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COLLEGE OF SCIENCE AND TECHNOLOGY

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COMPARATIVE STUDY OF SELECETED HEAVY METALS REMOVAL FROM AQUEOUS SOLUTION BY USING CARBONIZED SUNFLOWER SEEDS HUSKS AND IMINE LIGANDS

A dissertation submitted in partial fulfillment of the requirements for the degree of Master of Science (MSc) in Environmental Chemistry, School of Science, College of Science and Technology, University of Rwanda

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DECLARATION

I, UWINEZA MUZIRAKE Audace, declare that this dissertation **"Comparative study of selected heavy metals removal from aqueous solution by using carbonized sunflower seeds husks and imine ligands."** is my own work and it has not been submitted for any other degree at the University of Rwanda or any other institution.

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I, Dr. Gratien HABARUREMA, the supervisor of this dissertation titled "**Comparative study of selected heavy metals** r**emoval from aqueous solution by using carbonized sunflower seeds husks and imine ligands.**" declare the approval submission of the master dissertation for final examination.

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Date:………/………./2022

DEDICATION

My lovely wife UMWIZA Jeanine

My daughter ITUZE Stella Hally

My whole family

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ABSTRACT

Heavy metal pollution is currently one of the most important environmental threats in the world. Because of their recalcitrance and persistence in the environment, the treatment of heavy metals is filled with difficulties. Several technologies for removing heavy the later analytes from wastewater have been developed in recent years. Adsorption is a very good solution for the removal of heavy metals from industrial effluent and other polluted streams, among all classic and current approaches. Various cheap plant materials can also be used as adsorbents to make the adsorption process more economical. This study was performed to evaluate the ability of carbonized sunflower seed husks and synthetized imine ligands to remove Cu (II), Pb (II) cations from wastewater. Both artificial and natural wastewaters through batch adsorption were used in this study. Sunflower seed husks have been cleaned to remove dirt before drying and then carbonized in the oven at 300°C. Next, carbonized peels were ground and sieved to a size less than 0.3mm and directly used in different adsorbent/metal ion ratios. Imine ligands were also synthetized [Tris(((di(pyridin-2-yl) methylene) amino) methyl) amine(L1), 1,1-di(pyridin-2-yl)-N-(pyridin-2-ylmethyl) methanimine (L2) and the product between Trisaminoethylamine and salicylaldehyde (L5)]. On the percentage of heavy metal removal, the effects of contact time, initial metal concentration, loading weight of adsorbent, and pH were examined. Optimum values obtained are (pH5.5, 15mg/l of initial metal concentration, 6g/L of adsorbent dose, and 1hour contact time by using carbonized sunflower husks as adsorbent) and kept constant in the following experiments. The removal percentage observed was 68% by CSH,43% by L_1, 67% by L_2, 65% by L_5 for Pb (II) ions, and 58% by CSH, 39% by L_1, 65% by L_2, 71% for Cu (II) ions. From the analysis, it was found that Carbonized sunflower seeds husks successfully removed heavy metals almost at the same level with imine ligands. Therefore, Sunflower seeds husks that are eco-friendly and cost-effective materials, can be utilized as adsorbents to successfully remove metal ions from aqueous solutions.

Keywords: Adsorption, heavy metals, Wastewater, imine ligands, carbonized sunflower seed husks

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LIST OF ACRONYMS AND ABBREVIATIONS

AAS: Atomic Absorption spectrometer

ABS: Absorbance

AC: Activated carbon

CSH: Carbonized sunflower seeds husks

DNA: Deoxyribonucleic Acid

ISP: International Science Program

pH: Potential of hydrogen

SSHB: Sunflower seeds husk biochar

CHAPTER 1: INTRODUCTION

1.1. Background

Heavy metal is defined as any metallic chemical element with a comparatively high density and it is poisonous or harmful even at low quantities. These elements have got also larger atomic weights [1-2]. Since the beginning of the agricultural and industrial revolutions, heavy metal pollution has grown to be a significant environmental issue, and the majority of water supplies are now contaminated. Due to widespread human activities like mining operations, farming practices, and the dumping of industrial waste materials [2-3], heavy metal concentration has increased to dangerous levels. Water pollution can also occur through natural processes, such as atmospheric deposition, rock weathering, erosion and runoff, but it is primarily due to human activity[3],[5]. The threat posed by toxic and trace metals in the environment is more serious than the threat of other pollutants due to their non-biodegradability, cumulative properties, and biological half-life[7].

Heavy metals in the environment and food are necessary for good health in small numbers, but in high quantities, they can be toxic or dangerous. They may be hazardous to the blood, kidneys, liver, lungs, brain, and other vital organs [7-9]. Long-term exposure results in degenerative changes to the body's cells, tissues, and nervous system that resemble illnesses including Parkinson's, Alzheimer's, muscular dystrophy, and multiple sclerosis. Loss of appetite, headaches, hypertension, stomach pain, renal failure, weariness, sleeplessness, arthritis, hallucinations, and vertigo are among symptoms of acute Lead (Pb) exposure [10]. Increased mercury exposure may cause tremors, cognitive problems, irritability, sight or hearing loss, timidity, and other symptoms [1]. Exposure to metallic mercury fumes at higher levels for a shorter length of time may result in lung problems, vomiting, diarrhea, nausea, skin irritation, and increased blood pressure [11].

The bioaccumulation of harmful substances in fish occurs as a result of heavy metal poisoning of rivers, lakes, and streams [12]. Fish can acquire heavy metals through a number of pathways, including ingesting food and absorbing soil particles [13]. Numerous invertebrates are important fish and other aquatic animals' food sources, and they also offer a useful route for the absorption of Lead, Copper, Zinc, and Cadmium. Another route of exposure to these hazardous chemicals is by immediate water absorption. Sediment is considered as the principal trace element repository in marine environments [14]. Significant and minor elements are transferred to living organisms in this ecosystem from abiotic (water or sediment) sources, where they accumulate in the organisms and contaminate the food chain [4],[16-17]. In food chains, organisms at higher trophic levels are more susceptible to biomagnification. According to bio amplification, greater trace element accumulation in animals at higher trophic levels may pose a hazard to these organisms or humans [18-21]. Because it is hard to totally eliminate heavy metals from the ecosystem [19], adsorption is a very suitable choice for heavy metal removal from industrial wastewater and other polluted waterways among all classic and current technologies. It is simple, cost-effective and adaptable. It has become the method of choice for removing harmful pollutants from wastewater [20-21].

1.2. Problem statement

Industrial effluent contains significant quantities of numerous toxins, including heavy metals, which can pollute water once released into the environment. These metals consist of Arsenic, Copper, Cadmium, Zinc, Chromium, Aluminium, Lead, , Iron, Nickel Mercury, and Silver [22]. At least 20 metals are poisonous, and almost half of them are released into the environment in proportions that are detrimental to the environment as well as human health [5], [23]. According to different studies, heavy metals come from mining, natural deposits, and industry [5]. Some of these industries have high concentrations of various metals that pollute coastal waters. So Governmental regulations and policies require technology to remove these metals from the environment [24].

The treatment procedures that have been utilized to get rid of heavy metals from wastewater are: Complexation of dry biomass, precipitation, ion exchange, flocculation adsorption and coagulation [25]. Adsorption is a technique used because of its inexpensive cost and large-scale application [23],[29-30]. All of the techniques listed above, however, have drawbacks such as inadequate metal removal, sludge production, high reagent and energy requirements, metal precipitate aggregation, and membrane fouling. The adsorption process is a relatively new process and is a potentially preferred alternative to heavy metal removal due to its design flexibility [28], high quality treated wastewater, reversibility and adsorbent regeneration [27]. The above method is typically performed using activated carbon, which is also costly. So low cost materials which are abundant in nature, that require little processing, can be used as adsorbents to make the adsorption process more economical [4]

1.2. Objectives of the study

General objective

The main objective of the study is to remove Copper and Lead from aqueous solution by using carbonized sunflower seed husks and imine ligands

Specific objectives of the project

i. Prepare and characterize sunflower seed husks and imine as adsorbents
ii. Optimize of adsorption factors for better efficiency removal
iii. Evaluate of Cu and Pb removal from aqueous solution by using sunflower seed husks and imines ligands.

1.4. Hypothesis

- Cu and Pb will be removed efficiently from synthetic wastewater by using carbonized sunflower seed husks (CSH) and imine ligands
- Cu and Pb will be removed from real wastewater more efficiently by using carbonized sunflower seed husks (CSH) and imine ligands

1.5. Significance of the Study

Heavy metal pollution is complex, even at very low concentrations, and is attracting attention due to its toxicological effects on the environment and human health [29]. The increasing rate of global industrialization and urbanization causes major problems of water pollution due to the release of toxic heavy metals commonly found in the chemical industry such as tanning, textiles, cement, metallurgy, photographic materials and corrosive paints [30]. For example, untreated industrial effluent yields significant concentration of heavy metals that, after being discharged into the environment, pollute groundwater and surface water. The non-biodegradability of heavy metals and their tendency to accumulate in living organisms cause several illnesses, disorders, and deaths [29]. Therefore, the removal of toxic heavy metals from industrial wastewater is of primary importance in terms of public health and environmental protection [31]. Currently, several conventional methods are used to treat wastewater, which have drawbacks such as high cost, low efficiency, large amounts of reagents and solvents, and the production of toxic sludge [22]. Therefore, in order to minimize the amount of toxic heavy metals from industrial wastewater, it is necessary to develop cheaper, environmentally friendly and efficient heavy metal treatment processes.

Herein, we reported the preparation and characterization of low-cost adsorbent using available bio-sorbent materials (sunflower seeds husks) and compared their performance with conventional adsorbents (imine ligands). Sunflower seeds husks, which are mainly available, are used as energy source [32], can also be used in the removal of toxic heavy metals from industrial wastewaters. This study assessed the efficiency of toxic metal removal by sunflower seeds husks compared with imine ligands as an alternative choice of commercial activated carbon in the removal of Pb (II), Cu (II) from aqueous solution in batch mode studies.

1.6. Scope of the work

The purpose of this research was to assess the removal of Cu, Pb from wastewater through batch adsorption process by using carbonized sunflower seeds husks and imine ligands. Carbonized sunflower seeds husks and imine have been used as adsorbents. Artificial wastewater was produced in the lab, the samples obtained were examined for each metal separately in order to optimize performance factors. Experiments started by adsorbent preparation, synthesis and then by optimization of performance factors (pH, initial metal concentration, adsorbent dosage, contact time). After optimization, the same obtained optimum conditions were applied in synthetic and real wastewater testing. The experiments were batch-based and carried out in a laboratory setting. Analyses of toxic metals in water samples were performed by use of Atomic Absorption Spectrophotometer (AAS).

CHAPTER 2: LITERATURE REVIEW

2.1. Generalities on heavy metals

Heavy metals are naturally occurring metal elements that have a relatively high density a least 5 times greater than that of water and are toxic even at low concentrations [2],[10]. Heavy metal exposure persists and even rises in various regions of the world despite the long-standing knowledge of several harmful impacts on health [33]. Emissions of toxic metals into the ecosystem occur through various processes and routes that contaminate air (incinerator, extraction, processing, etc.), water (release from spills, storage and transport), and soil. Air pollution tends to be of primary importance from the perspective of human health [24]. Lead emissions are most evenly distributed in the atmosphere as they are primarily related to road traffic [34].

While non-ferrous metal processing and fuel combustion are predominantly responsible for Cadmium emissions [35], the geographic distribution of anthropogenic mercury emissions reflects amounts of coal use in various regions. [36]. Additionally, due to their high toxicity, non-biodegradability, and high concentration accumulation, the release of heavy metal trash into wastewater during the past few decades has unavoidably introduced metallic compounds into the aquatic environment of the Earth. [37]. Production of batteries, ink and pigments, tanning facilities, petroleum refineries, mining smelting, electroplating, painting, and more recently point sources from wastewater and industrial wastewater from point sources resulted in chronic toxicity and elevated levels of heavy metals [41-42].

