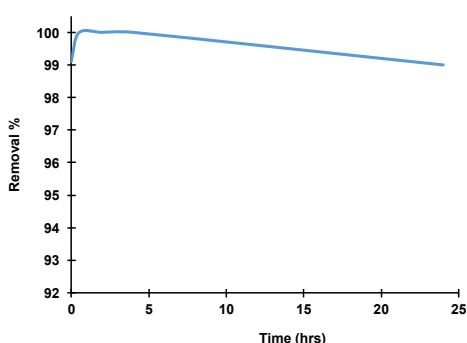
Sample	Time (hrs)	Removal %
S1	0	98
S2	0.5	100
S3	2	100
S4	4	100
S5	24	99

Figure 24 percentage removal of Hg2+ + ion with respect to time of 24 hrs.

5.5.4. Removal of mercury(II) from water in the presence of other metal ions

The effect of the presence of other metal ions in solution on the green chemical treatment approach was assessed. Natural water resources may contain various metal ions in solution, these metal ions may interfere with the chelation of mercury with the organic ligand by competing with Hg^{2+} ions. The effect of the presence of other metal ions was examined by preparing a sample of a fixed amount of analyte (Hg^{2+} ion). This sample was mixed with different amounts of metal ions and the adopted procedure was followed. Four different samples of mercury infused water (250 mg/L) were prepared. Sample 1 contained mercury (II) alone, sample 2 contained a binary system of mercury (II) and cadmium(II) ions with 1:1 stoichiometry, sample 3 contained another binary system of mercury(II) and zinc (II) ions with 1:1 stoichiometry, and sample 4 contained three metal ions: mercury (II), cadmium(II), and zinc (II) together with 1:1:1 stoichiometry. The four samples were treated with the organic ligand of stoichiometry 2:1 ligand to mercury(II) concentration (as optimized above), and left in contact for 30 mins. Later, the four treated samples were salted, filtered out, and analyzed by AAS for mercury ion removal. Results showed almost complete removal of mercury (99.9, 99.2, 100 and 100% respectively) removal efficiency in the four tested tubes. As it is seen,

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the presence of the above-mentioned metal ions have no considerable effect on the chelation/removal of Hg^{2+} ion by the organic ligand in water.

5.6. Analysis of precipitate generated from the complex

After confirming that the presented method efficiently removes mercury ions from water the generated precipitate, upon salting the solution and crashing the metal-organic complex out, was examined by scanning electron microscope (SEM) attached to an EDX (energy dispersive X-ray spectroscopy) micro-analyzer. The generation of the X-rays in SEM is a two-step process. In the first step, the electron beam strikes the sample and transfers part of its energy to the atoms in it. This energy can either make the atoms jump to a higher energy level or get knocked off from the atom, thus leaving behind a hole. The second step is when electrons from a higher energy level fill up this hole, and then the energy difference of this transition can be released in the form of an X-ray. This X-ray has an energy which is characteristic of the energy difference between these two levels and reflects the atomic number, which is a unique property of each element. Consequently, the X-ray is a fingerprint of each element and can identify which element is present in the sample and it is presented by EDX (Nanakoudis, 2018).

The EDX is an energy dispersive X-ray spectroscopy. It is a characterization technique that indicates elemental composition of various constituent elements in an analyzed material. The x-axis of the EDX spectrum indicates the ionization energy (Figure 25) while the y-axis indicates the counts. The higher the counts of a particular element reflects a higher presence of that element at that point or area of interest.

EDX results, illustrated in Figure 25, show peaks for carbon, nitrogen, fluorine, phosphorous, and mercury corresponding to the metal-organic complex and its counter ion, which confirms the formation and the crashing out of the metal-organic

