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SCHOOL OF SCIENCE

REMOVAL OF SELECTED TOXIC METAL SPECIES FROM POLLUTED WATER USING CELLULOSE EXTRACTED FROM SAWDUSTS

A dissertation submitted in partial fulfillment of the requirements for the Degree of Master of Science (MSc) in Environmental Chemistry

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Nyarugenge, January 2022

DECLARATION

Student:

I, Vedaste Nyandwi, declare that this dissertation titled “Removal of selected toxic metal species from polluted water using cellulose extracted from sawdust” is the result of my own work and has not been submitted for any other degree at the University of Rwanda or any other institution

Signature:

Main supervisor:

I, Prof. Theoneste Muhizi, the main supervisor of this dissertation titled “Removal of selected toxic metal species from polluted water using cellulose extracted from sawdust” declare the approval submission of the dissertation for examination.

Signature:

DEDICATION

To my mother who died early without seeing this great achievement,
To my spouse Claudine Nyirabahire,
To my daughter Sandra Leila Byosekumana,
To my son Mike Owen Mugisha Rugwiro, and
To the Almighty God

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ABSTRACT

This study aimed at investigating the efficiency of raw sawdust from *Eucalyptus saligna*, *Cupressus lusitanica*, and *Grevillea robusta* species and their extracted cellulose compounds for the removal of lead and cadmium from polluted water. Cellulose compounds were extracted using *n*-hexane and ethanol as solvents, and chemically characterized by Fourier Transform Infra-Red (FTIR) spectroscopy technique. Both sawdust and extracted cellulosic compounds were assessed for their capability to remove lead and cadmium from polluted water by using batch and column flow methods. The analysis of the extracted cellulosic compounds by FTIR confirmed their nature with the presence of the absorption bands at 3450-3300 cm^{-1} characterizing alcoholic functions O-H stretching, 2910 cm^{-1} indicating C-H bond stretching for non-aromatic compounds, and this was completed by the appearance of absorption bands between 1450-1300 cm^{-1} for C-H scissing. Sharp band at 1100-1250 cm^{-1} indicating C-O stretch was also detected in the isolated cellulosic compounds. Raw sawdust of *Eucalyptus saligna* showed high adsorption removal (43.50% for lead and 33.40% for cadmium) compared to *Cupressus lusitanica* and *Grevillea robusta* sawdust while cellulose-based compound from *Eucalyptus saligna* also showed high adsorption removal (83.00% for lead and 72.30% for cadmium). In this study, adsorption parameters that include adsorbents dosage, contact time, pH, temperature and initial concentration of toxic metal were optimized and were found to be 1.75 g, 2 hours, pH 6, 25 °C and 10.0 mg/L, respectively. Batch and column flow adsorption experiments were used and the results showed that column flow mode highest efficiency removal for lead (94.00%) was achieved by using cellulose-based compounds from *Eucalyptus saligna* species (compared to that of 83.00%) for batch experiment mode at the same adsorbent. On the other hand, the highest efficiency cadmium removal was found to be 82.00% and 72.30% for column and batch experiment mode, respectively. The optimum parameters found were also applied to real sample collected from car garages and car washes at Gatsata, Kigali city, and the results showed a high removal efficiency for cellulose-based compounds extracted from *Eucalyptus saligna* species (94.00% for lead and 81.90% for cadmium) in column flow mode while it was 83.60% for lead and 72.41% for cadmium in batch experiment mode

Key words: *Sawdust, cellulose-based compounds, cadmium and lead toxic metals, polluted water, batch and column flow experiment modes*

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LIST OF ABBREVIATIONS

AAS: Atomic Absorption Spectrophotometer

Ce: Equilibrium concentration

Cell-CM: Cellulose extracted from pineapple leaf modified with carboxymethly

Cell-EDTA: Cellulose extracted from pineapple leaf modified with Ethylenediamine tetra acetic acid

CH: Cellulose-based compounds extracted from *Cupressus lusitanica* sawdust

Co: initial concentration

CS: *Cupressus lusitanica* sawdust

EC: Electrical Conductivity

EDTA: Ethylene Diamine Tetraacetic Acid

EH: Cellulose-based compounds extracted from *Eucalyptus saligna* sawdust

ES: *Eucalyptus saligna* sawdust

FTIR: Fourier Transform Infrared spectrophotometer

GH: Cellulose-based compounds extracted from *Grevillea robusta* sawdust

GS: *Grevillea robusta* sawdust

pH: Hydrogen Potential

ppm: parts per million

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CHAPTER 1: GENERAL INTRODUCTION

1.1 Background

The discharge of untreated wastewater effluent in aquatic environment is a worldwide concern as it affects human health and the environment in general [1,2]. The removal of pollutants present in wastewater is recommended by local and international regulating agents to meet the required standards [3,4]. Toxic metals species such as arsenic (As), chromium (Cr), copper (Cu), zinc (Zn), cadmium (Cd), lead (Pb), nickel (Ni), and silver (Ag) are enormously present in wastewater discharged from chemical industries such as tannery, textile, cement, metallurgy, photographic material and corrosive paints [5–7].

In addition, toxic metal species may come from anthropogenic or economical activities including car garages, application of fertilizers in agriculture and use of refined petroleum products [1,8]. Because of their ability to bio-magnify and bio-concentrate in tissues, these chemicals are affecting human health, aquatic animals and plants even at lower concentrations [8–10]. Cadmium and lead are carcinogen and teratogen to human and well reported for impacting the lungs, kidney, liver, and reproductive systems [2,5,8]. The Rwanda Standard Board has imposed strict regulations on the maximum permissible concentration for cadmium and lead in discharged industrial wastewater as 0.1 mg/L for both toxic metals [3].

Nowadays, several methods of wastewater treatments for removing toxic metal species from contaminated water are known. These include electrochemical treatments, coagulation or flocculation, adsorption, ion exchange processes, reverse osmosis, bioremediation, solvent extraction, chemical precipitation and membrane process [9,11–13]. The adsorption process possesses many advantages over other technologies due to the easy availability and low cost of both the adsorbents used and operational procedures, its capability to regenerate adsorbents after use, its easiest application in industries, its high efficiency in removing toxic metal species in both ions and complexes forms, even at wide pH range and its, environmentally friendly characters through the use of these biomaterials which are considered as useless materials [7,14].

The adsorption of different toxic metal species has been studied including Cd (II), Co (II), Cu (II), Fe (II), La (II) and Pb (II), using either grape stems, potato peels or pineapple leaves biomass and found that they are versatile adsorbents with high adsorption removal efficiency [6,15,16]. Furthermore, many hydroxylated natural compounds including celluloses, lignin, chitosan, starch, phenolic compounds, lipids, proteins, simple sugars have showed a high potential bio-sorption capacity due to the chemical functional groups they contain [4–6,10].

For this purpose, this study aimed at investigating the removal capacity of cellulose-based compounds extracted from sawdust of *Eucalyptus saligna, Cupressus lusitanica,* and *Grevillea robusta* for cadmium and lead toxic metals from polluted water and wastewater collected from Gatsata car garages and car washes.

1.2 Problem statement

In Rwanda, most of the wastewater from industries, hotels, car garages and car washes is released into the environment without being treated [5,16,17]. According to Sekomo *et al*. (2018), a research conducted on fate transport of heavy metal species in the Nyabugogo swamp pointed out that both cadmium and lead were found in higher concentrations in water phase, sediments and fishes due to car garages activities that released contaminated wastewater by metals from car paints and oil [1]. This would result in contamination of surface and ground water used in different household activities such as cooking, drinking, swimming, fishing and irrigation [16].

Toxic metal ions were found to bio-accumulate in tissues of fishes and plants, and then can be transferred to human and animals during ingestion [12]. Some of these toxic metals such as cadmium, and lead, are carcinogens and teratogens to human, with negative effects on lungs, kidney, liver, and reproductive organs [2,5,8]. Depending to the dose and time of exposure, lead and cadmium may cause renal failure and even the death [4,18]. Sawdust from *Eucalyptus saligna*, *Cupressus lusitanica*, and *Grevillea robusta* are considered as solid wastes which are left in the environment where trees are sawed off [10,11,16].

The mismanagement and poor disposal of sawdust as solid wastes contribute to environmental pollution when they are taken in water bodies by rain runoff, where they are biodegraded, accumulated, and hence contribute to the increase of nutrients in water resulting to eutrophication phenomena [7]. However, sawdust contains cellulose-based compounds that can be used to remove these toxic metals in polluted water [11].Therefore the use of these solid wastes and their extracted cellullose-based compounds in water treatment may be benefic to both environment protection and quality of water [6,16,19].

1.3 Objective of the study

1.3.1 General Objective

The general objective of this research is to investigate the capability of compounds contained in sawdust to adsorb and remove some toxic metal species from contaminated water.

1.3.2 Specific objectives

The specific objectives of this study are:

1. To extract and characterize cellulosic compounds from sawdust of *Eucalyptus saligna, Cupressus lusitanica* and *Grevillea robusta*.
2. To investigate the adsorption removal capacity for cadmium and lead ions from wastewater by using raw sawdust and cellulosic compounds extracted from sawdust of *Eucalyptus saligna, Cupressus lusitanica* and *Grevillea robusta* trees.
3. To compare the adsorption efficiency of both batch and column flow systems for cadmium and lead ions.

1.4 Research questions

The research questions of this study are:

1. Can sawdust which are usually considered as useless be used as adsorbent for toxic metals from environment samples?
2. Can cellulosic compounds contained in sawdust contribute to adsorption capability of this waste?
3. What useful method can be used to maximize the adsorption capability of cellulosic compounds?

1.5 Significance of the study

Water is essential to sustain life. Improving access to safe drinking-water result in tangible benefits to health, hence effort should be made to avail safe drinking-water [4]. However, studies have indicated that in most of cases water, especially in urban areas, is contaminated mainly through effluent of polluted water from household, car garages, car washes, industries, hotels and restaurants, hospitals, and dumping sites [5,6]. In this regard, contaminants such as toxic metals, organic matter, inorganic nutrients, and microorganisms are frequent water pollutant.

Therefore, the removal of toxic metals in polluted water is recommended by different regulating agencies such as World Health Organization (WHO), United States of America Environmental Protection Agency (USA EPA), Rwanda Environment and management Authority (REMA) and Rwanda Standard Board (RSB) [3,4].

This research would contribute to the management of both solid and liquid wastes and to the valorization of solid waste by using cellulosic compounds extracted from sawdust to remove toxic metals from polluted water [10].

The methodology is appreciated to be less energy consuming, inexpensive, environmental-friendly and it will be beneficial to the surrounding population of the study area as it contributes to the environmental remediation by removing cadmium and lead ions from car garages and car washes effluent, then the risk of diseases attack from contamination with toxic metals is reduced. Also this methodology is beneficial to the government by reducing the cost which is paid for environmental monitoring and remediation. It will be conducted at Kigali City where effluents from car garages and car washes will be treated. Findings shall be used as reference for effective wastewater treatment in urban areas [20,21].