2.2. Possible methods used for heavy metal treatment

To remove soluble solids from wastewater in the most effective and economical manner possible, researchers have tested a number of different methods. Due to their dangerous and deadly effects when present in excessive quantities, metals have attracted a lot of attention. [23]. One method that has been employed or studied is precipitation [38], filtration [40], filtering Fluidized bed reactor [43], coagulation [41], ion exchange [40], magnetic fields [41–45], Flue gas purification [45], ion flotation, [44] reverse osmosis, membrane technology, evaporation recovery, oxidation or reduction [38],[46], and adsorption [47] are a few examples of electrochemical treatment. The majority of them are inefficient, costly, time-consuming, or unable to handle significant amounts of garbage [38],[48]. However, regardless of the concentration or amount of dissolved water, adsorption is a quick and inexpensive method of eliminating heavy metals from water. Adsorbents can be made of a number of substances to trap or adsorb heavy metals from wastewater. Waste materials and other organic materials work well as adsorbents, making it possible to remove particles from wastewater in an efficient and affordable way [33]. The challenge is to identify the ideal conditions and adsorbent for efficiently extracting a significant amount of a known metal. [23].

2.3. Production and characterization of biochar

Biochar is a solid substance made from biomass that has a high carbon content and is produced through pyrolysis, which gives it special qualities like adsorption capacity [49]. The lignin, cellulose, hemicellulose, fat, and starch in the feedstock are thermally broken-down during pyrolysis to produce biochar, a solid, bio-oil, and non-condensable gases (CO_2, CO, CH_4, and H_2) [50]. However, the yield of biochar and its properties are determined by the pyrolysis condition. Slow pyrolysis at a moderate temperature (350–500°C) and slow heating rate produces a higher yield (30%) of biochar than fast pyrolysis (600–700°C and fast heating rate) or gasification (temperature 700°C or above), which yields around 10% or less [52-53]. Depending on the type of feedstock and pyrolysis conditions used to create the biochar, surface area, polarity, atomic ratio, pH, and elemental makeup all fluctuate dramatically. These characteristics determine how biochar is effective in wastewater treatment [53].

Biochar has a wide range of applications in the treatment of water and wastewater due to its special features, such as adsorption capacity, specific surface area, microporosity [54], and ion exchange capacity [53]. The removal techniques for different pollutants are determined by how they interact with different biochar qualities, which rely on the pyrolysis temperature and feedstock type. The features of biochar are significantly influenced by the temperature at which it is pyrolyzed. The pyrolysis temperature of biochar increases with its carbon content, hydrophobicity, aromaticity, surface area, and microporosity [54]. Similar to this, as the pyrolysis temperature rises, the pH of the biochar also rises because the amount of ash in the biochar increases. Biochar has low polarity and acidity due to the loss of O and H-containing functional groups at high temperatures (>500°C). [42].

Various engineering techniques, in addition to the conventional pyrolysis technique, have been developed and applied to broaden the uses of biochar [55]. Engineered biochar is a biochar derivative whose physical, chemical, and biological characteristics (such as specific surface area, porosity, cation exchange capacity, surface functional group, pH), as well as its adsorption ability, have been enhanced [54],[56]. Some of the changes include anaerobic digestion of the feedstock prior to pyrolysis, steam/gas activation, microwave pyrolysis, ball milling, magnetic modification, chemical modification using hydrogen peroxide, alkali, or acid, and impregnation/coating with chemicals. [56].

2.4. Biochar and heavy metals

Heavy metals interact with biochar in a number of ways when it has a high organic carbon content (in the non-carbonized fraction), a porous structure, and various functional groups [57]. Heavy metal ion sorption by biochar is controlled by surface interaction through ion exchange and complexation between biochar functional groups (such as -OH, -COOH, and R-OH) and heavy metal ions [58]. Additional options include coordination of metal ions with the -electrons of biochar (C=C) and metal precipitation with inorganic components. Adsorption occurs throughout the biochar's matrix and is affected by the pyrolysis temperature, feedstock type, pH, and application rate [42],[57].

2.5. Activated carbon

Activated carbon has been utilized widely in earlier research [57],[59] because of its potent capacity to remove dangerous metals and other organics contained in water. To make activated carbon, a substance like pits or bark must first be heated to a temperature where the water has completely evaporated. The material is then carbonated in a furnace at temperatures between 500°C and 900°C after being impregnated with an acid [60]. After being rinsed in hot distilled water to the necessary pH level, the activated carbon is next crushed and sieved to the required diameter. Since it offers a higher surface area to volume ratio, carbon with a smaller diameter is preferable for adsorption. The ability of carbon to bind the dissolved dangerous metal is improved by a higher surface area ratio. In numerous earlier studies and experiments on adsorption, activated carbon was employed. Activated carbon was created using low-cost waste products such bark, date seed, food and agricultural waste, and other garbage [55]. The issue with activated carbon, on the other hand, is the considerable treatment necessary to make it. In other words, a lot of effort and money goes into maintaining particular conditions in order to create activated carbon. In addition to the usage of acidic chemicals, extremely high temperatures are necessary [61]. As a result, what began as a low-cost waste material ends up as a high-cost adsorbent after a long procedure [42].

Therefore, research has been done to determine how adsorption will affect materials that have not undergone rigorous processing to create activated carbon. Additionally, these studies looked at the impact of low-cost waste materials that had been cleaned, thoroughly dried to remove any moisture, and sieved to the necessary range of diameters [62].

2.6. Comparison between biochar and activated carbon

Low-cost materials with a high carbon content and low inorganic content were reported to be used as raw materials for AC manufacture [63]. Several studies have found a wide range of basic materials that can be utilized to make AC. Agro-industrial byproducts, for example, are commonly employed because of their renewability, high mechanical strength, low cost, abundance, and low ash content. Several studies have reported the use of agricultural waste biomass residues in AC production, including rice husks as coal, jujube seeds, sawdust, tropical wood, palm shells, durian peel, corn cobs, coconut shells, walnut shells, watermelon, tobacco stems, bean husks, hazelnut shell, banana peels, and mangosteen shells [65-66]. Non-agricultural resources, such as waste-automobile tires, were also discovered to be inexpensive sources of activated carbon. The structure of the raw materials and the manufacturing procedures have a big impact on the maximal adsorptive capacity of AC [66]. In comparison to biochar, activated carbon has a large specific surface area [42].

Biochar is a lightweight black carbon residue made by pyrolysis, which removes water and other volatile elements. Several researchers have employed a variety of feedstocks to make biochar: Agricultural trash like wheat, rice, and sugarcane, as well as forest leftovers including water hyacinth, beech trunk, and sawdust [48],[55],[65-66]. Biochar, which is a pyrolysis byproduct, is comparable to activated carbon, which is an industrial product [42].

2.7. Adsorption process

Adsorption, as previously noted, is one of the most cost-effective strategies for removing hazardous metals from wastewater. Depending on the environment used to eliminate the metals, most notably the pH, other types of removal may take place. Precipitation is one among them. Precipitation is a time-consuming and expensive operation that cannot be done properly on its own. Sorption refers to the removal of metals by means other than adsorption, such as the creation of solutes or precipitates [67]. The process of adsorbing dissolved substances in water to the surface of the materials being used, or adsorbent, is called adsorption. Adsorption has not been used to treat wastewater very often, but as the need for better water quality grows, extensive research on the technique has been carried out to give better water quality and decreased toxicity. Adsorption with activated carbon, which was used as a "polishing step" to remove some of the remaining dissolved compounds in the water after treatment, was the most often used technique. Furthermore, to operate with activated carbon, several adsorption methods necessitate high temperatures and pressures [68].

The effect of various materials in adsorbing, or collecting, dissolved inorganics in water has been studied. Testing has been done on a variety of water sources throughout the years, including drinking water, domestic sewage, industrial effluent, and the ocean [68-69]. Each of these types of water has particular kinds of dissolved substances depending on the location, source, and use of the water, as well as on governmental laws and requirements [71]. Purification and treatment operations also produce different effects depending on the methods utilized and the effluent. When it comes to harmful metals dissolved in water, industrial effluent generates the highest concentrations [37].

Adsorbents that have been employed in the past usually require a chemical process to manufacture. This is typically related to a difficult or lengthy procedure, or one that generates a lot of waste or byproducts [60]. In order to create activated carbon, organic materials such nuts, leaves, shells, bark, pits, and wood must be burned at high temperatures and put through rigorous processes [57]. Nevertheless, the production of activated carbon takes a long time, therefore until recently, adsorbents that are widely present in the environment and have a history of success were not used. Many of the adsorbents that have recently been used are by-products of other processes or natural waste materials that can be found in the environment. Activated carbon is a well-known product [72]. In the case of organic molecules and activated carbon, specific adsorptions take place between the surfaces of the adsorbent and the various functional groups of the adsorbate [73]. The following mechanisms, such as chemical adsorption chemical reactions [74], exchange adsorption electrical attraction, and physical/ideal adsorption Van Der Waal force attraction [75], cause the adsorbate and the adsorbent to be attracted to one another. Additionally, a material's solubility in water influences adsorption since a substance's capacity to be adsorbed increases with hydrophobicity in water and decreases with hydrophilicity [76].

To illustrate the equilibrium in adsorption, the amount of solute, or metals in this case, adsorbed per unit weight of the adsorbent (Qe) is plotted versus the concentration of the solute still present in the solution(C). This results in the formation of an adsorption isotherm. Langmuir and Freundlich are the most commonly utilized equations for water and wastewater treatment [77].

The amount of heavy metal adsorbed onto the adsorbent is dictated by the capacity of the adsorbents, which may be calculated using the mass balance equation (1)[78-79].

$$Qe = \frac{co - ce}{m} \times V \quad (1)$$

Where Qe denotes the adsorbent concentration following equilibrium (mg absorbate/g absorbent), V indicates the total volume of the solute solution (in L), Co represents the solute's initial concentration (in mg/L), Ce symbolizes the solute's residual equilibrium concentration (after adsorption) (in mg/L), and m defines the weight of the adsorbents used (in g).

The total removal efficiency (R%) was calculated using Equation (2)[79- 80].

$$R(\%) = \frac{Co - Ce}{Co} \times 100 \quad (2)$$

2.8. Cheap materials used in adsorption process

Adsorption that uses cheap materials, makes it a low-cost approach. Various less expensive adsorbents have been utilized, and others are continuously being researched [81]. Peat, for example, has been used to adsorb several heavy metals, while marine algae have been utilized to adsorb Cd^{2+} and Pb^{2+} ions. Heavy metals can be removed from water using inexpensive materials like clays, maize cob, bagasse, and palm fruit bunch. [82]. Microorganisms have also been proven to be excellent at removing heavy metal ions [83]. The technique for obtaining and processing the materials is straightforward and does not call for the use of extra materials, substances, or procedures. The most recent study material for effective adsorption only needs to be thoroughly washed and dried to remove moisture before being sieved. Tree leaves, date pits, cashew and hazelnut shells, barks, agricultural debris, maize kernels, and sawdust were tested for their potential to adsorb different metals in various environments[48]. The ideal pH, contact time, agitation speeds, beginning metal concentrations, and adsorbent dosage are all conditions that are evaluated [81]. For different metals and adsorbents, different circumstances provide different outcomes. As a result, what works for one set of experimental conditions, metals, and adsorbents may not work for another.

2.9. Sunflower seeds husks

In most sunflower-growing countries, sunflower is an important agricultural crop. It is planted for its edible oil and fruits, which are consumed by both humans and livestock. The sunflower seed is the fruit of the sunflower plant [84]. The husks of sunflower seeds contain surface active groups (hydroxyl, carboxyl, amine, and carbonyl) that can bind to some hazardous metals [85]. The presence of N-H, stretched O-H (hydroxyl), -NH (amine), asymmetric C-H, aromatic C-C, and alkenes C-H functional groups were found in the FTIR spectra of SSHB. The FTIR spectra of activated carbon also showed bands that were comparable to those of biochar [27]. Because a higher number of functional groups promote adsorption, carbonized sunflower seed husks are a promising choice for usage. This research enables these sunflower seed husks to be used not only for energy production, but also as an unusual means of extracting heavy metals from wastewater, particularly water released by industry, which contains the greatest number of dissolved hazard compounds [85].

2.10. Some of heavy metals

As mentioned above, a metal is considered a heavy metal if its density is five times that of water. Chromium, Nickel, Copper, Cobalt, Manganese, Mercury, Lead, Zinc, Cadmium, Silver, Arsenic, and Barium are the metals that are most frequently found in wastewater.[33]. These metals come from industrial wastewater that is discharged into nearby bodies of water. However, due to their toxicity, they must be removed from wastewater before being discharged into bodies of water. Lead and Copper were chosen for this study because of their prevalence in wastewater and their toxicity levels [86].