complex, and emphasizes the results obtained with AAS, assuring the removal of the metal complex from water.
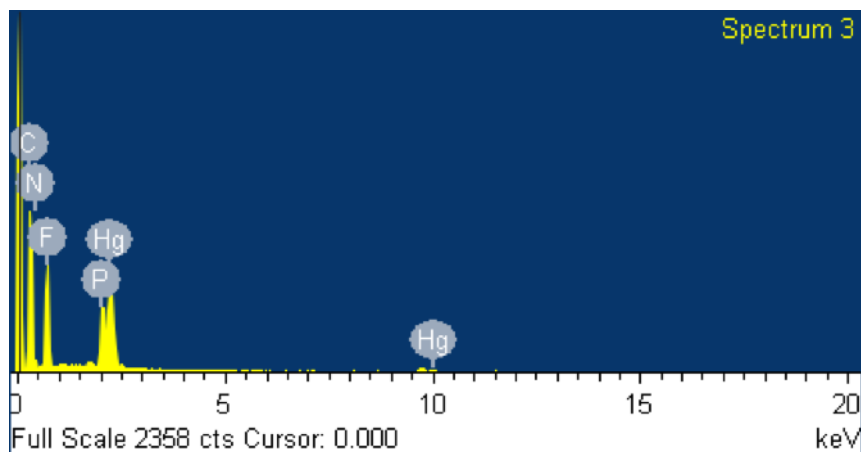
Figure 25 EDX analysis for the precipitate generated from crashing out the metal-organic complex.

5.7 Efficiency of Hg^{2+} removal in the proposed system

The present experiments have demonstrated that the aniline-aldehyde system is effective in the removal of Hg^{2+} ion by metal chelation mechanism. The optimum stoichiometry 2:1 ligand to metal concentration and an optimum contact time of 30 minutes at ambient conditions (pH 7; T= 22°C). Moreover, preliminary studies indicate that the presence of different metal ions do not affect the chelation of Hg^{2+} ion to the organic ligand (no competition between the other metals and the ligand), and do not affect the removal efficiency.

CHAPTER 6
REGENERATION OF THE PYRIDYLIMINE LIGAND

6.1. Introduction

The term "green chemistry" was coined in 1991 by Paul T. Anastas, the father of green chemistry who defined the field as, "Green chemistry is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design manufacture and application of chemical products"(Anastas and Warner, 2000). The purpose of applying green chemistry principles is to aid the design of chemicals and chemical processes that are less harmful to humans and their environments. Moreover, green chemistry protects the environment not by cleaning it up, but rather by introducing new chemical processes that do not pollute it.

Heavy metals can be easily absorbed by vegetable and fish due to their high solubility in aquatic environments, thus, that is how they reach and accumulate in human bodies (Bazrafshan *et al.*, 2015). These heavy metals should be removed from water to protect the environment and living organisms. Several techniques have been used to remove heavy metals from water, like coagulation filtration, reverse osmosis, distillation, granular activated carbon, electrocoagulation and lime softening. Although these treatment methods exhibit high removal efficiency of heavy metals, but they have their disadvantage lies in the production of hazardous sludge/waste, high operational cost (in the case of reverse osmosis, electrocoagulation and distillation) (Chowdhury *et al.*, 2014; Tripathi and Rawat Ranjan, 2015), thus the need for cheaper and safer methods for water treatment.

As mentioned in the introduction, the main objective of this project is to develop a "green" chemical approach for the removal of heavy metals - with the focus

on mercury- from water. Classical chemical treatment approaches would either result in the formation of hazardous by-products or entail the disposal of chemicals after the treatment process. Very few reported studies recycle the chemicals used to capture heavy metals after water treatment. Reducing chemical waste, recycling chemicals, with minimal energy input and using cost effective methods are among the principles of green chemistry. The three aforementioned principles will be applied in this study (chapter 2), where a dynamic ligand is employed to ensure its regeneration after sequestering mercury in water.

The regeneration process can be conducted in different scopes, some studies achieved regeneration by changing the pH of the medium to break the coordination bond between the ligand and the metal, thus separating the metal and ligand (Mal *et al.*, 2008; Cheng *et al.*, 2017). Other studies suggest to regenerate the ligand by introducing a competitive chelating agent (chelating resin), which will bind to the metal releasing the ligand alone (Dolev *et al.*, 2019). In this study we used the change in pH to trigger the regeneration of the ligand.