1.6 Scope of the study

This study was done in order to evaluate the adsorption capability of cellulose extracted from sawdusts to remove selected toxic metal species from polluted water and car garages and carwashes wastewater collected from Gatsata, Kigali City. This dissertation is presented in four chapters where, Chapter 1 presented a general introduction with background, problem statement, objectives, research questions, significance and scope of the study. Chapter 2 described the literature review on characteristics of toxic metals and their environmental impacts, toxic metals occurrence, toxicity of toxic metals, and toxic metals removal technologies. Chapter 3 presented the materials and methods of the study that involves the extraction of cellulose, chemical characterization of the adsorbent and the determination of adsorption efficiency of both sawdust and extracted cellulose. Chapter 4 showed the results and their discussions about the removal efficiency of the sawdust and cellulose extracted from sawdust to remove lead and cadmium toxic metals from synthetic wastewater and car garages and car washes wastewater. Chapter 5 showed conclusion and some recommendations for better management of both solid and liquid wastes.

CHAPTER 2: LITERATURE REVIEW

2.1 Characteristics of toxic metals and environmental impacts

Toxic metals are non-biodegradable [22] and have a carcinogenic and teratogenic effect at any concentration [2,5,8]. Some of the toxic metals such as lead and cadmium are commonly present in the effluents of mining, batteries manufacturing factories, car garages, car washes and paint industries [1,8,22]. They have been given an extraordinary concern as they are toxic pollutants and thus, a treatment is required before wastewater is being discharged into the environment [23]. Furthermore, cadmium and lead are harmful toxicants since many of their uses tend to propagate them widely in the environment and thereby making recycling and recovery very difficult [24].

2.2 Toxic metals occurrence

Toxic metals are natural constituents of every compartment of the environment. They take part in bio-geochemical reactions and can be transported between environmental compartments by natural processes, mainly by anthropogenic activities while others are introduced to natural waters by domestic and industrial waste streams and by agricultural runoff, particularly in areas where phosphate fertilizer has been applied [21,23]. Cadmium, copper, lead and zinc are all chalcophilic elements and are in close association in sulphidic ore deposits [23]. Further, toxic metals can be transported by natural weathering processes such as erosion or dissolution, or as a direct result or side effect of human activities [6,25]. For example, acid mine drainage takes away metals from rocks and soils. Furthermore, oxides of cadmium and zinc are vaporized and released to the air during smelting, while lead is emitted from automobile exhaust pipes. Toxic metals get into water systems by atmospheric washing [13]. Once the toxic metals reach natural aquatic system, they can undergo a variety of transformations which results in dissolved metals speciation such as precipitation and oxidation/ reduction that can drastically alter the mobility of the toxic metals [23,24].

2.3 Toxicity of toxic metals

Toxic metals are toxic to every trophic level from microbial population to the human being mainly through the food web [4,16]. Among the toxic metals, cadmium deserves attention because of its high toxicity and deleterious effects on humans and the environment, even at low concentrations [23,26]. One of the main problems associated with cadmium is its final destination in the food chain, as it can reach the soil or the air, by the burn of municipal waste or fossil fuels, thus polluting the environment and causing damage to the ecosystem [16].

In humans, the inhalation of this toxic metal may cause problems in respiratory tract and kidneys, in the case of oral intoxication. When a significant amount of cadmium is ingested, it may generate an immediate poisoning and damage to the liver and kidneys and may affect genes. Besides cadmium, an increased level of lead ions in the blood leads to an increase in blood pressure, fertility problems, nerve disorders, muscles and joints pain, irritability and memory loss [11,18,26]. Their toxicity is due to their ability to coordinately bond to the proteins through the carboxylic acid (–COOH), amine (–NH_2), and thiol (–SH) groups leading to the formation of complexes which affect their structures and other important enzymes [27].

2.4 Toxic metals removal technologies

Different physical and chemical processes used to remove toxic metal ions from contaminated environments include solvent extraction, chemical precipitation, ion exchange, chelation, reverse osmosis, coagulation–precipitation, electrochemical operation and filtration [11,12]. Each of the mentioned methods have advantages and drawbacks [27,28]. Some of the treatment methods with their respective advantages and drawbacks are listed below:

2.4.1 Chemical precipitation

This occurs as chemical interaction between the metal ions and a precipitant agent such as lime and calcium carbonate. Precipitation by sulphide ions is effectively more used for toxic metals removal from industrial waste effluents [5,16]. However, chemical precipitation consumes a large amount of chemicals and produce a huge amount of sludge which pose an environmental problem while disposing them [27].

2.4.2 Ion exchange

The ion exchange method is specifically based on the capability to exchange cations between the materials and the wastewater. Different types of materials are used, some may be natural (alumina, carbon, silicates) while others are synthetic (zeolites and resins). Among them, zeolites are mostly used in the ion exchange process [9]. The ion exchange process takes place by both cations and anions exchange in aqueous medium by ion exchanger. This method presents the disadvantages of being highly sensitive to the pH of the solution, and the ion exchange is non-selective in operation. It has also difficulties to handle concentrated metal solution [27].

2.4.3 Chemical coagulation

Coagulation technique is mainly used to prepare colloids. Mostly used coagulants are aluminum, ferrous sulfate and ferric chloride that uptake impurities present in wastewater or water.

Ferric chloride solution and polyaluminium chloride (PAC) coagulants are used in toxic metal removal. This technology suffers drawback as it can’t remove toxic metals in concentrated metal solution [9,16,27].

2.4.4 Adsorption

Adsorption is a surface phenomenon that is characterized by the concentration of a chemical species (adsorbate) from its vapor phase or from a solution near the surfaces or pores of a solid (adsorbent). The surface excess occurs when the attractive energy of a substance with the solid surface (adhesive work) is greater than the cohesion energy of the substance itself. Adsorbate is the substance that concentrate at the surface while adsorbent is the material at whose surface the adsorption takes place [11]. Adsorption is an environmental friendly method as it uses different types of waste which may have adverse effect to the environment to solve another environmental issues [7].

2.4.4.1 Types of adsorption

We distinguish three types of adsorption, namely exchange adsorption or ion adsorption, physical adsorption and chemical adsorption [27,29]. Exchange adsorption is a process by which ions of one chemical substance concentrate at a surface due to electrostatic attraction to charged sites at the surface [27]. In the absence of other specific sorption effects, the charge of an ion, for two potential ionic adsorbates, is the governing factor for exchange adsorption (ion with a high valence is adsorbed faster) [27].

In case of ions with equal charge, the size of the molecule will determine which one is adsorbed first where the smaller one is easily coming closer to the adsorption site [7,10]. Physical adsorption is due to weak Van der Waals forces of attraction. The adsorbed material is not located at a fixed site but is free to move by translation movement. Physical adsorption takes place with the formation of multilayer of adsorbate on adsorbent. It has low enthalpy of adsorption *i.e.* takes place at low temperature below boiling point of adsorbate. It has a very low activation energy, hence it is a reversible and exothermic process [11,29]. Chemical adsorption or chemisorption happens because of a chemical bond being formed between the molecule of the adsorbate and adsorbent. Adsorbed molecules are located at specific sites and are not free to move on the surface [27]. Chemisorption takes place with the formation of unilayer of adsorbate on adsorbent. It has high enthalpy of adsorption and takes place at all temperature. It has high activation energy, hence it is practically irreversible and exothermic process [5,20].

2.4.4.2 Types and characteristics of adsorbents

Generally, adsorbents are classified into natural adsorbents, synthetic adsorbents, bioadsorbents [9,29]. Natural adsorbents refer to the types of adsorbents occur naturally such as zeolites, clay minerals, charcoal, red mud, sediment and soil, ore minerals, *etc* [30,31]. They are low cost in acquisition and abundant in supply. They can be easily modified and increase their adsorption capabilities [20,29]. Synthetic adsorbents are adsorbents that are prepared from raw materials such as household waste, industrial wastes, agricultural waste, sewage sludge and polymeric adsorbents, *etc*. They are expensive compared to natural adsorbents [12,29]. Bio-adsorbents are agricultural and plant wastes that are used for wastewater treatment [5,10,32]. They are classified as (i) non-living biomass like bark, lignin, shrimp, krill, squid, crab, shell, etc (ii) Algal biomass, (iii) microbial biomass such as algae, bacteria, fungi and yeast [20,33–35]. Agricultural waste are promising bio-adsorbents such as potato peels, sawdust, citrus peels, mango peels, corn cob, grape bagasse, orange waste, almond shell, tea waste, dried parthenium powder, sugar cane bagasse, peanut shell, sunflower stalk, banana peels, rice husk, maize cobbs, maize husks, black gram husk [5,10]. Bio-adsorbents are composed mainly of cellulose, hemicellulose, lignin and extractives, and many other compounds such as lipid, starch, hydrocarbons, simple proteins, tannins, *etc* [14,36].

Cellulosic biomaterials have good adsorption potential due to the presence of hydroxyl functional groups. Cellulose can be chemically modified to form many derivatives with regards to waste treatment. Cellulose modification processes come through esterification, halogenations, etherification, oxidation, grafting [5,7]. The purpose of modification is to enhance the adsorption capacities compared to original cellulose [5,9].

2.4.4.3 Factors affecting adsorption

Adsorption process is generally affected by various factors that include characteristic of adsorbent, nature of adsorbate, ion concentration, pH and temperature [29,37–39]. The surface area of adsorbent is proportional to the adsorption capacity, *i.e.* the adsorption of certain solute increases with an increase of surface area or decrease in particle size [37]. The chemical composition of an adsorbent is also a key factor for adsorption as the extent of adsorption depend on the type and density of the adsorption sites that are present in the adsorbent [27]. As the solute –solvent interaction increases due to high solubility, the extent of adsorption becomes low since it requires to break the solute-solvent interactions before adsorption take place. Raw water samples may contain a mixture of ions and compound; adsorption of a single ion is affected by ionic strength of the solution where adsorption capacity increases as ionic concentration decrease.

The presence of more ions may cause interference or may promote adsorption [8]. The pH of a solution from which adsorption occurs was found to influence the extent of adsorption [37,40]. Since, hydrogen and hydroxide ions are quite strongly adsorbed, the adsorption of other ions is influenced by the pH of the solution. In addition, the concentration of H_3O^+ ions is high at lower pH values and they compete with metal ions in the solution for the active sites on the adsorbent material and thereby reducing adsorption capacities of the adsorbents [40].

The adsorption process also depends on temperature because toxic metal removal is usually significantly high at relatively higher temperatures. Temperature effect on adsorption equilibrium are generally not significant over the range of temperature practically encountered in water and wastewaters. Thus small variations in temperature do not alter the adsorption process to any significant extent [41]. On the other hand, it is worth noting that extremely higher temperatures do not favor adsorption process as they lead to the formation of complex adsorbent-adsorbate which will be dissociate and thereby hindering toxic metal removal [41,42].