2.10.1. Copper

Copper is a hazardous element that is abundant in wastewater [87]. Several sectors make extensive use of copper, including paints, fertilizer, printing circuits, dye and textile manufacturing, metallurgy, plating, and printing circuits. Copper is incredibly toxic to people and can harm the liver, lungs, mucous membranes severely, irritate the nervous system, induce necrotic changes in the liver and kidney, harm broad capillaries, harm hepatic and renal organs, and can even lead to depression.[78-80]

2.10.2. Lead

Lead is a common metal that is used as a petroleum additive, in batteries, paints, and dyes, and in a variety of other applications. Lead mining is one of the most prominent anthropogenic sources of primary Lead [35],[88]. Municipal solid waste, sewage sludge, and industrial waste water discharge all have high levels of Lead. Lead contamination in surface dust soil near houses or buildings, as well as home dust, can be caused by the use of Lead in paints. The use of Lead-containing fertilizers in agricultural fields has the potential to contaminate soil, surface water, and ground water [89]. Due to working with and being exposed to Lead or Lead-based products, high concentrations of Lead have a negative impact on human health. If Lead is dissolved in the water ecosystem, it can harm fish and other aquatic species. Lead is a proven carcinogen, causing direct DNA damage as well as inhibiting DNA synthesis and repair. Lead has the potential to harm DNA through oxidative stress [3],[88],[90].

CHAPTER 3: MATERIALS AND METHODS

3.1. Generalities

To achieve the objective of the research, carbonized sunflower seeds husks, as an effective suitable material has been chosen. Batch tests were performed to obtain effective toxic metal removal and different imine ligands have been synthetized and characterized. The experimentation was started by adsorbent preparation, run batch tests for optimization of performance parameters (pH, adsorbent dosage, contact time, and initial metal concentration) in synthetic wastewater and then assessed the toxic metal removal from real wastewater.

3.2. Description of the sampling area

On its upstream portion, Nyabugogo river that passes through Kigali city and has got so many tributaries, including Mwange, Rusine, and Marenge rivers. Other rivers from urbanized areas of Kigali, such as Rwanzekuma, Ruganwa, Mpazi, and Yanze, feed it later. Quarrying and mining that are known as pollution-producing industries, located near this Nyabugogo basin can be source of heavy metal pollution. In addition to that, the former Kigali industrial area, where Ruganwa river flows, there were also different types of industries that might have left some contaminants behind [4].

3.3. Location of sampling points

A total of 3 sampling sites were selected to assess the level of concentration of heavy metals in water in addition to the adsorption potential of carbonized sunflower seeds and synthetized imine ligands. Sampling sites and their spatial coordinates chosen are Ruganwa river (E00272129, N0995245) Rwanzekuma river (E00171567, N09886708) and Gatsata garage effluent (E00202889, N09969349).

3.4. Materials

Pyrolysis of biomass residues from agriculture and food processing industry can lead to production of biochar with various physical and chemical properties for applications in agriculture and environmental protection [91]. The materials that were prepared through pyrolysis process and used as adsorbent were raw sunflower seeds husks. The shells of sunflower fruits after the seeds have been removed are referred to as sunflower husks, also known as sunflower hulls and sunflower kernels [92]. It results from the industrial processing of sunflower seeds. Sunflower seed husks have first been purchased from the market and thoroughly cleaned in distilled water to get rid of any debris, dirt, and materials with adhesives that are insoluble.

After that, they were rinsed in distilled water to remove any ions that might have affected the results. Sunflower seed husks were then placed in the oven for drying after washing. The temperature was set at 70 ˚C for 24 hours to remove any moisture residing in the sunflower seed husks. Carbonization of sunflower seed husks was performed in an oven at 300°C for 3 hours, then ground and sieved to a size of less than 0.03 mm. The powder of carbonized sunflower seeds husks was then stored in a plastic bottle until it is utilized as adsorbents in the tests.

In the experiments, the carbonized sunflower seeds husks (CSH) were used immediately. Artificial wastewater prepared in the Laboratory was used for optimization of performance parameters and then optimized conditions were used treat synthetic and real wastewaters. This is because it was necessary to examine each adsorption factor's impact on metal removal separately since it would be challenging to determine how sunflower seed husks affected the adsorption behavior of the metal in the presence of other soluble and insoluble components in the water. There was just one metal solution dissolved in each prepared wastewater sample that was examined. Metal crystals were dissolved in the distilled water, this was done in order to remove any interference from other soluble materials that could be detected in actual wastewater. Distilled water was used to dissolve Copper ($Cu\ (NO_3)_2 \times 3H_2O$) and Lead ($Pb\ (NO_3)_2 \times 2H_2O$) crystals to obtain Cu and Pb solution respectively. The amount of metal crystal solids that was required to obtain an initial metal concentration of solution was calculated and used in the tests. The metal crystals were thoroughly dissolved in 1L of distilled water after being shaken. Optimized conditions were then used to assess the adsorption potential of various adsorbent in wastewater from polluted environment.


(a) (b)

Figure 1: (a) Raw and (b) Carbonized sunflower seeds husks.

3.5. Synthesis of Schiff bases

Due to their simplicity in synthesis, variety in structural design, and wide range of uses, Schiff bases are regarded as remarkable ligands for metal ion coordination complexes[93]. These ligands have shown remarkable performance in terms of steric properties and electronic soft tuning of their metal complexes and have been widely employed as polychelator ligands. Schiff bases were created by chemists as polydentate ligands and their complexes, and these have been used in a variety of chemistry-related fields. In this study, we focused on the synthesis, characterization and use of the ligands in heavy metal adsorption process [94]. Schiff bases have been synthesized by the condensation reaction of primary amines with aldehydes or ketones under organic solvent conditions (Methanol).

3.6. Batch tests

The performance of the adsorbent and adsorbate under various circumstances was examined in batch tests conducted as part of experiments on the adsorption of metals using CSH. These parameters consist of pH levels [95], initial metal concentration, adsorbent concentration, temperature, agitation rate, and contact time. [86-89]. When one of these circumstances is modified, it produces different outcomes; nevertheless, the size and significance of the change differs between the conditions due to the fact that each of them affects the adsorption process differently. Adsorption occurs when the adsorbent and adsorbate interact, hence altering the environment can improve or worsen the pace and amount of adsorption. The release of H+ and OH- ions into the solution modifies adsorption procedures. More H^+ ions are released by an acidic pH, which could react with either the adsorbent or the adsorbate, altering the results. An alkaline pH solution, on the other hand, releases OH^-, which might react with the adsorbent or adsorbate [97]. As a result, it is critical to examine the procedure at various pH levels when doing batch tests [98]. Unfortunately, a universal pH value cannot be computed or set due to the wide variety of adsorbents used and their chemical composition. As a result, testing must be carried out to find the most effective pH value [99].

Contact time, like pH, is an important consideration when doing testing [100]. This is especially crucial since the adsorbents utilized are organic materials, which may cause the system to release more organic molecules. Allowing insufficient contact time will not successfully finish the adsorption process, resulting in unintelligible and void outcomes [88-90]. The longer the contact period, the more likely equilibrium has been achieved, and hence adsorption has attained its full potential [96].

Another crucial factor to check is agitation speed [98], which can either speed up or slow down adsorption. A faster agitation speed, on the other hand, does not always imply a faster rate of adsorption. Testing is required to identify the speed at which adsorption is highest. [100].

The ability of the adsorbent to adsorb and remove metals from the solution is evaluated using various initial metal solution concentrations[92-93]. The better the adsorption, the lower the metal concentration [97], because there is less adsorbate for the adsorbent to remove [99]. Some adsorbents, on the other hand, behave exceptionally well at high starting adsorbate concentrations, and so have a higher adsorption capacity [96].Because of their capacity, these adsorbents are advantageous. The concentration dosage in the liquid solution must also be examined in order to test the capability of the adsorbent [100]. If only a small amount of the adsorbent is needed to remove a significant portion of the adsorbate, the adsorbent is advantageous. Similarly, the more the quantity necessary, the less desirable it is because its capacity is limited. Increasing the surface area of the adsorbent is one technique to lower the amount of adsorbent used. This can be accomplished by utilizing adsorbents with very small dimensions [100]. Because larger surface areas are more effective at adsorption, the same adsorbent may require fewer dosages once ground than its bigger counterpart [96].

Batch experiments were conducted by putting conical flasks on stirring device. The required metal concentrations were prepared accordingly and the pH was stabilized by drops of HCl 0.1M and NaOH 0.1M. Carbonized sunflower seeds husks powder was also measured and dissolved in metal solution. The samples were placed on a stirring device and set to an agitation speed as required for specified time and temperature until it was assumed equilibrium was reached. The samples were filtered to get them ready for water quality testing after the stirring process was finished. The percentage of metal removed by the carbonized sunflower seed husks and imine ligands was calculated and then plotted on figures. Batch testing in synthetic wastewater were the first set of experiments, where the results of varying the initial metal content, the concentration of carbonized sunflower seed husks, the pH solution, and the contact period were assessed. Separate tests on each metal produced results that were ideal.

3.7. Analytical method

A wide variety of techniques used for analysis, from simple weighing to advanced techniques such as Atomic Absorption spectroscopy will be described in this part.

3.7.1. Heavy metal analysis

Firstly, adsorbents were prepared from sunflower seeds husks and Schiff bases (imine ligands) were synthetized and characterized on FTIR machine. Second, distilled water was used to make a solution of each metal sample separately. Samples for each metal were combined with Carbonized sunflower seeds husks at different dosages and to study different behaviors of metal under different conditions. The prepared mixtures that were put in the suitable bottles put on a stirring device and forced to shake for 60mn, at 200rpm agitation rate. After stirring, samples were filtered to lessen the impact of suspended solids based on the findings and the analysis tool. To preserve the samples, 5mL of HNO_3 have been added to each of the sample, to allow a long time of storage that can reach to six months. The samples were examined for the presence of Cu and Pb analytes using an AAS equipment, and the results were then discussed. To be sure that there were no leftovers that would have an impact on the outcomes of subsequent tests, the sample bottles for the batch tests were properly rinsed with distilled water.

CHAPTER 4: RESULTS AND DISCUSSIONS

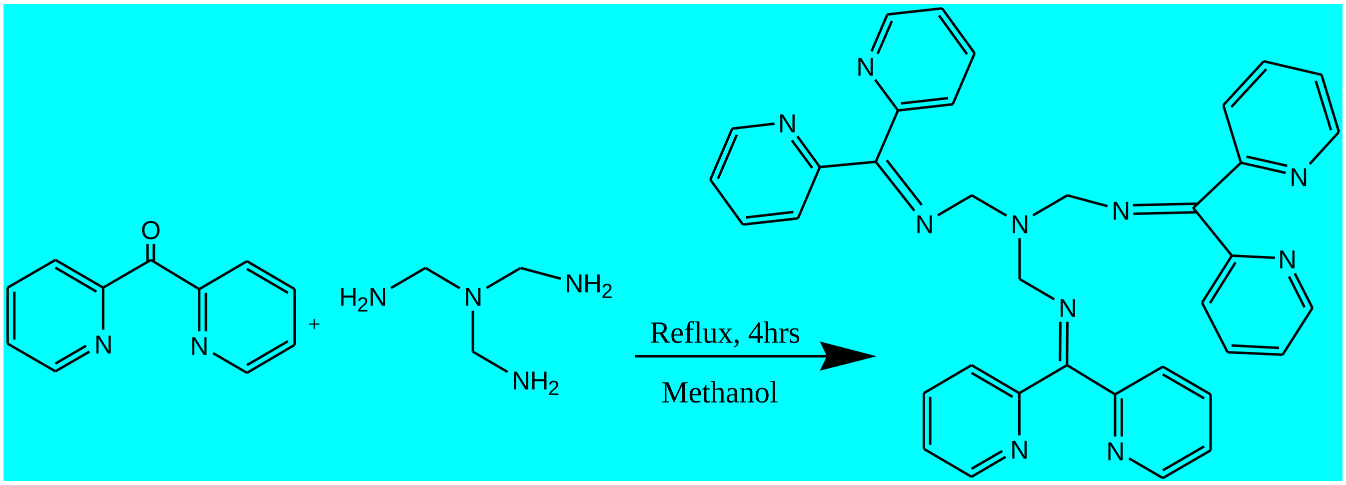
This section has objectively reported the findings, and the discussion on the meaning of the results.