6.2. Objective

Our approach, described in this work, is employing a dynamic pyridylimine organic ligand capable of chelating to the metal reversibly. Upon changing the pH of the solution, the insoluble metal-organic complex will break releasing the pyridylimine ligand, that is soluble in water (supernatant) leaving behind insoluble Hg(II) ion (precipitate). The release of the ligand alone can be re-used to remove Hg(II) through another cycle of treatment.
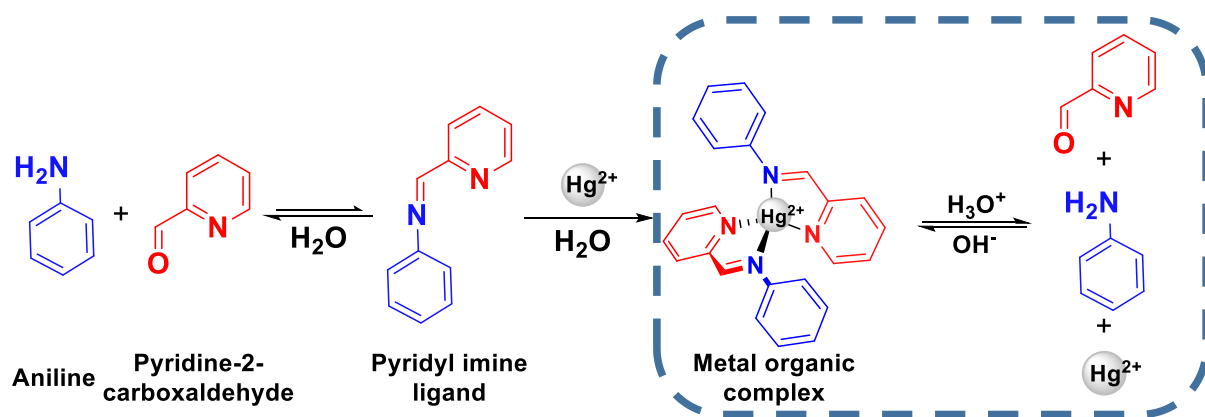
Scheme 2 Regeneration of the pyridylimine ligand in solution.

6.3. Experimental

6.3.1. Instruments

In this section, both UV-vis and AAS were used to monitor the regeneration process and recycling the ligand for the removal of mercury respectively.

6.3.2 Reagents

All chemicals used in this work are of analytical reagent grade and were used without further purification.

Aniline, 2-pyridine carboxaldehyde, mercury(II)trifluoroacetate, and *p*-toluene sulfonic acid were purchased from Sigma Aldrich and were used throughout the analysis. Potassium hexafluorophosphate was purchased from ACROS. All chemicals were used without further purification.

6.3.3 Preparation of samples

The pyridylimine ligand was added to a mercury-induced water of a stoichiometry 2:1 ligand to metal concentration. After 30 minutes, KPF$_6$ salt was added to the water sample to change the solubility of the metal-organic complex resulting in a precipitate. Then the suspension was centrifuged at 1000 rpm for 10 mins, and the precipitate was filtered out. The supernatant (treated water) was analyzed by AAS.

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6.4 Results and analysis

AAS analysis indicated that almost 100% removal of mercury from water in a single treatment. The precipitate collected from the treatment process was re-dispersed in 3 ml distilled water to which *p*-toluene sulfonic acid was added to acidify the pH of the solution, in the aim of separating the metal-organic complex.

The experiment was conducted through the sequential addition of *p*-toluene sulfonic acid stock solution (14.6 mM) to the dispersed precipitate in distilled water, pH of the solution was recorded after each addition. This was done through the titration of different volumes of the acid (0-200 μL) to the suspended precipitate. At pH 3, the precipitate was fully dissolved in solution and the sample was analyzed by UV-vis to monitor the separation.