2.4.4.4 Calculation related to amount of toxic metal removal by adsorption

The removal efficiency and the adsorption efficiency can be calculated using the following Equation 1 and 2 [8,17].

$$R(\%) = \frac{(C_o - C_e)}{C_o} * 100 \qquad (1)$$

Where *R (%)* is the removal efficiency, C_o is the initial metal ion concentration in mg/L and C_e is the metal ion concentration after adsorption in mg/L

$$qe = \frac{(C_o - C_e)}{m} V \qquad (2)$$

where q_e is the amount (mg/g) of metal ion adsorbed by adsorbent, V is the volume (L) of the sample and m is the mass (g) of adsorbent

2.4.4.5 Disposal of used adsorbent

The used adsorbent (both sawdust and extracted cellulose based compounds) once returned in the environment, it becomes a pollutant as it binds toxic metals ions. The way of overcoming this challenge is to immobilize the used adsorbents in construction wall by mixing them with materials for making bricks [43]. Another way is the process of incineration which may reduce their mass in small quantity of ash and immobilize the ash in construction walls or in dumping site [36].

CHAPTER 3: MATERIALS AND METHODS

3.1 Extraction of cellulose

The sawdust of *Eucalyptus saligna*, *Cupressus lusitanica* and *Grevillea robusta* were collected from the Southern province of Rwanda in Kamonyi district, Musambira sector, Kivumu cell and Gahondo village (E00060130 N09972690), where trees are sawed off. After collection, sawdust samples were transported in the laboratory of chemistry of the University of Rwanda and dried in oven at 40 °C for 24 hours. Afterward, cellulosic compounds were extracted. To do this, the sample were grinded into smaller particles and sieved. The acquired powder (50 g) was feed into the Soxhlet apparatus and washing with different solvents separately starting by non-polar solvent which is *n*-hexane (200 mL), followed by polar solvent which is ethanol (200 mL), and finally washing with distilled water (200 mL), each washing was done in a period of one hour. Thereafter, the remaining materials was retained in oven at 80 °C to dry. After, it was mixed with an aqueous solution of sodium hydroxide 5% (w/v) in a ratio of 1:100 (m/v) and kept for 30 min in autoclave at 121 °C. Thus, the filtrate was mixed with a solution of hydrogen peroxide 2% (v/v) and ethylene diamine tetra acetate 0.2% (w/v) in ratio 1:25 (g /ml) and the obtained mixture was stirred for 12 hours, at 48 °C. The shapeless mass was submitted to bleaching I through filtration and washing using ethanol and distilled water, respectively. Most polar materials such as hemicelluloses, lignin and pectin were eliminated through this bleaching process. The raw cellulose was purified in bleaching II by treating the raw material with acetic acid 80% (v/v) in ratio, 1:33 (g/mL), and concentrated nitric acid 65% (v/v) in a ratio 1:4 (g /mL) at 120 °C for 30 minutes, under mechanical stirring. Finally, cellulose was filtered and washed with ethanol and distilled water to obtain a solution with pH about 7 [25,32,44]**.**

3.2 Chemical characterization of the adsorbent

The identification of functional groups available in the adsorbents before and after adsorption was performed by Fourier transform-infrared spectrophotometry (Bruker Alpha II, 111311, Germany) equipped with a Diamond Crystal ATR (Attenuated Total Internal Reflectance) accessory. The FT-IR spectra of adsorbents were recorded in the wavelength range of 4000 to 400 cm^{-1} with the scanning resolution set to 4.0 cm^{-1} for 24 scans [6,16].

To conduct this chemical characterization, the diamond crystal plate of FT-IR spectrometer was cleaned using acetone solvent. The crystal plate was allowed to dry before scanning for the background spectrum. The powdered sample (small amount) was put on diamond crystal plate surface (high refractive index surface) and the anvil tip was pressed and brought into contact with the sample so that the IR beams will pass through the powdered sample and internally reflected toward the IR detector (computer-aided readout). Thereafter, the FT-IR spectrum was generated and recorded as transmittance (%) versus wavenumber (cm^{-1}) [25,44].

3.3 Determination of the adsorption efficiency of both sawdust and extracted cellulose

The adsorption efficiency of sawdust and extracted cellulose were assessed on both synthetic wastewater and wastewater sampled from Gatsata car garage and car washes.

3.3.1 Preparation of lead and cadmium synthetic wastewater

Lead nitrate (99 %), cadmium nitrate tetrahydrate (99.0%) were separately used to prepare polluted waters (synthetic wastewater) by toxic metals. Stock solutions of these toxic metals with concentrations of 1000 ppm were prepared by dissolving firstly 2.744 g of cadmium nitrate ($Cd(NO_3)_2.4H_2O$) and secondary 1.598 g of lead nitrate ($Pb(NO_3)_2$) in 1000 mL of distilled water to obtain solutions having 1000 mgL^{-1} of each metal ion. Working solutions of 10 to 40 mgL^{-1} were prepared by serial dilutions of the stock solution [8,24].

3.3.2 Sampling of wastewater from Gatsata car garages and car washes

In order to assess the pollution status of wastewater from Gatsata car garages and car washes, grab wastewater samples were collected manually in 500 mL clean plastic bottles. Wastewater samples were collected systematically from downstream to upstream for five different sampling locations (Figure 1) on the effluent from Gatsata garage. The sampling sites indicated by S1, S2, S3, S4, and S5 were characterized by their GPS coordinates which were, E00136452-N09585713; E00169504-N09785844, E00253314-N09919323, E00202889-N09969349 and E00135859-N09852692, respectively.

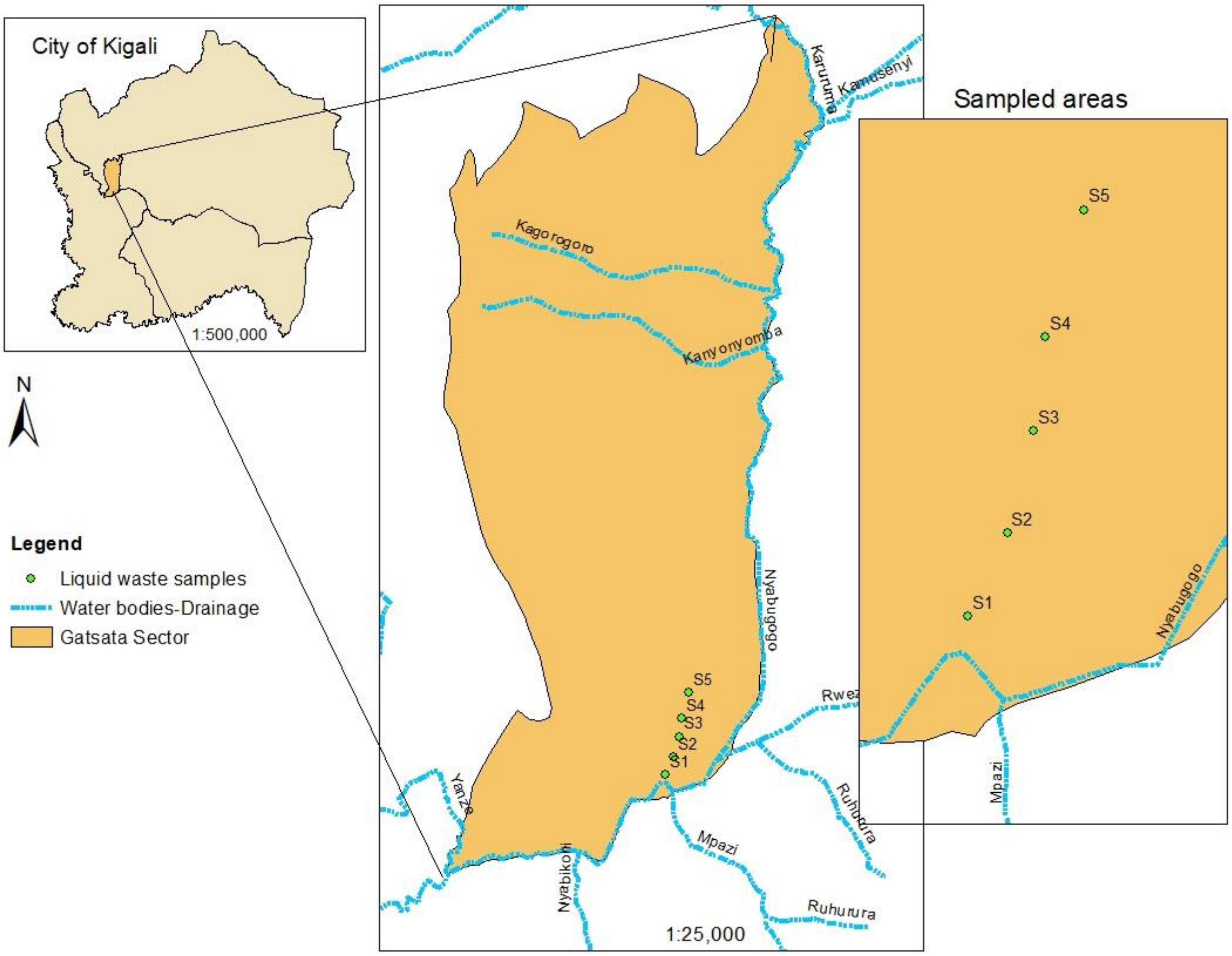

Figure 1: Location of the sampling sites in Gatsata sector, Kigali city

3.3.3 Instrumental Analysis

The concentration of cadmium and lead present in synthetic wastewater and wastewater sampled from Gatsata car garages effluents was analyzed by using Atomic Absorption Spectrophotometer (AA Shimadzu -6800 with wizard software), (Figure 2). The adsorbents were characterized using the Fourier Transform Infrared Spectrophotometer (Bruker Alpha II, 111311, Germany) equipped with a Diamond Crystal ATR (Attenuated Total Internal Reflectance) accessory, (Figure 3).

Figure 2: Atomic Absorption Spectrophotometer (AA Shimadzu -6800 with wizard software)

Figure 3: Fourier Transform Infrared Spectrophotometer (Bruker Alpha II, 111311, Germany)

3.3.4 Assessment of the adsorption capabilities of sawdust and cellulosic based materials using Atomic Absorption Spectrophotometer

To assess the capability of sawdust and extracted cellulose in removing toxic metals from polluted water, both batch adsorption method and packed column flow system method were used. To proceed, a volume of 100 mL of either synthetic wastewater containing 10 ppm of lead and cadmium ions separately or wastewater from Gatsata car garages and car washes, was shaken with one gram (1 g) of each adsorbent at 25° C, at uniform oscillation of 200 rpm for two hours and the pH was fixed at 6.0 using *Cupressus lusitanica* sawdust (CS), *Grevillea robusta* sawdust (GS), *Eucalyptus saligna* sawdust (ES), Cellulose-based compounds extracted from *Cupressus lusitanica* sawdust (CH), Cellulose-based compounds extracted from *Grevillea robusta* sawdust (GH) and Cellulose-based compounds extracted from *Eucalyptus saligna* sawdust (EH). The obtained suspension was then centrifuged, filtered and the filtrate was analyzed using Atomic Absorption Spectrophotometer. The obtained remaining toxic metal ion concentration after adsorption process was recorded.