4.1. Spectroscopic characterization of Adsorbent

Using FTIR machine, different synthetized imine ligands and carbonized sunflower seeds husks described above were characterized to know exactly the functional groups that are involved in adsorption process.

4.1.1. Spectroscopic characterization of Tris(((di(pyridin-2-yl) methylene) amino) methyl) amine (L1)

Tris(((di(pyridin-2-yl) methylene) amino) methyl) amine was synthetized through the reaction between 2,2-Dipyridylketone and Trisaminoethylamine in the proprtion (3:1 molar ratio). To synthetise this Tris(((di(pyridin-2-yl) methylene) amino) methyl) amine, 0.5g of 2,2-Dipyridylketone was mixed with 0.15g of Trisaminoethylamine in 30ml of methanol and heated under reflux. After 4 hours of heating, cooling for 12hours and rotary evaporating of the solvent, red crystals were obtained.The scheme 4.1.1 shows the main routes of the reaction.



Scheme 4.1. 1: Synthetic route of Tris(((di(pyridin-2-yl) methylene) amino) methyl) amine(L1).

IR spectrum of Tris(((di(pyridin-2-yl) methylene) amino) methyl) amine(L1) shows different peaks which show the presence of aliphatic amine at 3371cm^{-1} and imine peaks at 1680 cm^{-1} and 1579 cm^{-1} (Figure 2).

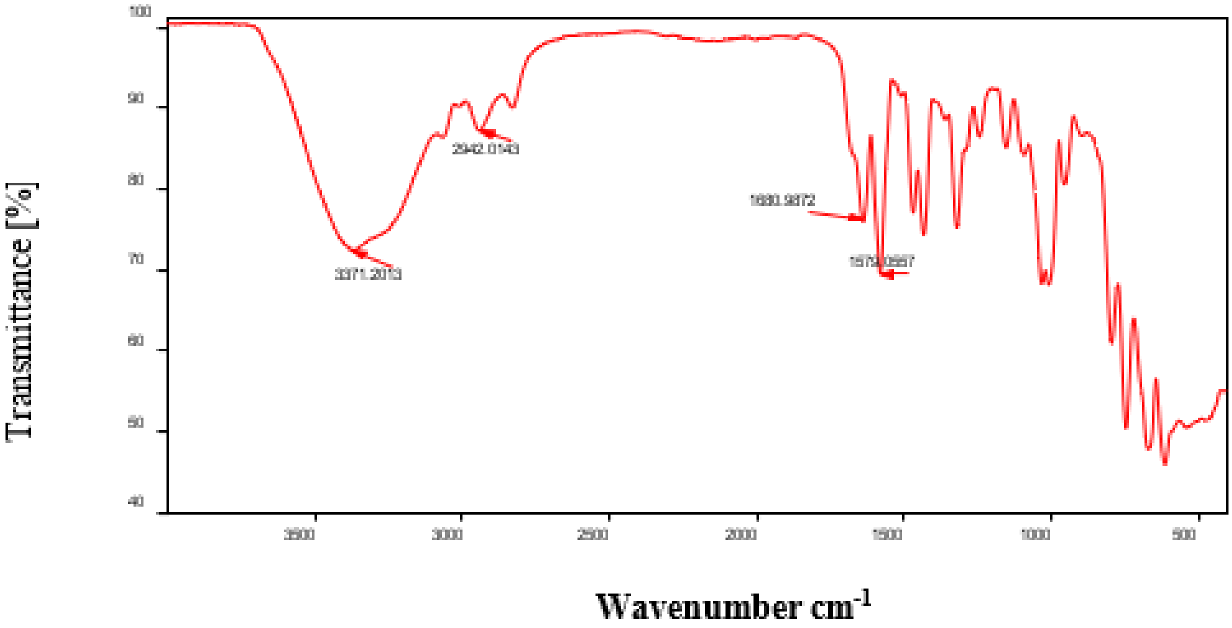
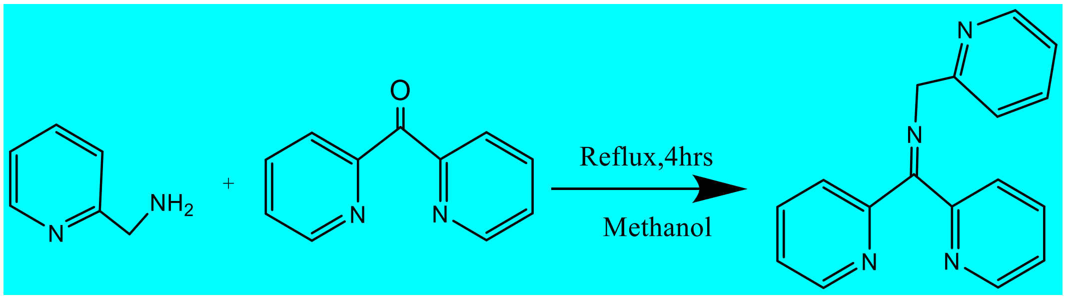


Figure 2: IR spectrum of Tris(((di(pyridin-2-yl) methylene) amino) methyl) amine(L1).

4.1.2. Spectroscopic characterization of 1,1-di(pyridin-2-yl)-N-(pyridin-2-ylmethyl) methanimine (L2)

To synthetize 1,1-di(pyridin-2-yl)-N-(pyridin-2-ylmethyl) methanimine (L2), 2,2-Dipyridylketone 0.5g and 0.30ml of picolylamine in the proportion of 1:1(molar ratio) have been mixed together. After mixing,yellow solution was formed. Refluxing heating was done in 4hours time and then red crystals were harvested after cooling and evaporation of the solvent.The scheme 4.1.2 below illustrates the main reaction components:



Scheme 4.1. 2: 1,1-di(pyridin-2-yl)-N-(pyridin-2-ylmethyl) methanimine (L2).

The FTIR analysis of 1,1-di(pyridin-2-yl)-N-(pyridin-2-ylmethyl) methanimine (L2) showed the presence N-H (Aliphatic amine) and N-H (secondary amine) at 3351cm^{-1}, C=N (Imine) at 1683 cm^{-1}, and -NH (Amine) at 1579cm^{-1} (Figure 3).

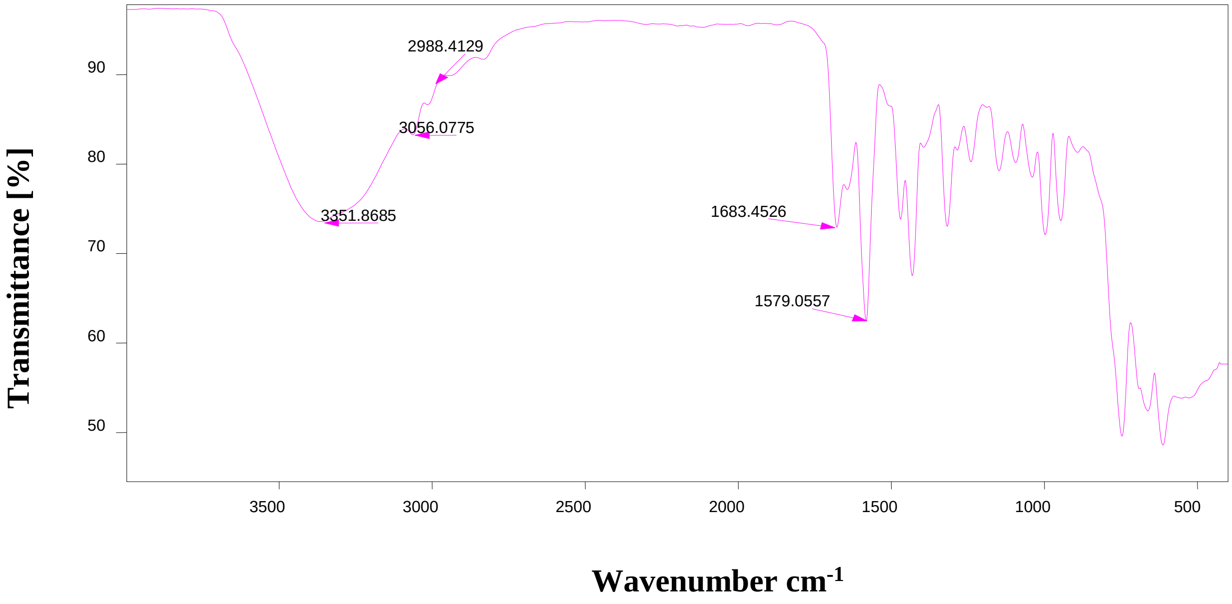
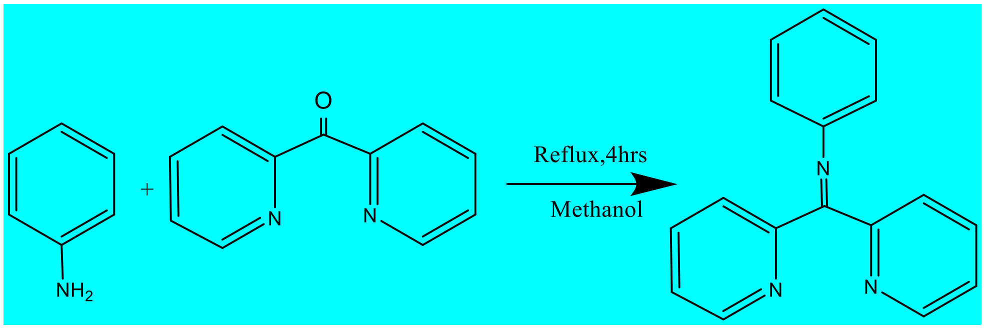


Figure 3: IR spectrum of 1,1-di(pyridin-2-yl)-N-(pyridin-2-ylmethyl) methanimine(L2).

4.1.3. Spectroscopic characterization of N-phenyl-1,1-di(pyridin-2-yl) methanimine (L3)

The reaction of 2,2-Dipyridylketone 0.5g and aniline 0.3g in 30ml of methanol in the proportion of 1:1(molar ratio) lead to the formation N-phenyl-1,1-di(pyridin-2-yl) methanimine. Immediately after the mixing of the solution, clear yellow solution was formed. After 4hours of reflux heating, yellow crystals were produced. The reaction components are shown in the scheme 4.1.3



Scheme 4.1. 3: Synthesis routes for N-phenyl-1,1-di (pyridin-2-yl) methanimine (L3).

The ligand N-phenyl-1,1-di (pyridin-2-yl)methanimine (L3) shows the presence of N-H (Aliphatic primary amine),-OH (Alcohol),-OH (Carboxylic)at 3357 cm^{-1} and -OH (Alcohol),-OH (Carboxylic) and imine at 3056cm^{-1} ,C=N (Imine) at 1679cm^{-1} and N-H (Amine) at 1598cm^{-1}, which means that it can bind heavy metals (Figure 4). The presence of -OH functional group can be due to the contamination of the product by methanol used as solvent and the byproducts of carbonyl group reactions.