6.4.1 Monitoring the regeneration process through UV-vis

The regeneration of the pyridylimine ligand was investigated using UV- vis spectrophotometry studies. The metal-organic complex (precipitate) was suspended in distilled water, where it was subjected to the addition of *p*-toluene sulfonic acid gradually to change the pH of the solution. Absorption peaks at different reaction pHs are presented in figure 1.
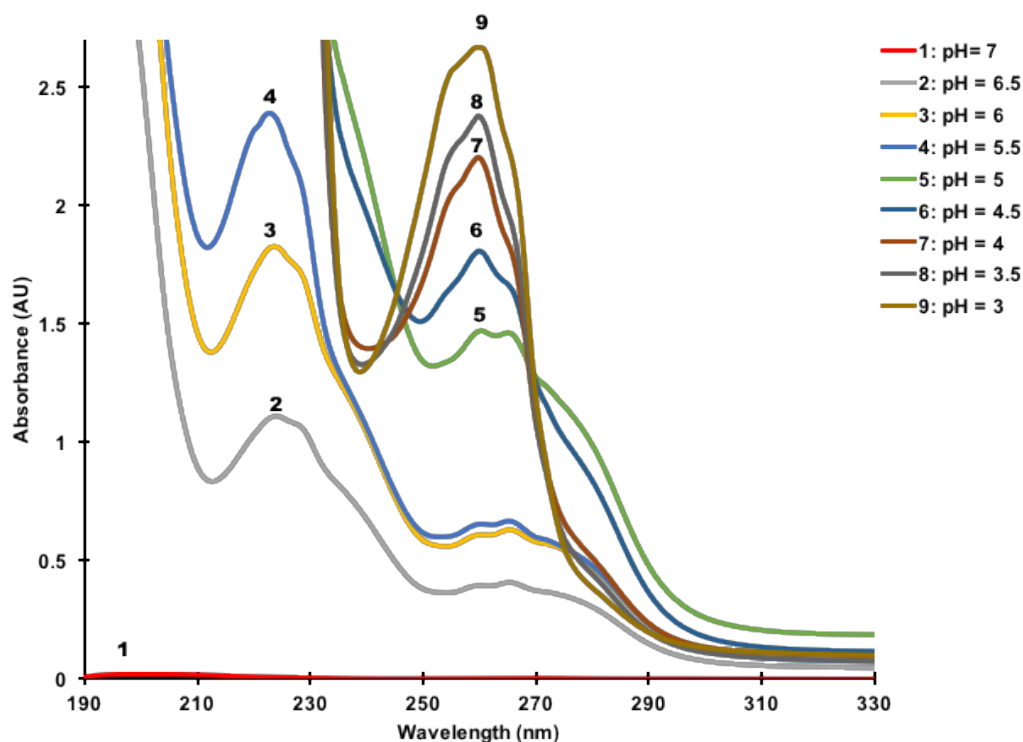
Figure 26 UV- visible absorption spectra of the addition of p-toluene acid to metal-organic ligand precipitate.

Two different spectral behaviors were observed during the acid titration experiment as demonstrated in Figure 26.

The first spectral change, entitled spectra (2, 3, and 4) of respective pH values: 6.5, 6, and 5.5, where the spectra are similar to the reference pyridylimine ligand's spectrum as shown in Figure 27 . Absorption spectra 2, 3, and 4 exhibit the same behavior as the ligand's spectrum with two shoulder peaks at around 230 nm and 270 nm. This shows that the pyridylimine ligand is regenerated at a pH of 5.5 with no signs of the metal in solution.
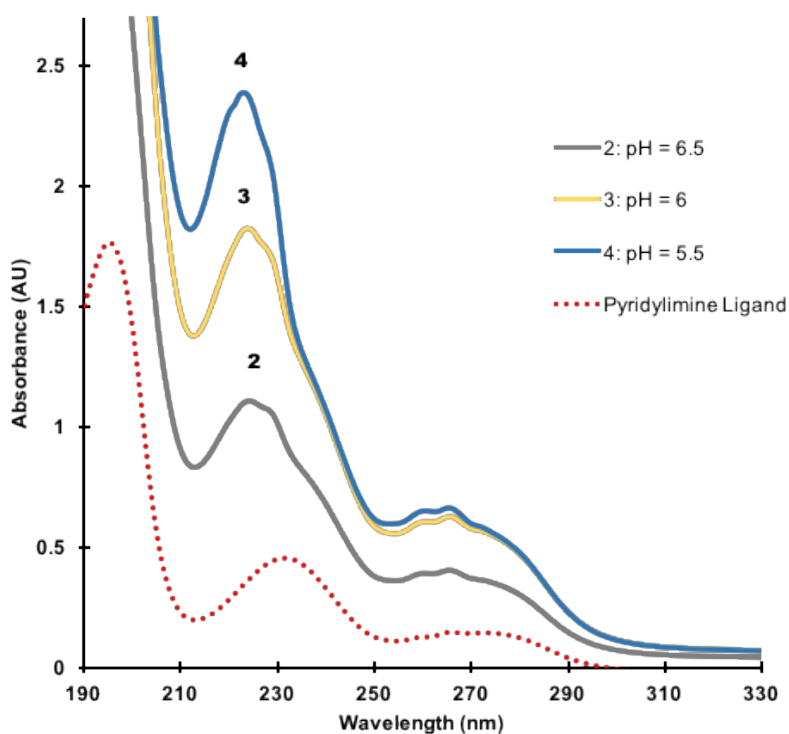
Figure 27 UV-visible absorption spectra of behavior 1 compared to the pyridylimine ligand's spectrum.