3.3.4.1 Batch adsorption method

In the present study, batch experiment mode of operation, (Figure 4) (no liquid flow across a bed of particles like in dynamic experiments) was used to measure the adsorption progress. For this purpose, either synthetic wastewater (polluted water) (100 mL) or wastewater from Gatsata car garages and car washes (100 mL) was mixed with a measured mass of dried sawdust or extracted cellulose in a 250 mL conical flask, which is covered by an aluminium foil. The solutions in contact with the adsorbent were maintained at a constant temperature, the mixture being vigorously stirred by means of a magnetic stirrer at 200 rpm for two hours. The sampled solutions were centrifuged at 5000 rpm for 15 min with a centrifugation machine, then after filtration was done in a 45µm filter paper. The concentration of residual metal ions in the solution was measured using a Shimadzu atomic absorption spectrophotometer (AA Shimadzu -6800 with wizard software) [8].

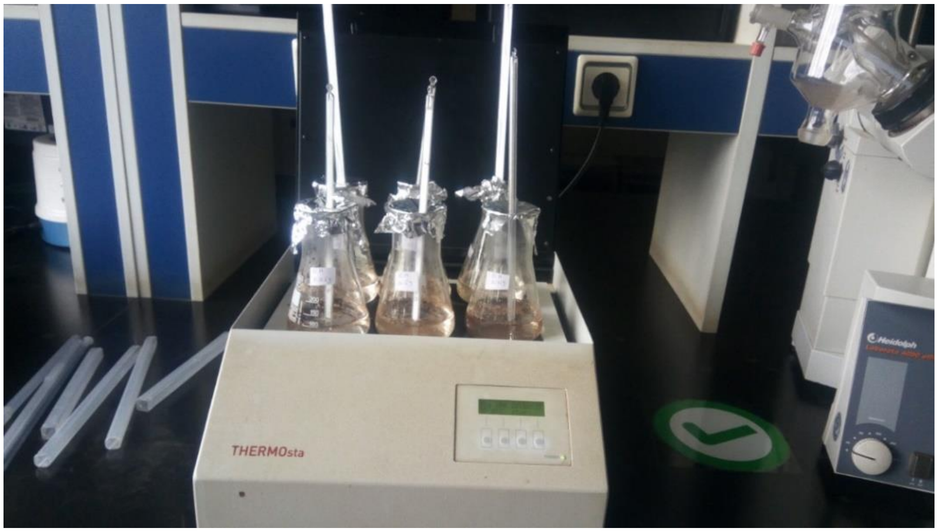

Figure 4: Batch adsorption experiments

3.3.4.2 Packed column flow system method

Laboratory columns of 15 cm height and 1 cm in diameter were used. The columns were filled with known mass of dried samples of sawdust or cellulosic compounds (Figure 5).

The cadmium and lead synthetic water with known concentration were continuously fed to the top of the columns at 50 mL/h flow rate. Eluates were collected and analyzed for their residual cadmium and lead concentrations using the Atomic Absorption spectrophotometer (Shimadzu, AA-6800) [45].

Figure 5: Packed column flow adsorption experiments

3.3.5 Determination of the optimum conditions for adsorption

To assess the good working conditions for adsorption of lead and cadmium, the impact of concentration of adsorbent, initial concentration of the toxic metals, working pH, temperature and the duration of the adsorption process were assessed in this study.

3.3.5.1 Assessment of the effect of adsorbent dose on the adsorption of Pb (II) and Cd (II)

The adsorbent dose is varying from 0.25 g to 2.25 g to determine the optimum adsorbent dosage for the removal of Pb^{2+}, Cd^{2+} at equilibrium. The experiment was carried out in triplicate at 25° C, pH of 6.0, and concentration of 10 ppm for metal ion. Samples were then shaken at uniform oscillation of 200 rpm for two hours, centrifuged, filtered and analyzed using Atomic Absorption spectrophotometer (AA Shimadzu -6800 with wizard software) for remaining toxic metal ion concentration after adsorption process takes place [5,11].

3.3.5.2 Assessment of the effect of initial concentration of toxic metals on adsorption of Pb (II) and Cd (II)

The effect of initial concentration on adsorption of toxic metal ions was studied by using 1.75 g of each studied adsorbent and 100 mL of the Pb^{2+} and Cd^{2+}solutions while varying their concentrations in the range of 10 - 40 ppm. The mixtures were shaken at a 200 rpm for two hours while maintaining a temperature at 25 °C and pH 6.0. Thereafter, samples were centrifuged, filtered and the resulting filtrates were analyzed for the remaining metal ions concentration using the Atomic Absorption spectrophotometer (AA Shimadzu -6800 with wizard software) [17,24].

3.3.5.3 Assessment of the effect of pH on the adsorption of Pb (II) and Cd (II)

Adsorption experiments were carried out at various pH values while maintaining the temperature at 25 °C and the initial concentrations of 10 ppm. The pH of the solutions was adjusted by addition of 0.1 M nitric acid and 0.1 M sodium hydroxide dropwise using a pipette. Thereafter, the adsorbents powder was weighed accurately (1.75 g) and added to 100 mL solution of Pb^{2+} or Cd^{2+} at pH 2.0, 5.0, 6.0, 7.0, 9.0 and 12.0, respectively and the mixtures were shaken for two hours. The resulting mixtures were centrifuged, filtered and the remaining concentrations of Pb^{2+} or Cd^{2+} were analyzed using Atomic Absorption Spectrophotometer (AA Shimadzu -6800 with wizard software) [9,16,23].

3.3.5.4 Assessment of the effect of temperature on the adsorption of Pb (II) and Cd (II)

Adsorption experiments were carried out at various temperatures (20, 25, 30, 35, and 40 °C) in a water bath using constant dosage of 1.75 g for each of the adsorbents, contact time of two hours, shaking speed of 200 rpm, pH 6.0 and initial concentration of 10 ppm for cadmium and lead. The resulting mixtures were collected, centrifuged, filtered and analyzed for the remaining concentrations of Pb^{2+} and Cd^{2+} by using Atomic Absorption Spectrophotometer (AA Shimadzu -6800 with wizard software) [29].

3.3.5.5 Assessment of the effect of contact time on the adsorption of Pb (II) and Cd (II)

Adsorption experiments were carried out at different contact time (30, 60, 90, 120, 150, and 180 minutes). One hundred milliliters (100 ml) of 10 ppm of Pb^{2+} or Cd^{2+} were transferred in stoppered conical flask and agitated with 1.75 g of the adsorbent. Shaking was carried out at constant speed rotation of 200 rpm and samples were filtered and analyzed for the remaining toxic metals ions concentration using Atomic Absorption Spectrophotometer (AA Shimadzu -6800 with wizard software) [9].

3.3.6 Assessment of the adsorption capabilities of sawdust and cellulosic based materials using FTIR

The adsorption capabilities of sawdust and cellulosic based materials was assessed through a Fourier Transform Infrared Spectrophotometer. This assessment was done by analyzing both samples of sawdust and cellulosic based materials before the adsorption process. Thereafter the same samples were used to adsorb selected toxic metals from polluted water and then dried after adsorption process, these dried samples were analyzed on FTIR. The obtained spectra were compared in order to examine the observable changes occurred in functional groups due to the adsorption process of lead and cadmium toxic metals.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Extraction yield of cellulose-based compounds

From 50 g of each *Eucalyptus saligna*, *Cupressus lusitanica* and *Grevillea robusta* sawdusts, masses of 22.5 g, 16.5 g and 13.5 g of the cellulose-based compounds was obtained, respectively. These mean yields of 45, 33 and 27% for *Eucalyptus saligna*, *Cupressus lusitanica* and *Grevillea robusta* sawdust, respectively. *Eucalyptus saligna* sawdust have high yield in cellulose-based compounds than *Cupressus lusitanica* and *Grevillea robusta* sawdust as it has a large wood density, fast growing rate which results in higher height, high photosynthesis rate and it is more competitive and hence *Eucalyptus saligna* store more cellulose in its stem and develop thick cell wall helping them to adapt to different environmental conditions [46,47]. Similar results were reported by Jamshaid et *al.* (2017) while conducting a study on cellulose- based materials for the removal of heavy metals from wastewater and reported that the cellulose-based compounds content varied depending to the tree species [5]. The presence of cellulose based compounds in agricultural waste materials was also successfully presented by Zarubica et al. (2011) while studying the biosorptive removal of lead, cadmium and zinc ions from water by *Lagenaria vulgaris* shell [48].

4.2 FTIR Characterization of extracted cellulose-based compounds

Commercial cellulose was used as reference material to allow exact characterization of extracted cellulosic compounds. Commercial cellulose (Figure 6; red spectrum) showed a broad band at 3450 – 3300 cm^{-1} due to the stretching vibrations of O-H and the medium peaks near 2900 cm^{-1} for aliphatic C-H (*sp*^{3} hybridization) symmetric and asymmetric stretches. The band peaks around 1450 cm^{-1} are associated to the stretching and bending vibrations of C-C and O-H that are present in the cellulose backbone. The figure 6 (green spectrum) is indicating also how sawdust of *Eucalyptus saligna*, for example, appeared in FTIR. Different absorption bands were observed in raw sawdust and were interfering with cellulosic ones. Large absorption band is appearing in the zone between 3500 and 3300 cm^{-1} indicating OH functions while pronounced absorption band at 1450 cm^{-1} was attributed to C-C and O-H stretch that are present in the cellulose backbone. For the extracted cellulosic compounds (Figure 6; black spectrum) absorption bands between 3450-3300 cm^{-1} indicated alcoholic functions O-H stretching while band at 2910 cm^{-1} wavelength was attributed to C-H bond stretching for cellulose based compounds which are non-aromatic compounds. This attribution was confirmed by the existence of other absorption bands between 1450-1300 cm^{-1} characterizing O-H scissing. Furthermore, bands at 1250 -1100 cm^{-1} were given to C-C stretch of the cellulosic compounds.

Remarked various similarities between three spectra on Figure 6 confirmed the existence of cellulose based compounds in sawdust and the extracted compounds from sawdust were cellulose based compounds. Similar results were presented by Kullasatri et al. (2014) while carried out extraction and characterization of cellulose from sugarcane bagasse by using environmental friendly method [44] and by Sulwaniizzatibinti et al. (2017) while extracting cellulose from sawdust using ionic liquid [25].