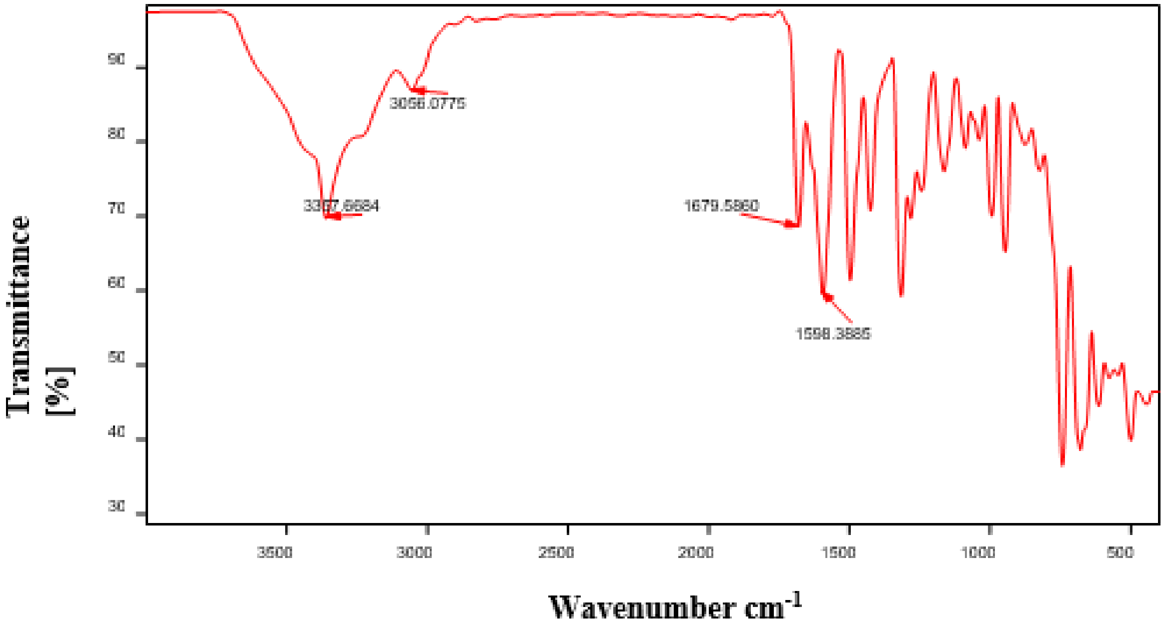
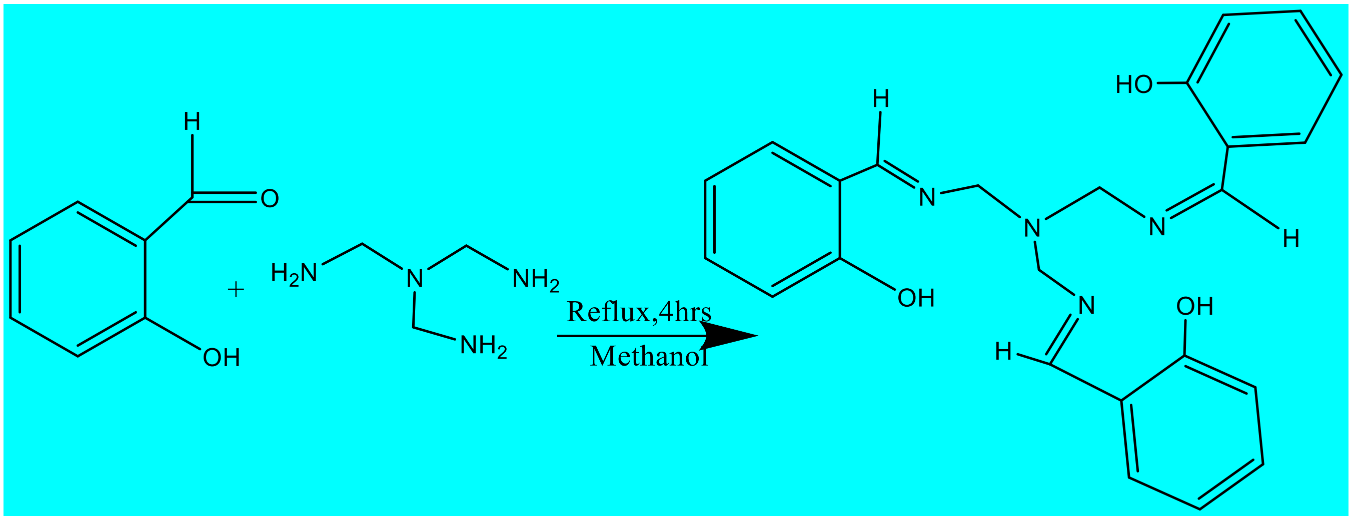


Figure 4: IR spectrum of N-phenyl-1,1-di (pyridin-2-yl) methanimine (L3)

4.1.4. Spectroscopic characterization of Ligand (L5)

This ligand L5 was obtained from the reaction between Trisaminoethylamine 0.15g and salycyaldehyde 0.37g in the proportion of 1:3 (molar ratio) in 30 ml of methanol. The solution after mixing was yellow and crystals formed after 4hours under reflux heating were also yellow. The crystals were obtained after evaporation of the solvent at room temperature. The Scheme 4.1.4 shows the details of the reaction.



Scheme 4.1. 4: Scheme for the synthesis of Ligand (L5)

The analysis of ligand L5 (Product of the reaction between Trisaminoethylamine and salicylaldehyde) on FTIR machine showed -OH (Alcohol) at 3061cm^{-1}, and N-H (Amine) at 1669-16623cm^{-1}. As it can be seen from the Figure 5, the ligand L5 has got so many functional groups that can bind heavy metals.

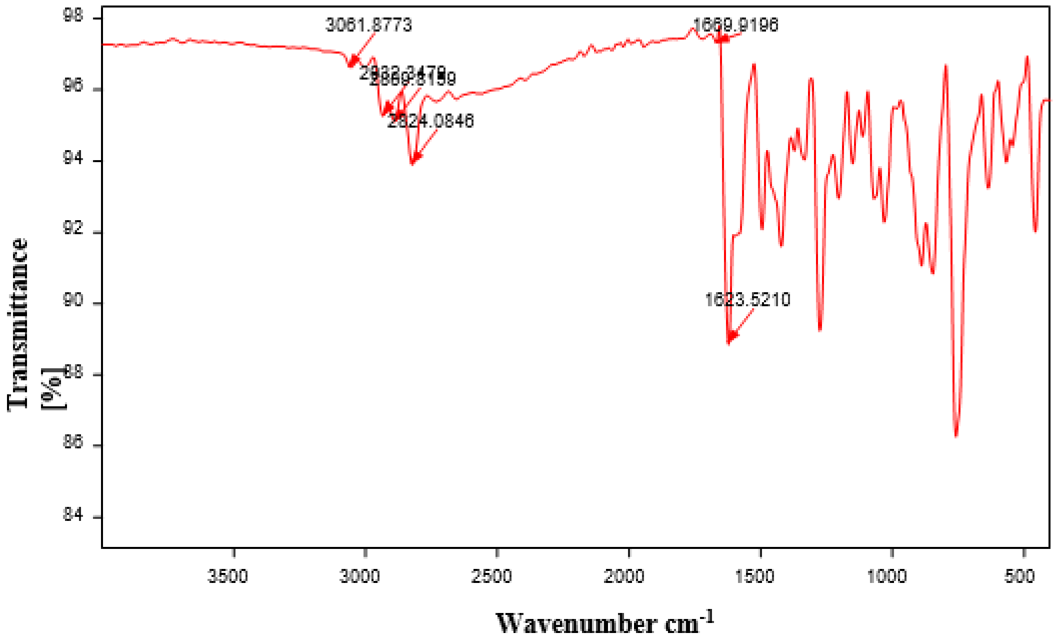


Figure 5: IR spectrum of ligand (L5)

4.1.5. Spectroscopic characterization of sunflower husks

Carbonized sunflower seeds husks has been analyzed on FTIR machine. The results show the peaks for N-H (Aliphatic primary Amine) at 3390cm^{-1}, -OH (carboxylic and alcohol) and at 3038cm^{-1}, N-H (Amine salts) at 2978cm^{-1}, C=O (Carboxylic) at 1716cm^{-1}, C=N (Imine) at 1658 cm^{-1}, and N-H (Amine) at 1617cm^{-1}. As it can be seen from Figure 6, there so many functional groups that are able to bind toxic metals. This is the same like what Srđan Stanković, *et al* 2019 [101] found in his research.

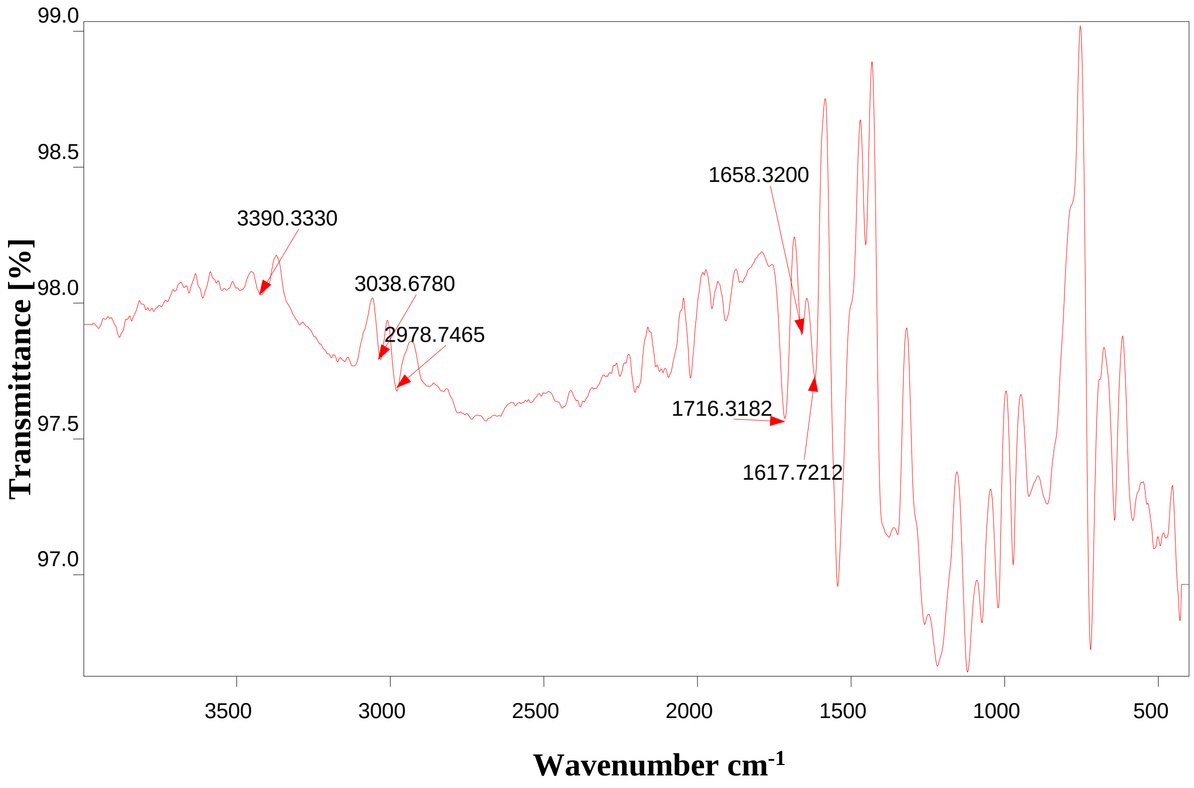


Figure 6: IR spectrum of Carbonized Sunflower seeds husks (CSH).

4.3. Adsorption process optimization

In this study, adsorption experiments were carried out to investigate the influence of major affecting parameters in the removal of Lead and Copper from wastewater under various conditions. The conditions like solution pH, amount of adsorbent, contact time, initial metal concentration were studied for the removal of Lead and Copper by batch method. A mechanical stirrer device was used and a desired amount of adsorbent were weighed, mixed with desired metal concentration sample and added to a 100ml conical flask. The room temperature was maintained throughout the experiment. Then, the adsorbents were separated from the sample by using filter paper and the absorbance of a filtered solution was measured.

4.3.1. Calibration curves

Calibration curves have been used to understand the AAS response to Lead and Copper. In this study, a set of standard samples have been prepared by diluting a 100mg/l standard solution at different concentrations (0.5mg/l, 1mg/l, 2mg/l, 2.5mg/l, 5mg/l, 7.5mg/l, and 10mg/l) for both Copper and Lead. These prepared standards were analyzed on AAS, and the response (absorbance) at each concentration was recorded. Table 1 and Figure 7, Table 2 and Figure 8 below are calibration table and Figure for Pb and Cu respectively. As it can be seen on the Figure 7 and 8, the response is linear.

Table 1: Pb calibration curve results.