However, behavior 2 is well presented in spectra 5, 6, 7, 8, and 9 of pH 5, 4.5, 4, 3.5, and 3 respectively (Figure 28, A). The exhibited spectra are similar to that of the metal organic-complex spectra resulting of titrating the Hg metal ion with pyridylimine ligand (Figure 28, B). As previously mentioned, the metal-organic complex formation is shown through the formations of a new peak at wavelength 260 nm. This peak clearly formed at pH=5, and it enhanced as the pH decreased, until pH 3 which is the point at which all the precipitate was soluble in solution. Thus, at pH values less than 5, Hg^{2+} start dissolving into solution (disappearance of the precipitate) forming the metal-organic complex.

A: Regeneration spectra

B: Titration of the mercury to the ligand spectra
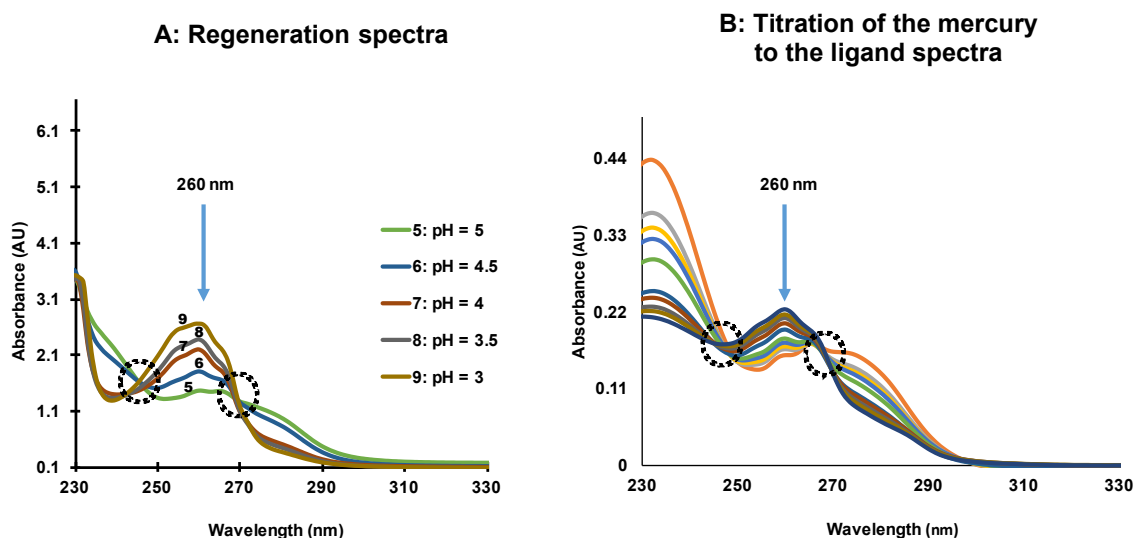
Figure 28 Comparing the UV- visible absorption spectra of behavior 2 at pH 5 to that obtained upon titrating mercury to the ligand forming the metal-organic complex.

Furthermore, to confirm the results presented by UV-vis, AAS analysis were conducted to detect the removal of Hg^{2+} by the regenerated ligand solution. A volume of 3 ml water were added to the generated precipitate from the first cycle followed by the addition of 16 μL of *p*-toluene sulfonic acid (14.6 mM), which showed the pH to be 5.5, then the residual precipitate (which contained the Hg^{2+} ion) was filtered out and the solution containing the ligand was added to mercury infested water.