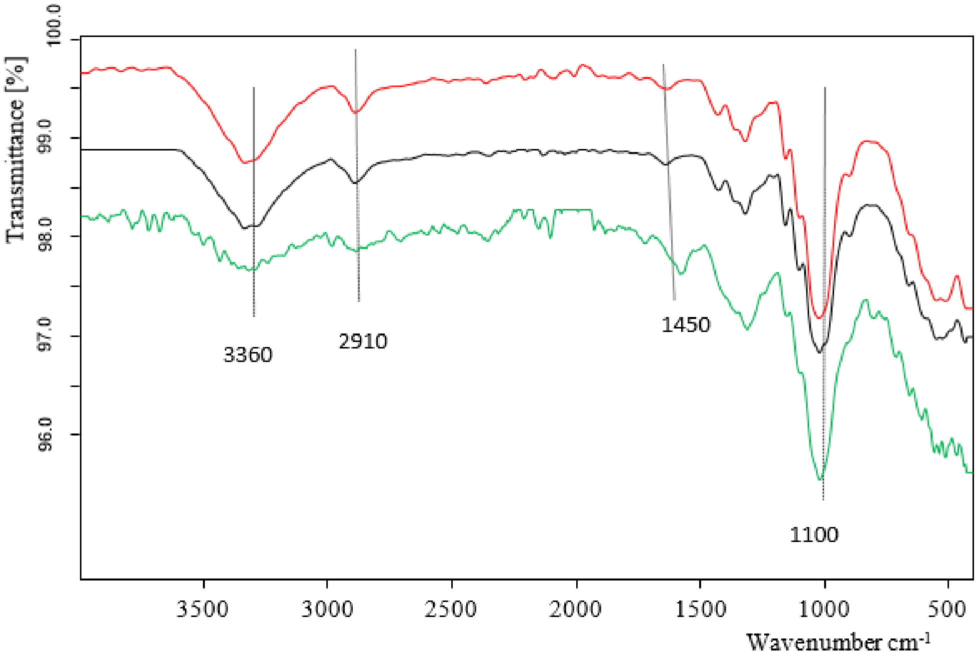

Figure 6: FTIR Spectra of commercial cellulose (red), extracted cellulose (black) and sawdust (green)

4.3 Adsorption capabilities of sawdusts and extracted cellulose-based compounds on cadmium and lead

The preliminary batch adsorption experiments were done to check the capability of *Cupressus lusitanica* sawdust (CS), *Grevillea robusta* sawdust (GS), *Eucalyptus saligna* sawdust (ES), Cellulose-based compounds extracted from *Cupressus lusitanica* sawdust (CH), Cellulose-based compounds extracted from *Grevillea robusta* sawdust (GH) and Cellulose-based compounds extracted from *Eucalyptus saligna* sawdust (EH). After adsorption process, the quantity of the non-adsorbed toxic metals was determined using Atomic Absorption Spectrophotometer and obtained results were recorded in Table 1 and Table 2.

These results indicated that concentration of both lead and cadmium decreased from the same initial concentration of 10 mg/L to 9.69, 9.70, 8.01 mg/L and 10 mg/L to 9.70, 9.73, 8.61 mg/L for lead and cadmium using *Cupressus lusitanica* sawdust (CS), *Grevillea robusta* sawdust (GS) and *Eucalyptus saligna* sawdust (ES) respectively (Table 1).

Table 1: Preliminary results on adsorption of lead and cadmium using sawdusts

	Lead adsorption			Cadmium adsorption		
Adsorbent	Ce (mg/L)	Removal (%)	qe (mg/g)	Ce (mg/L)	Removal (%)	qe (mg/g)
CS	9.69	3.10	0.031	9.70	3.00	0.030
GS	9.70	3.00	0.009	9.73	2.70	0.027
ES	8.01	19.91	0.199	8.61	13.91	0.139

Cellulose-based compounds extracted from *Cupressus lusitanica* sawdust (CH), Cellulose-based compounds extracted from *Grevillea robusta* sawdust (GH), Cellulose-based compounds extracted from *Eucalyptus saligna* sawdust (EH) and commercial cellulose were also used to access their adsorption capabilities with respect to lead and cadmium contained in synthetic wastewater. With their hydroxyl chemical functions, cellulose-based compounds bound to lead and cadmium ions from synthetic wastewater, complex them hence their concentrations in synthetic wastewater decreases from 10 mg/L to 7.34, 9.50, 5.25, 5.19 mg/L and from 10 mg/L to 7.55, 9.55, 7.25, 7.21 mg/L for lead and cadmium respectively (Table 2).

Table 2: Preliminary results on adsorption of lead and cadmium using extracted cellulose and standard cellulose

	Lead adsorption			Cadmium adsorption		
Adsorbent	Ce (mg/L)	Removal (%)	qe (mg/g)	Ce (mg/L)	Removal (%)	qe (mg/g)
CH	7.34	26.60	0.266	7.55	24.50	0.245
GH	9.50	5.00	0.050	9.55	4.50	0.045
EH	5.25	47.50	0.475	7.25	27.50	0.275
Commercial cellulose	5.19	48.10	0.481	7.21	27.90	0.279

It was remarked that both *Cupressus lusitanica* and *Grevillea robusta* sawdusts and their extracted cellulose-based compounds have weak adsorption efficiency compared to *Eucalyptus saligna* sawdust and their extracted cellulose based compounds.

The difference in this adsorption capability may be due to different content quantities of cellulose-based compounds in these three species [5]. The extraction yields in cellulose based compounds obtained, which were 45, 33 and 27% for *Eucalyptus saligna*, *Cupressus lusitanica* and *Grevillea robusta* are supporting this assumption. The more the material is rich in cellulosic compounds, the more it contains high amount of hydroxyl functions and then complexing a high quantity of toxic metals. Similar findings were previously reported and support the results from this study [49,50].

Results obtained from the analysis by AAS were verified and confirmed by the analysis on Fourier Transform Infra-red spectrophotometer where the obtained spectrum after adsorption indicated many changes in its absorption bands (Figure 7 and Figure 8).

The obtained spectrum of sawdust after adsorption with lead (Figure 7, orange spectrum) and cadmium (Figure 7, purple spectrum) showed variations in broadness of the broad band around 3360 cm^{-1} indicating the use of OH functions in binding lead and cadmium. The pronounced absorption band at 1450 cm^{-1} disappeared completely in the spectrum after lead adsorption, this is due to the saturation of the OH functions that are present in cellulose backbone as it is highly adsorbed than cadmium because of weak nuclear attraction of lead compared to cadmium [6,48].

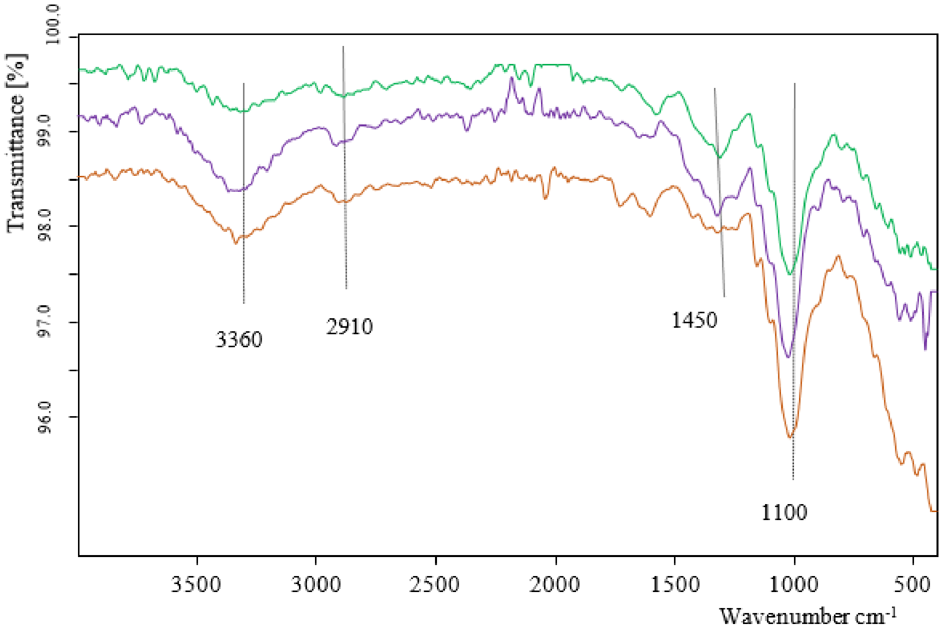

Figure 7: FTIR spectra of sawdust (green), sawdust after cadmium adsorption (purple) and sawdust after lead adsorption (orange)

The obtained spectra of extracted cellulose before and after adsorption with lead and cadmium were compared and showed changes confirming that adsorption process happened (Figure 8)

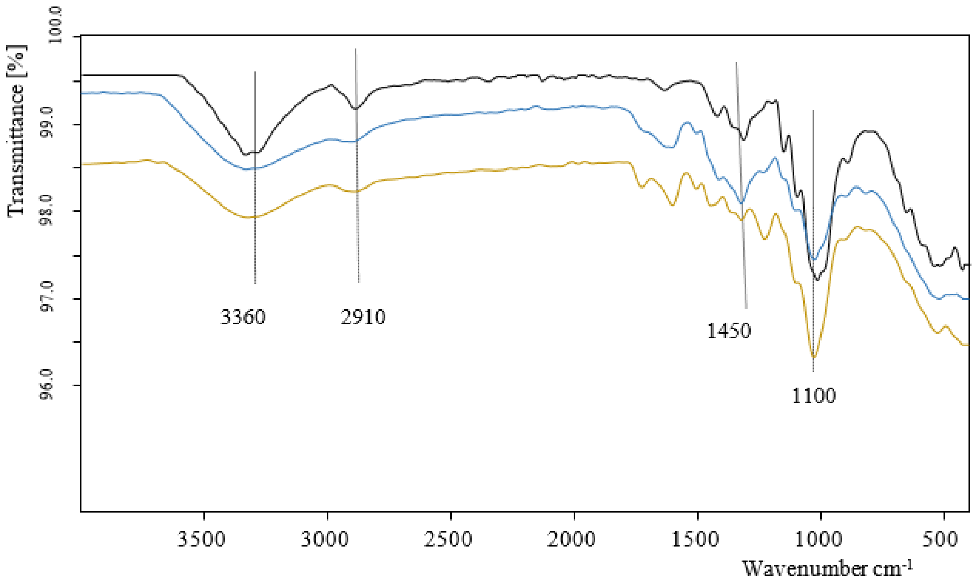

Figure 8: Spectra of extracted cellulose (black), extracted cellulose after cadmium adsorption (blue) and extracted cellulose after lead adsorption (marrow)

The O-H broad band at 3360 cm^{-1} is still observed after lead (Figure 8, marrow spectrum) and cadmium adsorption (Figure 8, blue spectrum) albeit changes in intensities. This is due to the fact that cellulose-based compounds used as adsorbents are polyhydroxylated compounds and some O-H groups were used to bind lead and cadmium while others left, reason why a persistence in OH-broad band was observed even after adsorption. In addition, some of the lone pairs electrons of oxygen in the O-H groups are not free to bind lead and cadmium metals due to steric hindrance effect and, conformational (axial and equatorial) constraints [23,51]. Furthermore, lead adsorbs completely onto cellulose based compounds, this is due to the larger size and weak nuclear attraction in lead than in cadmium and hence lone *d* orbitals in lead are free to accept lone pairs of electrons from cellulose-based adsorbents, hence the pronounced absorption band at 1450 cm^{-1} due to O-H groups present in cellulose backbone disappeared completely in the spectrum after lead adsorption [8,49]

4.4 Impact of the physico-chemical parameters on the adsorption process

4.4.1 Effect of adsorbent dose on the adsorption of Pb (II) and Cd (II)

The experiment was carried out in order to study effects of adsorbents dose on the adsorption removal process of lead and cadmium ions by using CS, GS, ES, CH, GH, and EH at 25 °C within 2 hours contact time.