STD (X)	0.5000	1.0000	2.0000	2.5000	5.0000	7.5000	10.0000
ABS (Y)	0.0053	0.0082	0.0149	0.0122	0.0268	0.0492	0.0634

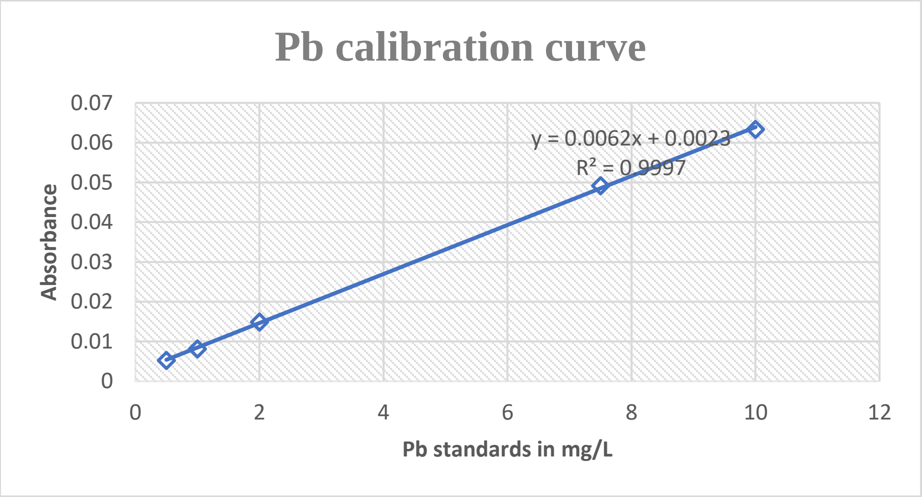


Figure 7: Pb calibration curve.

Table 2: Cu Calibration curve results

STD (X)	0.5000	1.0000	2.0000	7.5000	10.0000
ABS (Y)	0.0053	0.0082	0.0149	0.0492	0.0634

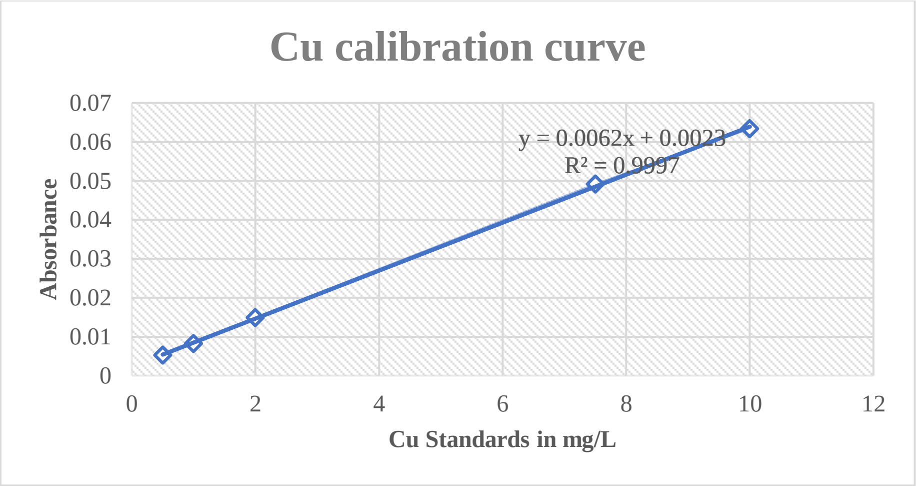


Figure 8: Cu calibration curve.

4.3.2. Effect of pH on adsorption process

The effect of pH on Lead and Copper adsorption was checked by fixing all the parameters, only pH values keep changing from 2 to 7 (see Table 3). The adsorbent dose was 10g/L; whereas the initial metal concentration was 10mg/L. The time and temperature were 120mn and 25°C respectively. The agitation rate of 200rpm was applied. The Figure 9 shows the effect of pH on adsorption process.

Table 3: Effect of pH on adsorption process.

			Removal efficiency by pH variation			
Metal	Adsorbent dose(g/L)	pH variation	Co(mg/l)	Ce(mg/l)	Co-Ce(mg/l)	% Removal
Pb (II)	10	2	10	3.2	6.8	68
	10	3	10	3	7	70
	10	4	10	1.6	8.4	84
	10	5	10	1	9	90
	10	6	10	1.3	8.7	87
	10	7	10	2	8	80
Cu (II)	10	2	10	4	6	60
	10	3	10	3.6	6.4	64
	10	4	10	1.9	8.1	81
	10	5	10	1.3	8.7	87
	10	6	10	0.8	9.2	92
	10	7	10	2.2	7.8	78

The pH of the aqueous solution is a significant parameter for the removal of metal ions by adsorption as it is also affecting precipitation as by causing competitions between [H^+] ions and metal ions on the adsorption sites [101]. For that reason, these adsorption experiments were conducted at pH 2-7 to prevent possible precipitation of Cu $(OH)_2$, Pb $(OH)_2$, which would introduce uncertainty into the interpretation of the results. As it can be seen from Figure 9, aqueous solution of metal ions has the lowest removal percentage of Cu and Pb at pH2 (60% and 68% respectively) and it slowly rises together with increase of pH value [101]. When pH value is low the protons competes with metal ions for sorption sites at CSH, resulting in low removal percentage [101].As the pH value of the solution raises the Cu and Pb ions have tendency to substitute the protons, which results in higher sorption capacity and hence higher removal percentage. However, at pH value larger or equal to pH 6,the process of Cu and Pb hydroxides formation occurs [25]. Since both processes (sorption and precipitation) are happening at the same time, the removal percentage is higher near pH 6, due to the false positive results [102]. In this study the optimal pH value for Cu and Pb sorption was chosen at pH5.5.

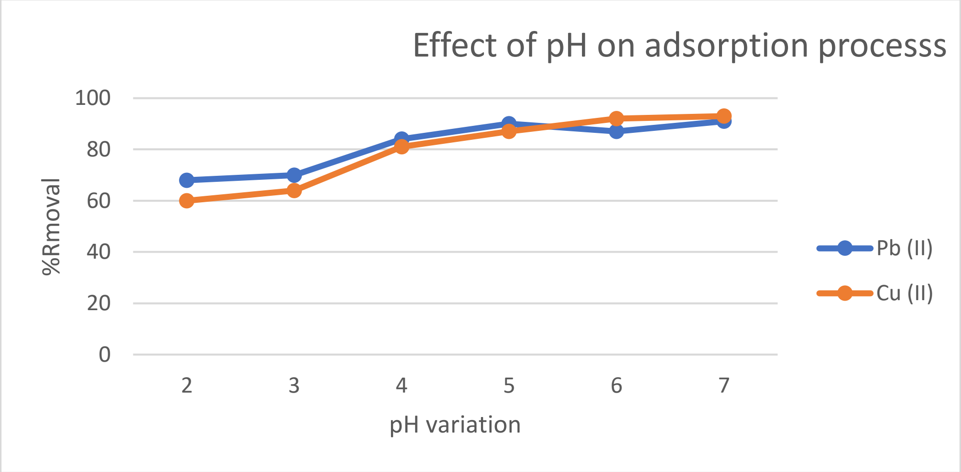


Figure 9: Effect of pH on adsorption process.

4.3.3. Effect of initial metal concentration

Lead and Copper solutions with several initial concentrations in the range of 5–25 mg/L have been considered, whereas optimized pH (5.5) was also used. Other parameters were kept constant including, adsorbent dose :10g/L, time :120mn, temperature:25°C, as well as agitation rate :200rpm. The Figure 10 shows the effect of initial metal concentration for Lead and Copper.

Table 4: Effect of initial metal concentration

		Removal efficiency of initial metal concentration			
Metals	Adsorbent dose(g/L)	Co(mg/l)	Ce(mg/l)	Co-Ce(mg/l)	% Removal
Pb (II)	10	5	2.1	2.9	58
	10	10	3	7	70
	10	15	1.65	13.35	89
	10	25	3.5	21.5	86
	10	25	3.75	21.25	85
Cu (II)	10	5	2.4	2.6	52
	10	10	2	8	80
	10	15	1.95	13.05	87
	10	25	3.25	21.75	87
	10	25	4.25	20.75	83

Generally, adsorption dosage is strongly affected by initial concentration of heavy metals [101],[103]. Several studies have shown that removal efficiency of heavy metal from aqueous solution is concentration dependent and there exist decreasing trend if there is further increase of initial concentration. In this study, 5-25mg/l of initial concentration for Cu and Pb in aqueous solution have been used. According to [25]. The amount of heavy metal being adsorbed per unit mass of adsorbent increased with an increasing heavy metal concentration of the solution. From the Figure10, it can be seen that from 5-15mg/l, there is an increase percentage removal as the metal concentration increases. But at 15mg/l and above, there is slight decrease in percentage removal because the adsorbent was saturated [100],[97-100]. Therefore, 15mg/L was considered as the optimum value.

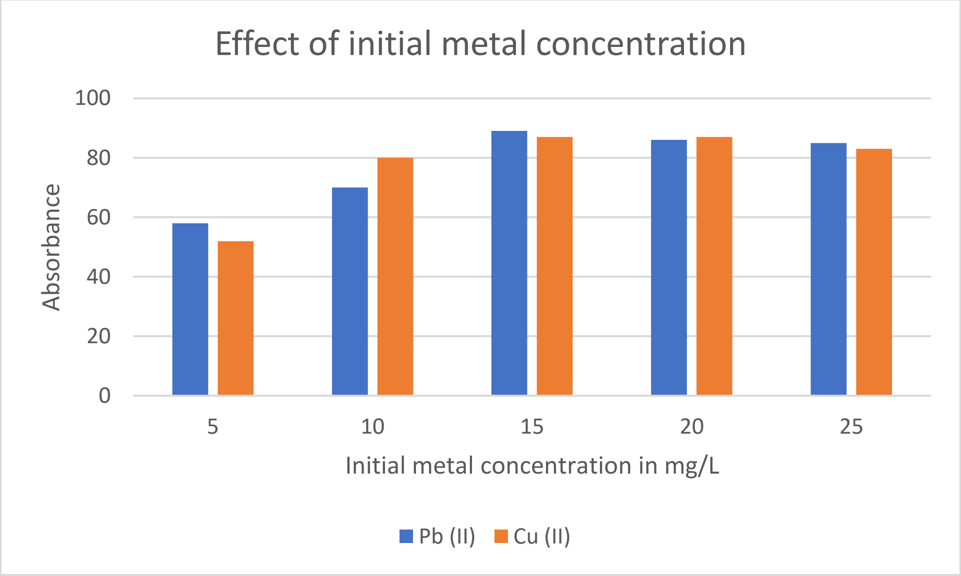


Figure 10: Effect of initial metal concentration.

4.3.4. Effect of adsorbent dose

Adsorbent dose is a mainly important parameter in adsorption which determines the amount of removal as well as the economics of process. To examine the effect of adsorbent dosage on Lead and Copper adsorption, different amounts of CSH from 2-12g/L have been used. Other parameters like initial metal concentration: 15mg/L, Time: 120minutes; Temperature:25°C; the agitation rate:200rpm and pH (5.5) were also used including the optimized ones.

Table 5: Effect of adsorbent dose variation

Metal	Adsorbent dose(g/L)	Removal efficiency by adsorbent dose			
		Co(mg/l)	Ce(mg/l)	Co-Co(mg/l)	%Removal
Pb (II)	2	15	12.6	2.4	16
	4	15	1.95	13.05	87
	6	15	2.1	12.9	86
	8	15	2.4	12.6	84
	10	15	2.85	12.15	81
	12	15	2.55	12.45	83
Cu (II)	2	15	12.75	2.25	15
	4	15	6.15	8.85	59
	6	15	3	12	80
	8	15	1.8	13.2	88
	10	15	2.1	12.9	86
	12	15	2.25	12.75	85

Dose of adsorbent also is one of the main points to determine the capacity uptake of heavy metals by adsorbents. Usually, increase in the dose of adsorbents will increase in the adsorbed capacity until it reaches a limit. If further increases the dose, the adsorption capacity will be constant [103]. In this study, 2-12g/L of adsorbent have been used in the experiment. From Figure 11, it can be seen that there is a rapid increase of removal percentage of 15-90% in the range of 2-6g/L of adsorbent [105]. When the concentration of adsorbent goes above 6g/L, there is a slow increase in removal percentage slightly above 90%. The increase of sorbent dosage often induces particle aggregation and mixing difficulties, which can decrease effective surface area and active sites and slow down the mass transfer [101]. In this adsorption process experiment, the value of 6g/L of carbonized sunflower seeds husks (CSH) was considered as the optimum dose for Cu (II) and Pb (II) removal from aqueous solution.