Reuse of the recycled ligand showed removal of 55.3% of Hg^{2+} from mercury spiked water, this marks cycle 2. Cycle 3 showed 40% removal and cycle 4 showed 22.5% removal.

The regeneration process is yet to be further optimized considering different parameters like: (a) stirring, (b) contact time, and (c) concentration of the components in water.

CHAPTER 7
CONCLUSION

Based on the discussions provided in previous chapters of this report, it is a grand challenge to be involved in discovering ways to carry out water treatment processes utilizing green and sustainable chemistry approaches. This builds on the ultimate premise of green chemistry; that it is better to prevent waste than to clean it up after it is formed. Achieving this grand challenge is mostly attributed to the production of no secondary hazardous waste, using less energy, and lower cost of operation.

The proposed method suggests a more sustainable water treatment method for the removal of mercury (II) ions from water. This is achieved through employing a dynamic pyridylimine ligand, capable of chelating to mercury ions in solution forming a metal-organic complex. The metal-organic complex's formation and identity were monitored in solution using UV-vis spectrophotometric techniques. UV-vis analysis revealed that two receptors bind to one Hg(II) ion tightly in water. The tight binding of the metal-organic complex was quantified through a titration experiment, to be $K_G = 7.8 \times 10^7$ M^{-1}.

Formation of this metal-organic complex (2L : Hg) and its consequent removal from water would lead to treating mercury-contaminated water. Removal of the metal-organic complex was achieved through changing its water solubility; addition of a PF_6 salt renders the metal-organic-complex insoluble in water, where the soluble complex crashes out as solid. Removal of this solid leaves behind a treated water. The efficiency of the method in removing mercury was assessed by Atomic absorption, where concentrations of mercury before and after the treatment were compared. It was observed that the employed organic ligand can effectively remove 250 ppm Hg(II) ions

from mercury-contaminated water, where almost 100% removal of mercury from water was completed in 30 minutes under ambient conditions.

Heading towards a more sustainable approach and emphasizing on the green chemistry title, the formation of the metal-organic complex can be reversed by changing the pH of the metal-organic complex in solution. The change in pH triggers breaking down the metal-organic complex, allowing for the separation of the aqueous pyridylimine ligand and the insoluble form of the metal ion. The infested ligand was used, for four other cycles of water treatment.

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Appendix

APPENDIX A

The different concentrations used in the titration experiments are shown in the tables below.

Table A1. Different concentrations of Hg(II) ion used in the titration

Sample Name	Concentration of Ligand (M)	Concentration of Hg^{2+} ion (M)
C1	1.1×10^{-5}	7.3×10^{-6}
C2	1.1×10^{-5}	1.1×10^{-5}
C3	1.1×10^{-5}	1.4×10^{-5}
C4	1.1×10^{-5}	1.6×10^{-5}
C5	1.1×10^{-5}	1.8×10^{-5}
C6	1.1×10^{-5}	2.2×10^{-5}
C7	1.1×10^{-5}	2.5×10^{-5}
C8	1.1×10^{-5}	3.0×10^{-5}
C9	1.1×10^{-5}	3.4×10^{-5}
C10	1.1×10^{-5}	6.0×10^{-5}

Table A2. Different Ligand concentrations used in titration experiment

Sample Name	Hg: L (ratio)	Concentration of Ligand (M)	Concentration of Hg^{2+} ion (M)
C1	1 to 0.2	5.98E-06	2.99E-05
C2	1 to 0.4	1.20E-05	2.99E-05
C3	1 to 0.6	1.79E-05	2.99E-05
C4	1 to 0.8	2.39E-05	2.99E-05
C5	1 to 1	2.99E-05	2.99E-05
C6	1 to 1.2	3.59E-05	2.99E-05
C7	1 to 1.4	4.19E-05	2.99E-05
C8	1 to 1.8	5.38E-05	2.99E-05
C9	1 to 2.0	5.98E-05	2.99E-05
C10	1 to 3.0	8.97E-05	2.99E-05
C11	1 to 4.0	1.20E-04	2.99E-05
C12	1 to 6.0	1.79E-04	2.99E-05
C13	1 to 8.0	2.39E-04	2.99E-05
C14	1 to 10.0	2.99E-04	2.99E-05
C15	1 to 16	4.78E-04	2.99E-05