The adsorbent dose was increased from 0.25 g to 2.25 g and the adsorption of lead and cadmium was found to increase till the establishment of the equilibrium state for an adsorbent dose of 1.75 g, (Figure 9) (Appendix A1 *vibe infra*). This is due to the fact that for doses higher than 1.75 g, there was no significant change in the removal capacity of cadmium and lead (Figure 9); consequent 1.75 g of adsorbent was found to be the optimum dose, a dose which is required to reach the maximum toxic metal removal. This was probably due to toxic metal concentration shortage in solution as the dose of adsorbent increases despite availability of more active sites on adsorbent's surface [21,33]. This happens because as the adsorbent dose increase also the functional group site responsible for adsorption increases [38,39]. From Figure 9, it is clearly seen that lead was more removed for all adsorbents used than cadmium. This is due to the fact that the nuclear attraction in lead is weaker than that in cadmium (cadmium ions are small in size than lead ions and a strong charge density is observed for cadmium than for lead) and hence the free *d*-orbital in lead are more free to accept lone pairs of electron from adsorbent (chemisorption) than cadmium [2].

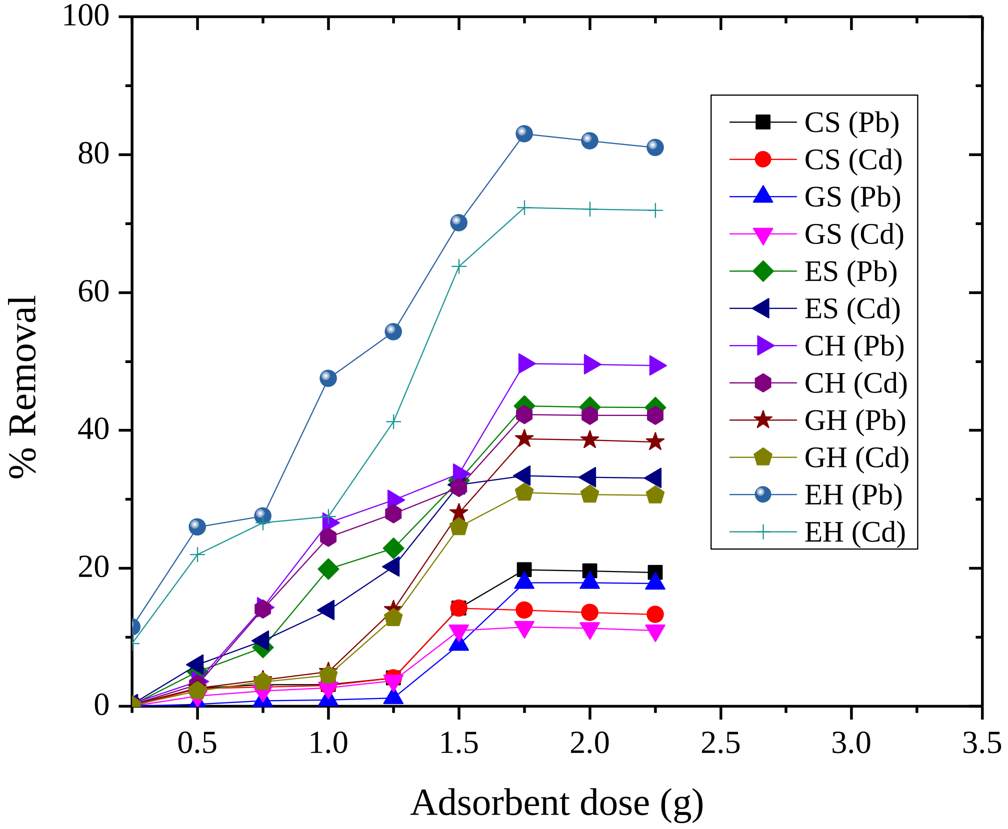

Figure 9: Dose effect on adsorption process of lead and cadmium by using CS, GS, ES, CH, GH, and EH at 25°C within two hours contact time

4.4.2 Effect of pH on the adsorption of Pb (II) and Cd (II)

Generally, adsorption process was found to be affected by pH. In this study, it was pointed out that adsorption of lead and cadmium onto CS, GS, ES, CH, GH and EH adsorbent was strongly affected by pH (Figure 10) (Appendix A2 *vibe infra*)). From Figure 10 it is clearly seen that adsorption of lead and cadmium increase with the increase in pH values from 2 to 6 for both adsorbents and the adsorption removal start to decrease at higher pH values (pH > 6). These findings are in good agreement with those reported by Daochalermwong *et al. (*2020) [6] and Mopoung and Kengkhetkit (2016) [40]. At higher pH values, lead and cadmium ions form hydroxyl precipitate as well as hydroxyl complex for lead in particular, which dissolves in nitric acid, hence their adsorption decreases while at lower value of pH, hydronium ions and toxic metals ions are competing towards the active site of adsorbents and consequently hindering the cadmium and lead removal process as it collaborates with the lower efficiency removal that were observed [6,40].

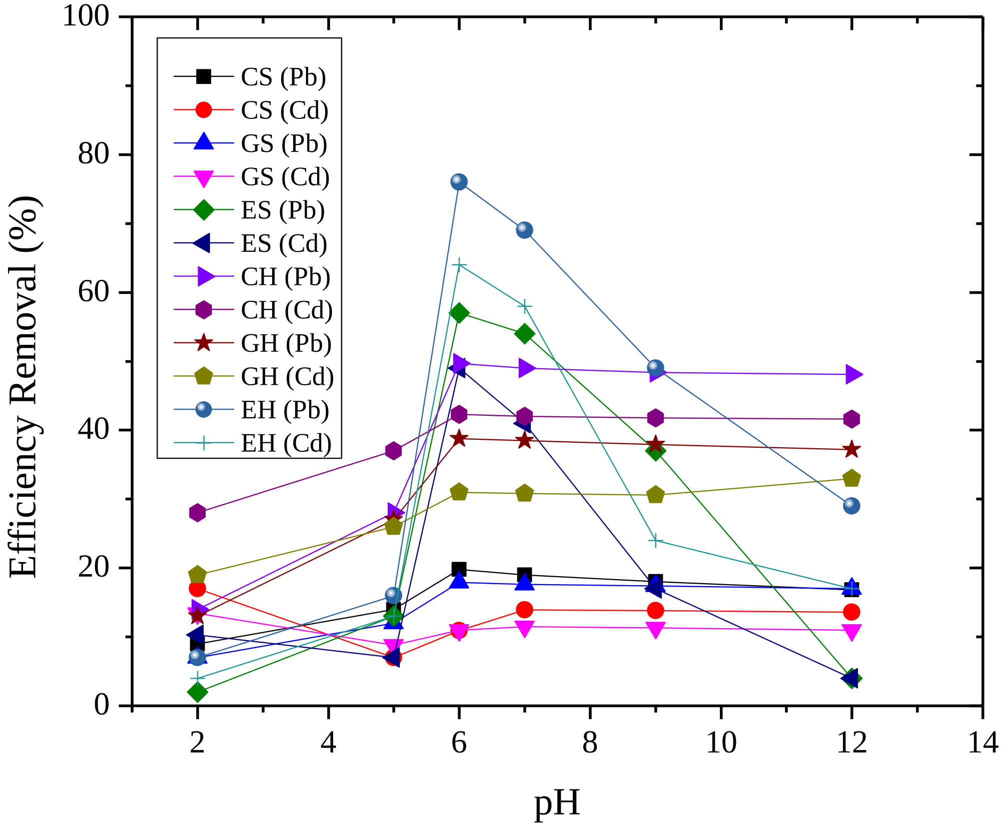

Figure 10: Effect of pH on adsorption of lead and cadmium

4.4.3 Effect of temperature on the adsorption of Pb (II) and Cd (II)

The effect of temperature on adsorption of lead and cadmium was studied for temperatures ranging from 20 to 40 °C. In this study, it was found that an increase in temperatures from 20 °C to 25 °C increased the adsorption removal efficiency for adsorbate (lead and cadmium) for all studied adsorbents (Figure 11) (Appendix A3 *vibe infra*)). The maximum percentages removal efficiency for lead were found to be 19.80, 17.90, 43.50, 49.70, 38.80 and 83.00% at 25 °C by using CS, GS, ES, CH, GH, EH adsorbents, respectively while the maximum percentages efficiency removal for cadmium were 13.90, 11.50, 33.42, 42.30, 31.00 and 72.30% using CS, GS, ES, CH, GH, EH adsorbents, respectively. On the other hand, for temperatures greater than 25°C, the adsorption was found to decrease because at higher temperature there might have been the dissociation of the complex adsorbate-adsorbent. Similar results were reported in other studies by Sarada *et al*. (2017) on the study about biosorption of cadmium using *Araucaria heterophylla* as green plant biomass and suggest that at high temperature the thickness of the boundary layer was decreased and the metal ion escape from the biomass surface and pass into the solution phase resulted in a decrease in the adsorption efficiency [49] and Mbugua Moses (2015) for the study on effectiveness of cactus biomass and its combusted products in removal of colour, turbidity and selected metal ions from contaminated water and confirmed that at high temperature, the adsorption capacity decreases due to weak interaction between active site of the adsorbent and the adsorbate [24].

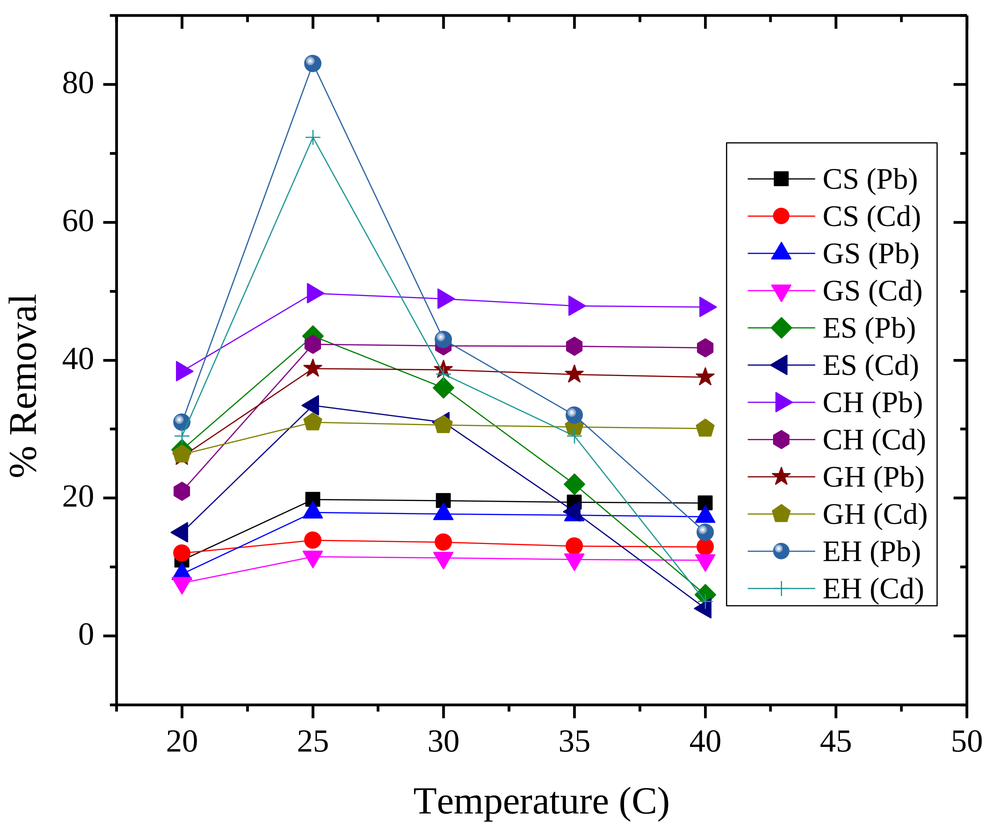

Figure 11: Effect of Temperature on adsorption of lead and cadmium onto various adsorbent