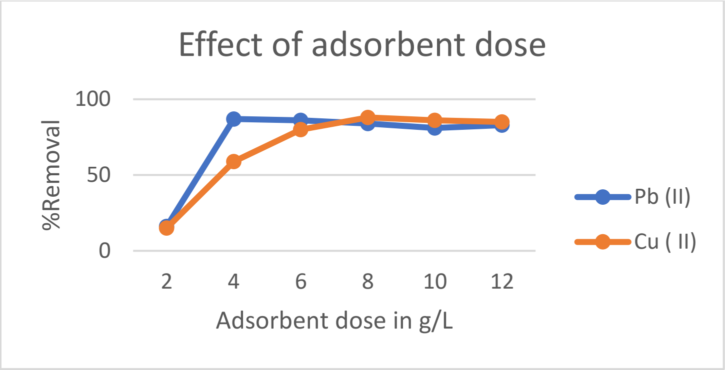


Figure 11: Effect of adsorbent dose.

4.3.5. Effect of contact time

The removal efficiency of Lead and Copper was investigated as a function of contact time while other parameters were kept constants including the optimized one. Adsorbent dose: 6g/L; Initial metal concentration: 15mg/L; Time:120mn; Temperature:25°C; Agitation rate:200rpm; pH (5.5). Table 6 and Figure 12 highlight the effect of contact time on adsorption process.

Table 6: Effect of contact time on adsorption process

		Removal efficiency by time variation			
Metal	Time variation	Co(mg/l)	Ce(mg/l)	Co-Ce(mg/l)	%Removal
Pb (II)	5	15	1.5	13.5	90
	20	15	0.75	14.25	95
	40	15	0.3	14.7	98
	60	15	0.45	14.55	97
	90	15	0.15	14.85	99
Cu (II)	5	15	6	9	60
	20	15	2.55	12.45	83
	40	15	0.6	14.4	96
	60	15	0.45	14.55	97
	90	15	0.45	14.55	97

The effect of contact time between Carbonized sunflower seeds husks (CSH) and metal solution is presented in this report. In this experiment, the time interval from 5-90mn was considered. As it can be seen from the (Figure 12), two phases have been observed: first very rapid phase (up to 10 minutes), followed by the second phase (10-20mn) where equilibrium has been reached [25],[103]). The first phase of the process of Cu and Pb adsorption onto CSH is very intensive due to the large concentration gradient and due to the large numbers of available active sites on surface. After that phase, very small changes in the percentage removal are observed due to saturation of surface sites, and very slow diffusion of solution into the interior of CSH [101]. From this experiment, the optimal time to reach equilibrium of the adsorption process was considered as 60minutes.

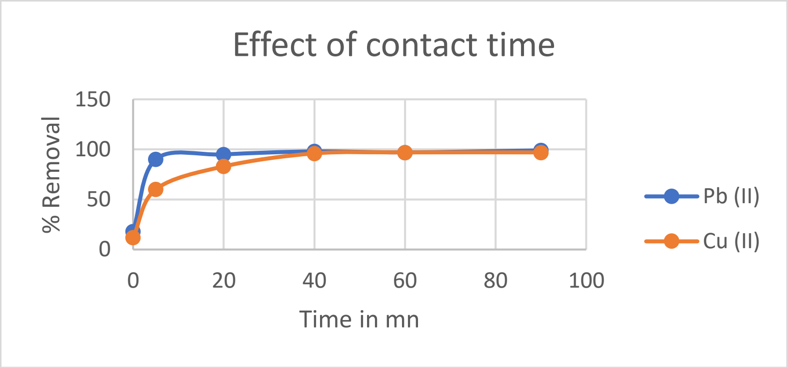


Figure 12: Effect of contact time.

Briefly, the obtained optimum values are: pH value (5.5), 15mg/L of initial metal concentration, 6g/L of CSH and 1hour contact time. After optimization, experiments on synthetic and real wastewater were made.

4.4. Heavy metal adsorption from aqueous solutions

Adsorption process though batch tests have been conducted to evaluate the adsorption potential of prepared and synthetized adsorbents (carbonized sunflower seeds husks and imine ligands).

4.4.1. Metal removal efficiency from synthetic wastewater

This experiment was done in 3 replicates and the reactor contents were separately filtered into plastic bottle using filter paper. AAS was used to determine Pb ad Cu concentration in the filtrate. Triplicate AAS values were averaged and the amount of Pb and Cu removed, was calculated from the difference between the initial concentration and the equilibrium concentration of the ions (Table 7). The Figure13 below is the chart for the removal performance of metal from synthetic wastewater.

Table 7: Metal performance removal from synthetic wastewater

Test type	Metals		Efficiency removal from synthetic wastewater by different adsorbents				
			Blank	CSH	L1	L2	L5
Test1	Cu (II)	Co(mg/l)	15	15	15	15	15
		Ce(mg/l)	14.55	2.25	6	2.4	1.8
		Co-Ce(mg/l)	0.45	12.75	9	12.6	13.2
		% Removal	3	85	60	84	88
	Pb (II)	Co(mg/l)	15	15	15	15	15
		Ce(mg/l)	13.95	4.5	4.95	3.6	3
		Co-Ce(mg/l)	1.05	10.5	10.05	11.4	12
		% Removal	7	70	67	76	80
Test2	Cu (II)	Co(mg/l)	15	15	15	15	15
		Ce(mg/l)	14.4	5.1	6.6	4.65	5.85
		Co-Ce(mg/l)	0.6	9.9	8.4	10.35	9.15
		% Removal	4	66	56	69	61
	Pb (II)	Co(mg/l)	15	15	15	15	15
		Ce(mg/l)	13.8	3	5.55	3.9	3.6
		Co-Ce	1.2	12	9.45	11.1	11.4
		% Removal	8	80	63	74	76
Test3	Cu (II)	Co	15	15	15	15	15
		Ce	14.7	6.15	7.8	3	2.85
		Co-Ce	0.3	8.85	7.2	12	12.15
		% Removal	2	59	48	80	81
	Pb (II)	Co(mg/l)	15	15	15	15	15
		Ce(mg/l)	14.55	1.65	3.45	4.2	3.6
		Co-Ce(mg/l)	0.45	13.35	11.55	10.8	11.4
		% Removal	3	89	77	72	76

From the Figure 13, it can be seen that either carbonized sunflower seeds husks or synthetized imine ligands can remove efficiently both Cu or Pb from aqueous solutions. CSH itself has got the efficiency removal of [80% (Pb), 70% (Cu)], [54% (Cu), 69% (Pb)] by L1, [77.7% (Cu), 74% (Pb)] by L2, and [77.6% (Cu) ,77.3% (Pb)] by L5. L1 is weakly removing heavy metals because of shielding from its chemical structure. The difference observed between Copper and Lead might be caused by the affinity of the metal vis-a-vis the adsorbent whereas CSH generally behaves in the same way like most of the ligands used together. As it can be seen form Figure 13, there are also removal percentage variations between tests which can be due to analytical errors.

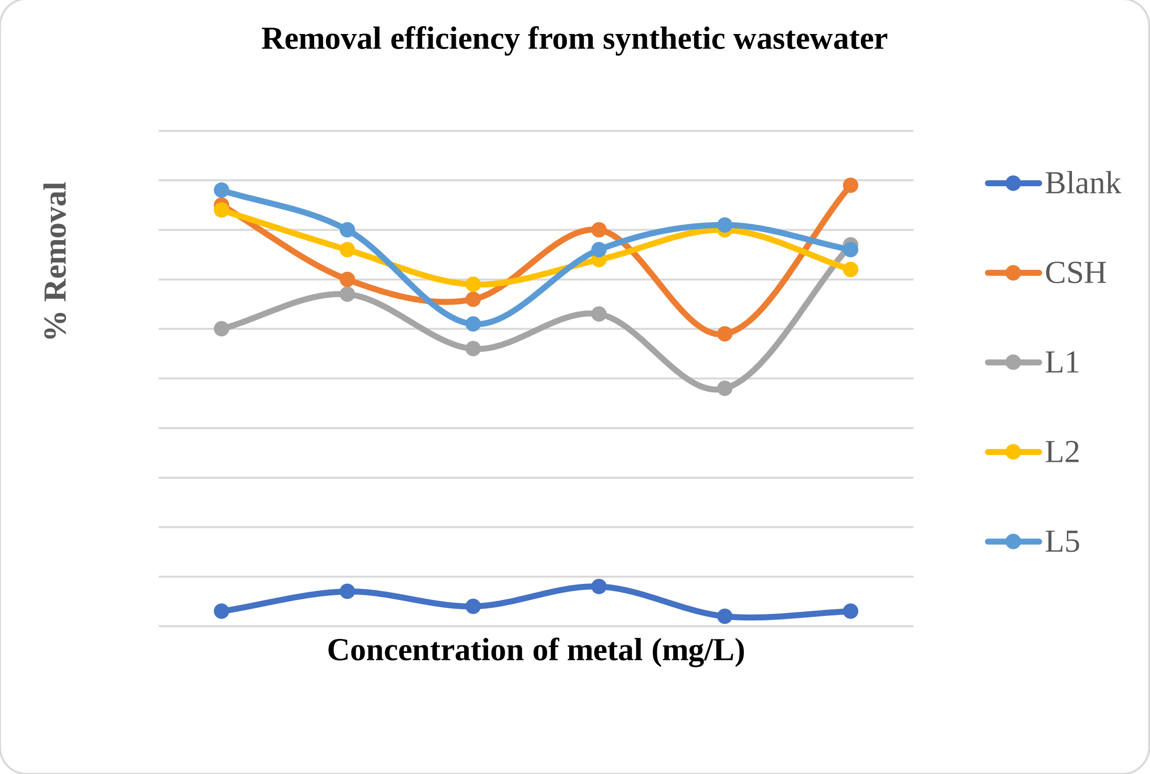


Figure 13: Removal efficiency of toxic metal from synthetic wastewater.

4.4.2. Efficiency metal removal from real wastewater

To test the real wastewaters, grab samples from Nyabugogo river tributaries, such as Kibumba river, Gatsata garages effluent, and Rwanzekuma river sites have been sampled and composite sample was made. From sample analysis, Cu(0.18mg/L) and Pb(0.31mg/L) were found. The same optimum conditions obtained by using CSH were also applied in adsorption process by using synthetized SCHIFF bases. The Figure 14 below is the chart for heavy metal removal from real wastewater.

Table 8: Heavy metal removal from real wastewater.

			Efficiency removal by Different adsorbents				
Sample type	Metals		Blank	CSH	L1	L2	L5
Sample1	Cu (II)	Co(mg/l)	0.15	0.15	0.15	0.15	0.15
		Ce(mg/l)	0.1275	0.045	0.078	0.0525	0.0495
		Co-Ce(mg/l)	0.0225	0.105	0.072	0.0975	0.1005
		% Removal	15	70	48	65	67
	Pb (II)	Co(mg/l)	0.37	0.37	0.37	0.37	0.37
		Ce(mg/l)	0.296	0.148	0.185	0.1184	0.1369
		Co-Ce(mg/l)	0.074	0.222	0.185	0.2516	0.2331
		% Removal	20	60	50	68	63
Sample2	Cu (II)	Co(mg/l)	0.21	0.21	0.21	0.21	0.21
		Ce(mg/l)	0.1743	0.0945	0.126	0.0861	0.0861
		Co-Ce(mg/l)	0.0357	0.1155	0.084	0.1239	0.1239
		% Removal	17	55	40	59	59
	Pb (II)	Co(mg/l)	0.3	0.3	0.3	0.3	0.3
		Ce(mg/l)	0.255	0.09	0.165	0.075	0.084
		Co-Ce(mg/l)	0.045	0.21	0.135	0.225	0.216
		% Removal	15	70	45	75	72
Sample3	Cu (II)	Co(mg/l)	0.18	0.18	0.18	0.18	0.18
		Ce(mg/l)	0.1476	0.09	0.126	0.0522	0.0234
		Co-Ce(mg/l)	0.0324	0.09	0.054	0.1278	0.1566
		% Removal	18	50	30	71	87
	Pb (II)	Co(mg/l)	0.26	0.26	0.26	0.26	0.26
		Ce(mg/l)	0.208	0.065	0.169	0.104	0.104
		Co-Ce(mg/l)	0.052	0.195	0.091	0.156	0.156
		% Removal	20	75	35	60	60

Figure 14 showed that carbonized sunflower seeds were removing Cu and Pb at 58% and 68% respectively from wastewater. Different synthetized Imine ligands have got the following removal efficiencies: [39% (Cu),43% (Pb)] by L1, [62% (Cu), 67.6% (Pb)] by L2, [71% (Cu), 65% (Pb)] by L5. Ligand L1 shows the lowest removal potential compared to other adsorbents or ligands, this can be attributed to the shielding caused by its chemical structure. But it is also seen that there is a decrease in overall removal percentage compared to synthetic wastewater. This might be due to other contaminants that may compete with metal ions and analytical errors.

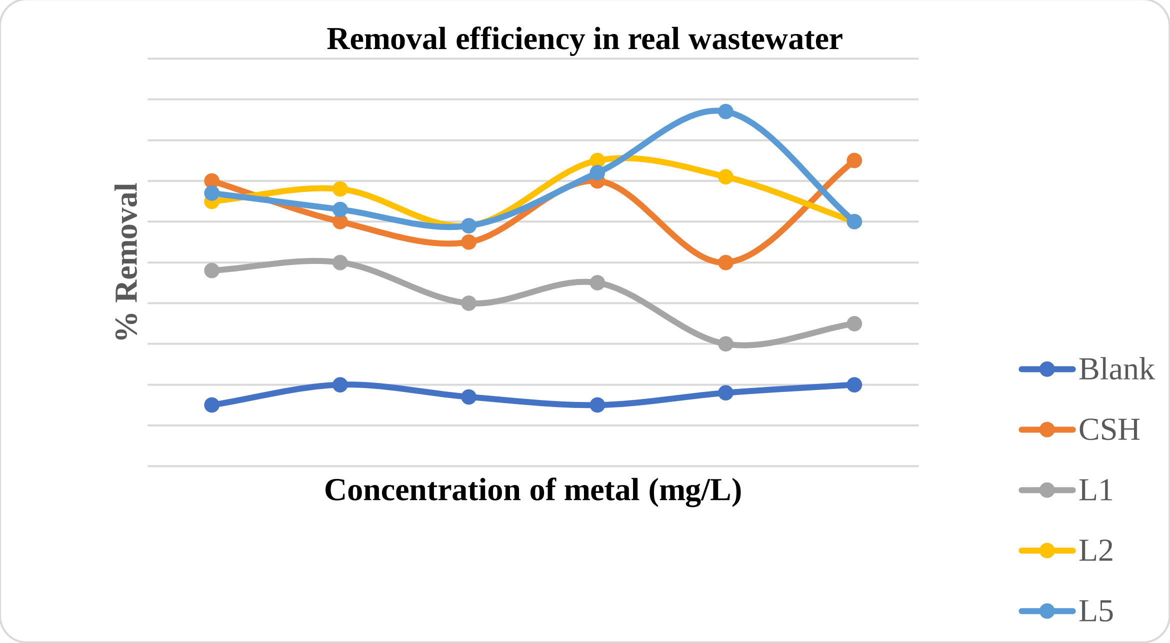


Figure 14: Toxic metal removal from real wastewater.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

Heavy metal contamination is one of the most serious environmental problems today. The treatment of heavy metals is difficult due to their recalcitrance and persistence in the environment. Among all the classic and current developed techniques for removing heavy metals from aqueous solutions, adsorption is a very good answer. In order to remove Lead and Copper from wastewater, a variety of natural and artificial adsorbents were used. Carbonized Sunflower seeds husks were used as a natural adsorbent, whereas synthetized imine ligands were considered as artificial ones. In this study, carbonized sunflower seeds husks were prepared and different imine ligands synthetized [Tris(((di(pyridin-2-yl) methylene) amino) methyl) amine(L1),1,1-di(pyridin-2-yl)-N-(pyridin-2-ylmethyl) methanimine (L2) and the product between Trisaminoethylamine and salicylaldehyde(L5)] and compared between themselves for their performance in removing toxic metal from wastewater. During the study, the effect of contact time, initial concentration of metal ion and loading weight of adsorbent, pH on the percentage of heavy metal removal were assessed and optimized. The obtained optimal conditions for batch adsorption method were pH (5.5), 15mg/l of initial metal concentration, 6g/L of adsorbent dose, and 1hour contact time by using carbonized sunflower husks as adsorbent. FTIR analysis revealed the presence of specific functional groups such as amine and imine on both CSH and synthetized imine ligands that are responsible for sequestrating Cu and Pb ions from aqueous solutions. The removal percentage observed was 68% by CSH, 43% by L_1, 67% by L_2,65% by L_5 for Pb (II) ions, and 58% by CSH, 39% by L_1, 65% by L_2, 71% for Cu (II) ions in real wastewater. From the results, it was found that Carbonized sunflower seeds husks successfully removed the heavy metals almost at the same level with imine ligands. Therefore, as a natural adsorbent, CSH can more preferably be used in wastewater treatment because they are low cost materials compared to synthetized imine ligands.

Recommendations

- Modification of sunflower seeds husks can further be explored for enhanced stability and effectiveness in all wastewater types.
- Recovery and reuse of sunflower seeds husks have to be developed to ensure environmental sustainability.
- Assess whether the combination of modified sunflower seeds and imine ligands can enhance wastewater treatment performance.

- Finally, applying sunflower seeds husks as natural adsorbent on the industrial scale requires further investigation as a strategy that will fulfill the goals of the circular economy.

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Appendixes

			Removal efficiency by pH variation(trial1)			
Metal	Adsorbent dose(g/L)	pH variation	Co(mg/l)	Ce(mg/l)	Co-Ce(mg/l)	% Removal
Pb (II)	10	2	10	1.8	8.2	82
	10	3	10	1.7	8.3	83
	10	4	10	1.3	8.7	87
	10	5	10	1.3	8.7	87
	10	6	10	0.9	9.1	91
	10	7	10	2	8	80
Cu (II)	10	2	10	2.5	7.5	75
	10	3	10	4.1	5.9	59
	10	4	10	1.9	8.1	81
	10	5	10	1	9	90
	10	6	10	1.2	8.8	88
	10	7	10	3.2	6.8	68

			Removal efficiency by pH variation(trial2)			
Metal	Adsorbent dose(g/L)	pH variation	Co(mg/l)	Ce(mg/l)	Co-Ce(mg/l)	% Removal
Pb (II)	10	2	10	3.4	6.6	66
	10	3	10	2.6	7.4	74
	10	4	10	2.4	7.6	76
	10	5	10	1.4	8.6	86
	10	6	10	2	8	80
	10	7	10	2.3	7.7	77
Cu (II)	10	2	10	2.1	7.9	79
	10	3	10	2.7	7.3	73
	10	4	10	1	9	90
	10	5	10	1.8	8.2	82
	10	6	10	0.7	9.3	93
	10	7	10	2	8	80

			Removal efficiency by pH variation(trial3)			
Metal	Adsorbent dose(g/L)	PH variation	Co(mg/l)	Ce(mg/l)	Co-Ce(mg/l)	% Removal
	10	2	10	4.6	5.4	54
	10	3	10	3.7	6.3	63
	10	4	10	1.1	8.9	89
	10	5	10	0.3	9.7	97
	10	6	10	1	9	90
Pb (II)	10	7	10	2.7	7.3	73
	10	2	10	7.4	2.6	26
	10	3	10	4	6	60
	10	4	10	2.8	7.2	72
	10	5	10	1.1	8.9	89
	10	6	10	0.5	9.5	95
Cu (II)	10	7	10	1.4	8.6	86

		Removal efficiency of initial metal concentration(trial1)			
Metals	Adsorbent dose(g/L)	Co(mg/l)	Ce(mg/l)	Co-Ce(mg/l)	% Removal
	10	5	2.6	2.4	48
	10	10	4	6	60
	10	15	2.1	12.9	86
	10	25	5.75	19.25	77
Pb	10	25	5.25	19.75	79
	10	5	2.2	2.8	56
	10	10	1.3	8.7	87
	10	15	1.95	13.05	87
	10	25	1.375	23.625	94.5
Cu	10	25	6.5	18.5	74

		Removal efficiency of initial metal concentration(trial2)			
Metals	Adsorbent dose(g/L)	Co(mg/l)	Ce(mg/l)	Co-Ce(mg/l)	% Removal
Pb (II)	10	5	2	3	60
	10	10	2.8	7.2	72
	10	15	1.5	13.5	90
	10	25	3.25	21.75	87
	10	25	3.75	21.25	85
Cu (II)	10	5	2.4	2.6	52
	10	10	2.5	7.5	75
	10	15	3.75	11.25	75
	10	25	1.25	23.75	95
	10	25	3	22	88

		Removal efficiency of initial metal concentration(trial3)			
Metals	Adsorbent dose(g/L)	Co(mg/l)	Ce(mg/l)	Co-Ce(mg/l)	% Removal
Pb (II)	10	5	1.7	3.3	66
	10	10	2.2	7.8	78
	10	15	1.35	13.65	91
	10	25	1.5	23.5	94
	10	25	2.25	22.75	91
Cu (II)	10	5	2.6	2.4	48
	10	10	2.7	7.3	73
	10	15	1.95	13.05	87
	10	25	7.5	17.5	70
	10	25	3.375	21.625	86.5

		Removal efficiency by adsorbent dose(trial1)			
Metal	Adsorbent dose(g/L)	Co(mg/l)	Ce(mg/l)	Co-Co(mg/l)	%Removal
Pb (II)	2	15	11.25	3.75	25
	4	15	0.75	14.25	95
	6	15	4.05	10.95	73
	8	15	3.9	11.1	74
	10	15	3.15	11.85	79
	12	15	0.45	14.55	97
Cu (II)	2	15	11.85	3.15	21
	4	15	1.35	13.65	91
	6	15	2.1	12.9	86
	8	15	2.1	12.9	86
	10	15	2.55	12.45	83
	12	15	2.25	12.75	85

		Removal efficiency by adsorbent dose(trial2)			
Metal	Adsorbent dose(g/L)	Co(mg/l)	Ce(mg/l)	Co-Co(mg/l)	%Removal
Pb (II)	2	15	12.3	2.7	18
	4	15	1.5	13.5	90
	6	15	1.2	13.8	92
	8	15	1.95	13.05	87
	10	15	4.5	10.5	70
	12	15	2.4	12.6	84
Cu (II)	2	15	9	6	40
	4	15	2.7	12.3	82
	6	15	1.8	13.2	88
	8	15	1.5	13.5	90
	10	15	2.85	12.15	81
	12	15	3	12	80

		Removal efficiency by adsorbent dose(trial3)			
Metal	Adsorbent dose(g/L)	Co(mg/l)	Ce(mg/l)	Co-Co(mg/l)	%Removal
	2	15	6.15	8.85	59
	4	15	2.25	12.75	85
	6	15	1.05	13.95	93
	8	15	3.15	11.85	79
	10	15	5.85	9.15	61
Pb(II)	12	15	4.35	10.65	71
	2	15	12.6	2.4	16
	4	15	0.9	14.1	94
	6	15	0.6	14.4	96
	8	15	0.45	14.55	97
	10	15	0.9	14.1	94
Cu (II)	12	15	3	12	80

		Removal efficiency by time variation(trial1)			
Metal	Time variation	Co(mg/l)	Ce(mg/l)	Co-Ce(mg/l)	%Removal
	5	15	2.1	12.9	86
	20	15	1.5	13.5	90
	40	15	0.9	14.1	94
	60	15	1.2	13.8	92
Pb (II)	90	15	1.05	13.95	93
	5	15	3	12	80
	20	15	1.65	13.35	89
	40	15	1.05	13.95	93
	60	15	1.5	13.5	90
Cu (II)	90	15	1.2	13.8	92

		Removal efficiency by time variation(trial2)

Metal	Time variation	Co(mg/l)	Ce(mg/l)	Co-Ce(mg/l)	%Removal
Pb (II)	5	15	0.75	14.25	95
	20	15	0.75	14.25	95
	40	15	0.45	14.55	97
	60	15	0.15	14.85	99
	90	15	0.3	14.7	98
Cu (II)	5	15	10.2	4.8	32
	20	15	13.05	1.95	13
	40	15	12.75	2.25	15
	60	15	15	0	0
	90	15	14.85	0.15	1

		Removal efficiency by time variation(trial3)			
Metal	Time variation	Co(mg/l)	Ce(mg/l)	Co-Ce(mg/l)	%Removal
Pb (II)	5	15	1.8	13.2	88
	20	15	1.05	13.95	93
	40	15	0.9	14.1	94
	60	15	1.2	13.8	92
	90	15	0.9	14.1	94
Cu (II)	5	15	5.85	9.15	61
	20	15	3.15	11.85	79
	40	15	0.9	14.1	94
	60	15	1.05	13.95	93
	90	15	1.05	13.95	93