4.4.4 Effect of initial concentration of toxic metals on adsorption of Pb (II) and Cd (II)

According to the results obtained and presented in Figure 12 (Appendix A4 *vibe infra*), the removal efficiency for lead was changed from 19.80 to 15.70%, from 17.90 to 14%, from 43.53 to 7.00%, from 49.70 to 46.00%, from 38.80 to 37.00%, from 83.00 to 32.00% as the initial concentration of lead changed from 10 to 40 ppm while for cadmium, the removal efficiency was passed from 13.90 to 12.30%, from 11.50 to 10.50%, from 33.42 to 3.00%, from 42.20 to 40.90%, from 31.00 to 28.70%, from 72.30 to 27.00% as the initial concentration of cadmium was changed from 10 to 40 ppm for CS, GS, ES, CH, GH, and EH respectively. It is clearly seen that the removal efficiency decreased with an increase of initial concentration of lead and cadmium toxic metals for all adsorbents that were used. At lower concentrations of metal ions, most of the toxic metal ions in solution tends to be adsorbed onto vacant active sites of the adsorbents, thus resulting in significantly high metal ion adsorption removal [49].

The increase of lead and cadmium concentration in solution makes adsorbent active site unable to bind all lead and cadmium, as the actives sites become more saturated and leaving most of toxic metals in solution without being adsorbed. Similar findings were reported by Nyamunda *et al.* (2019) while conducting a research on removal of Zn (II) and Cu (II) ions from industrial wastewaters using magnetic biochar derived from water Hyacinth [17].

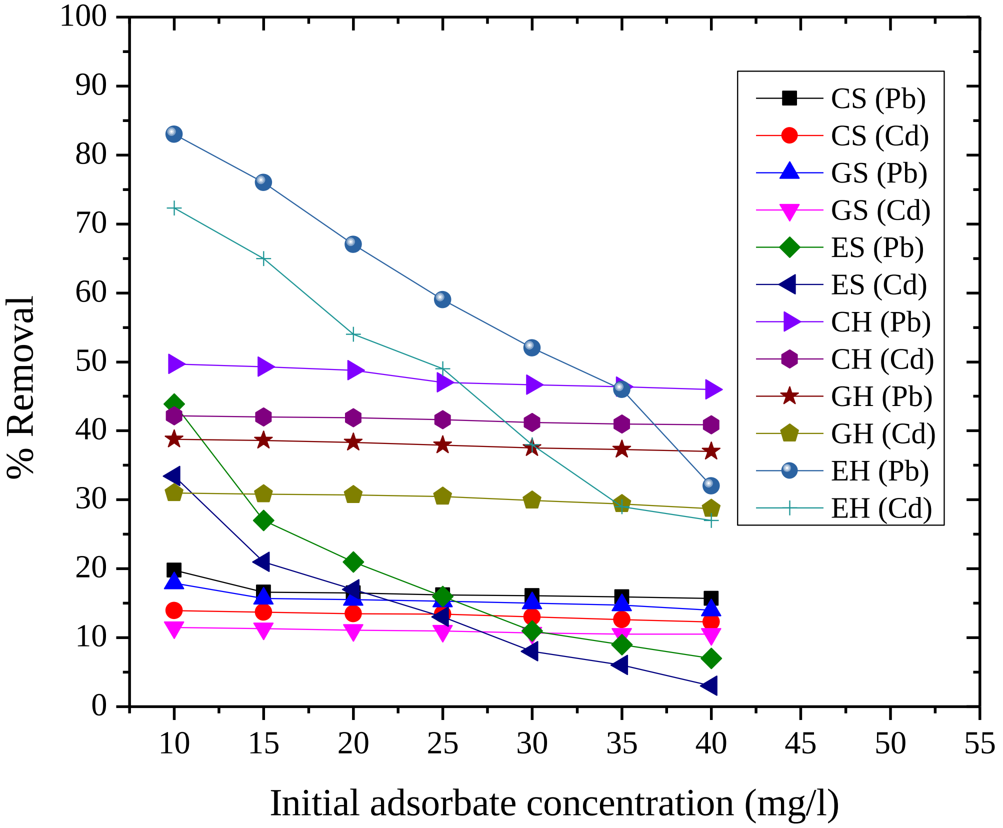

Figure 12: Effect of initial concentration of adsorbate

4.4.5 Effect of contact time on the adsorption of Pb (II) and Cd (II)

The Figure 13 (Appendix A5 *vibe infra*) shows adsorption removal percentage with respect to time. The adsorption of lead and cadmium onto CS, GS, ES, CH, GH, and EH increased with increase of contact time and remains constant when it reached to the equilibrium conditions.

Lead and cadmium uptake at the beginning was rapidly due to the availability of hydroxyl groups of adsorbents. The higher adsorption capacity happened after two hours and become constant as the adsorption reached the equilibrium.

The maximum uptake for lead was found to be 19.80, 17.90, 44.00, 49.70, 38.80, 83.00 for CS, GS, ES, CH, GH, EH adsorbents, respectively while the maximum uptake for cadmium was found to be 14.00, 11.50, 33.00, 42.30, 31.00, 73.00 for CS, GS, ES, CH, GH, EH adsorbents, respectively. The same trends were observed in the study on removal of heavy metal ions using modified celluloses prepared from pineapple leaf fiber [6] and Alkali modified jackfruit wood sawdust as bio adsorbent for removal of Pb (II) ions from wastewater [52]

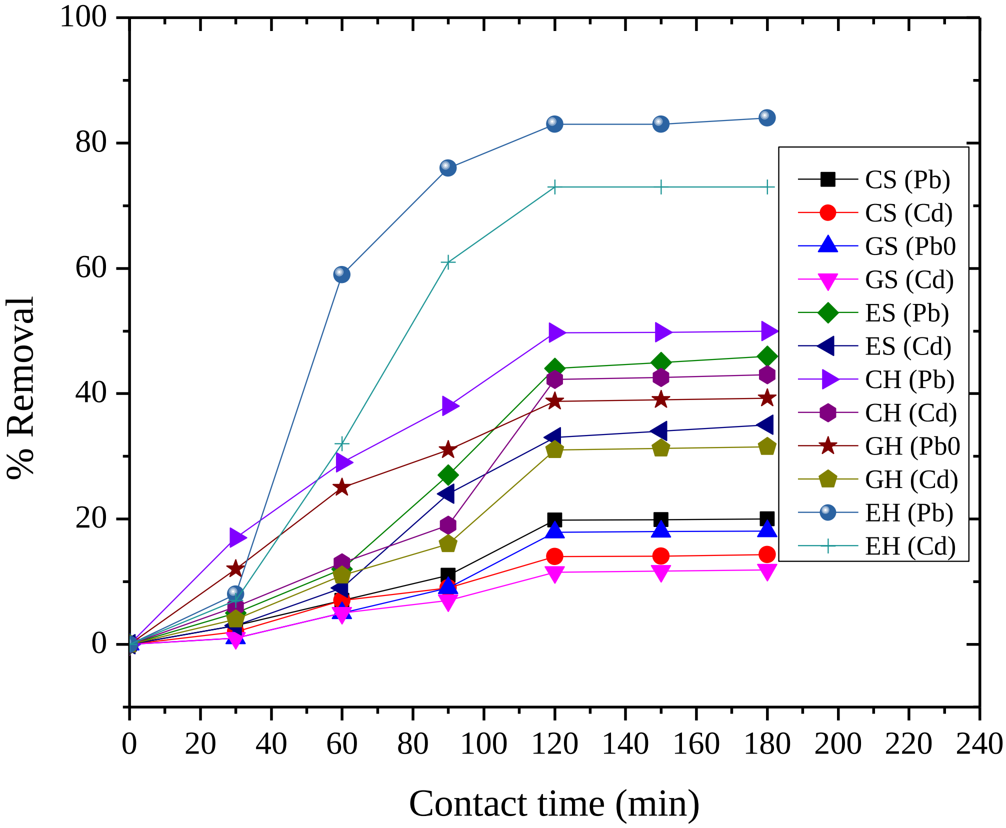

Figure 13: Effect of contact time on lead and cadmium adsorption by using CS, GS, ES, CH, GH, and EH

4.5 Impact of the adsorption methods used on toxic metal removal efficiency

The efficacy of the two methods, batch and column flow, for the removal of cadmium and lead was examined in this study. According to the Figure 14 (Appendix B *vibe infra*), it is shown that the adsorption removal efficiency is high for column flow technology than for batch adsorption.

The percentage removal for lead in batch mode was 43.00, 83.00, 19.80, 49.70, 17.90 and 38.80% using ES, EH, CS, CH, GS, and GH respectively while it was 55.00, 94.00, 39.00, 68.00, 33.00, 56.00% in column flow mode using ES, EH, CS, CH, GS, and GH respectively.

On the other hands for cadmium in batch mode it was 33.42, 72.30, 13.90, 42.30, 11.50 and 31.00% using ES, EH, CS, CH, GS, and GH respectively while in column flow mode it was 43.00, 82.00, 49.00, 79.00, 41.00 and 70.00% using ES, EH, CS, CH, GS, and GH respectively. These results can be explained by the fact that in column flow mode the toxic metals solution is continuously fed and allow the adsorption to take at each hydroxyl group and this results in higher adsorption than in batch mode where the whole volume of adsorbate is in contact with the adsorption and the first adsorption can become a barrier to the next leading to weak adsorption [10,45]. Similar trends were found in a study on modeling adsorption of Cu (II) using polyaniline-coated sawdust in a fixed-bed column [53].

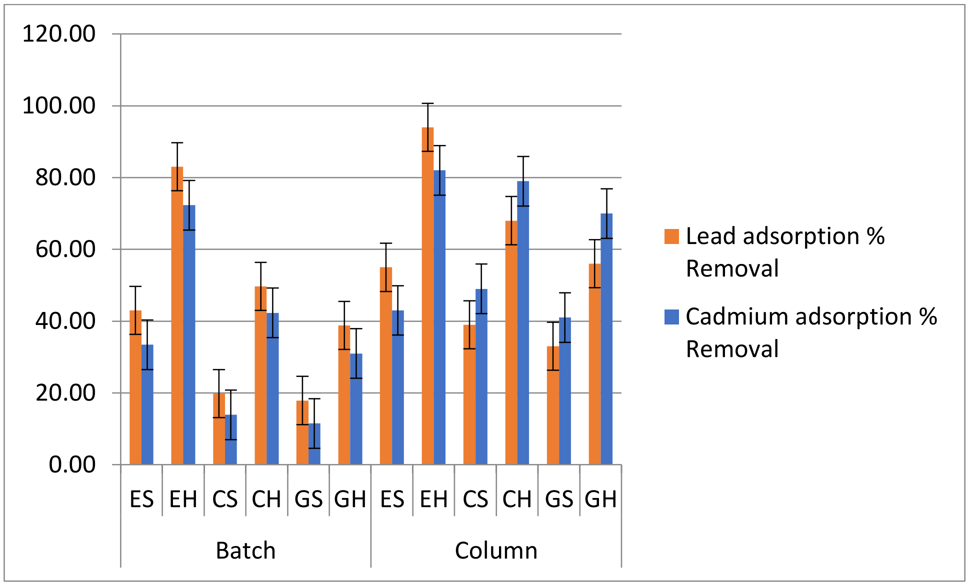

Figure 14: Lead and cadmium removal on batch and column flow adsorption technology from polluted water

4.6 Assessment of pollution by toxic metals of wastewater collected from Gatsata car garages and car washes effluents

The analysis was carried out on five different grab samples collected from the Gatsata car garage and car washes effluents at different sites. From the results (Table 3), it is clearly seen that both lead and cadmium toxic metals were present in effluent of the main discharge channel from the Gatsata car garages and car washes and exceed the tolerance limit of discharge of industrial wastewater that were fixed by the Rwanda Standard Board [3].

The absence of both cadmium and lead toxic metals in the upstream of the main discharge channel from Gatsata car garages and car washes confirms that lead and cadmium toxic metals found in the surrounding wetland comes from Gatsata car garages and car washes.

The presence of toxic metals in the stream passing through the rice plantation poses high risk to the population consuming the rice grown in this wetland. Therefore, the adsorption treatment before discharging the wastewater into the environment is required. Similar results were found by Sekomo *et al.* (2018) while conducting a study on the fate of heavy metals in an urban natural wetland : The Nyabugogo Swamp (Rwanda) [1].

Table 3: Results of pollution level of wastewater from car garages and car washes at Gatsata

Parameters	Site 1	Site 2	Site 3	Site 4	Site 5	Standards*
pH	6.99	6.89	7.18	6.83	7.02	5-9
EC(µs/cm)	1207	1391	1185	1419	1204	-
TDS (mg/L)	591	667	560	676	584	2000
Salinity (‰)	0.70	0.57	0.56	0.67	0.57	-
Cd (mg/L)	3.77	BDL	0.52	BDL	BDL	0.1
Pb (mg/L)	2.01	BDL	0.08	0.11	0.09	0.1

BDL: Below detection Limit * Standards RS 109: 2017 Water quality — Discharged industrial wastewater — Requirements

4.7 Toxic metal removal efficiency on batch and column flow adsorption technologies from car garage and car washes wastewater sample.

According to the Figure 15 (Appendix C *vibe infra*), it is shown that the adsorption removal efficiency is high for column flow mode than for batch adsorption mode. The percentage removal for lead in batch mode was 42.79, 83.58, 19.90, 50.25, 17.91 and 38.81% using ES, EH, CS, CH, GS, and GH respectively while it was 55.22, 94.03, 39.30, 68.16, 33.33 and 56.22% in column flow mode using ES, EH, CS, CH, GS, and GH respectively. On the other hands for cadmium in batch mode it was 33.42, 72.41, 13.79, 42.44, 11.41 and 31.30% using ES, EH, CS, CH, GS, and GH respectively while in column flow mode it was 42.97, 81.96, 49.07, 78.78, 41.64 and 70.03% using ES, EH, CS, CH, GS, and GH respectively.

For this case, it is shown that the percentage removal for lead and cadmium for both adsorbents is higher than those observed in the case of polluted water prepared in the laboratory and this is due to the initial concentration of adsorbate which is lower in the case of wastewater from car garage and car washes at Gatsata (2.01 mg/L and 3.77 mg/L for lead and cadmium respectively). Similar trends were found in a study on modeling adsorption of Cu (II) using polyaniline-coated sawdust in a fixed-bed column [53].

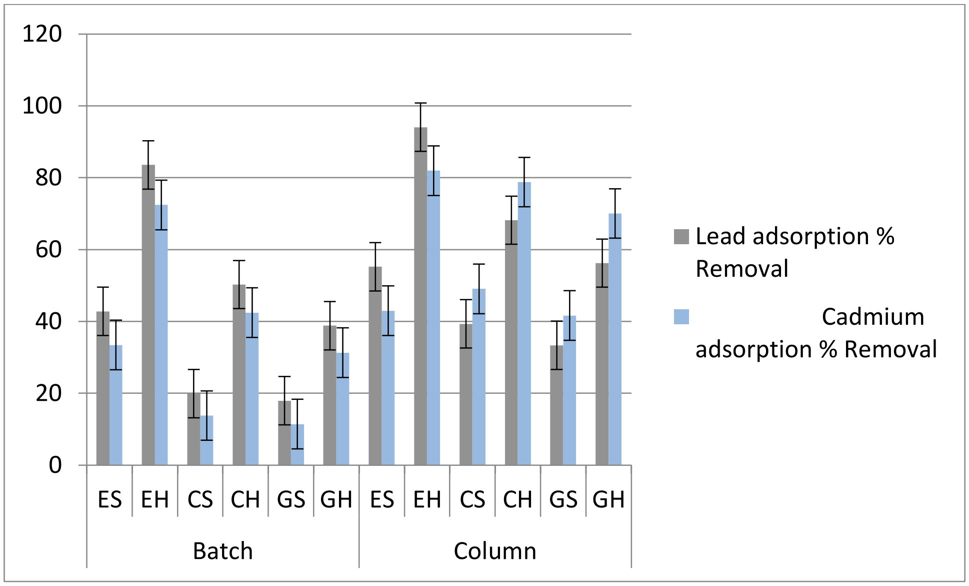

Figure 15: Lead and cadmium removal on batch and column flow adsorption technology from car garage wastewater

4.8 Comparison of obtained results with published data

Appendix D *vibe infra* shows different results on adsorption removal of lead and cadmium by using various adsorbents mainly cellulose-based bio adsorbents, this is due to various functional groups, such as hydroxyl, carbonyl, sulfate, phosphate, and amino groups [6,16,40,54]. The adsorption removal efficiency expressed in percentage of lead and cadmium found in this study is due to the presence of hydroxyl groups and ether groups in *Cupressus lusitanica, Grevillea robusta* and *Eucalyptus saligna* sawdust and their extracted cellulose-based compounds and are found in the same range of values as those found in different publications. Experimental conditions, that is pH, temperature, adsorbent dose and contact time, used in this study are also in the same range with those reported in different articles.

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The work reported in this dissertation aimed at investigating adsorption removal efficiency of cellulose-based compounds extracted from sawdust of *Eucalyptus saligna*, *Cupressus lusitanica* and *Grevillea robusta* for Cd^{2+} and Pb^{2+} from synthetic wastewater and Gatsata car garages and car washes wastewater. In this study, the adsorbents were characterized by using the FTIR spectroscopy technique. Based on the experimental results, it was found that efficiency removal of lead and cadmium were achieved with optimum dose of 1.75 g of EH adsorbent with maximum adsorption removal of 83.00 and 72.30% for lead and cadmium, respectively compared to other adsorbents that were used (CS, GS, ES, CH and GH). In addition, the same efficiency removal was achieved for contact time of 120 minutes (2 h) and 10 mg/L of initial adsorbate concentration in the removal of lead and cadmium. The optimum pH for the maximum adsorption of lead and cadmium (83.00 and 72.30%, respectively) was found to be pH 6.0 for all studied adsorbents. The optimum conditions were applied to real wastewater collected from car garages and car washes at Gatsata, which was found to contain lead and cadmium ions. In addition, it was found that EH showed higher adsorption efficiency removal of 83.58 and 72.41% for lead and cadmium, respectively. Within this work, batch adsorption and column flow adsorption experiment modes were used and the results showed that column flow adsorption removal for lead and cadmium were 94.00 and 82.00%, respectively onto EH adsorbent for polluted water, there was an increase of performance of approximately 10% for both toxic metals compared to batch mode. The same increasing performance was observed for the Gatsata car garages and car washes.

5.2 Recommendations

Taking into account of the obtained results and conclusions, the following recommendations can be suggested to car garages and car washes owners and future researcher:

1. Sawdust of *Eucalyptus saligna*, *Cupressus lusitanica* and *Grevillea robusta*, which is considered as solid waste with no valuable economic importance can be used to treat car garages and car washes wastewater to remove toxic metals especially lead and cadmium for the benefit of protecting human health.
2. More investigations should be done for adsorption removal of other toxic metals such as copper, nickel, zinc, manganese using sawdust and their cellulose-based compounds extracted from sawdust of *Eucalyptus saligna*, *Cupressus lusitanica* and *Grevillea robusta*.

iii. Further studies should be done in order to investigate the feasibility at industrial scale for the removal of lead and cadmium toxic metals from wastewater using sawdust and their cellulose-based compounds extracted from sawdust of *Eucalyptus saligna, Cupressus lusitanica* and *Grevillea robusta*.

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APPENDICES

Appendix A: Effect of different parameters on lead and cadmium adsorption removal

A1: Effect of adsorbent dose for CS, GS, ES, CH, GH and EH on lead and cadmium adsorption process

		Lead adsorption			Cadmium adsorption		
Adsorbent	Dose (g)	C_e (mg/L)	Removal (%)	q_e (mg/g)	C_e (mg/L)	Removal (%)	q_e (mg/g)
CS	0.25	9.99	0.1	0.004	10.00	0.00	0.000
	0.5	9.74	2.6	0.052	9.74	2.56	0.051
	0.75	9.69	3.1	0.041	9.72	2.80	0.037
	1	9.69	3.1	0.031	9.70	3.00	0.030
	1.25	9.59	4.1	0.033	9.59	4.10	0.033
	1.5	8.58	14.2	0.095	8.58	14.21	0.095
	1.75	8.02	19.8	0.113	8.61	13.90	0.079
	2	8.04	19.6	0.098	8.64	13.60	0.068
	2.25	8.06	19.4	0.086	8.67	13.30	0.059
GS	0.25	10	0	0.000	10.00	0.00	0.000
	0.5	9.97	0.3	0.006	9.85	1.50	0.030
	0.75	9.92	0.8	0.011	9.78	2.20	0.029
	1	9.91	0.9	0.009	9.73	2.70	0.027
	1.25	9.88	1.2	0.010	9.63	3.70	0.030
	1.5	9.11	8.9	0.059	8.90	11.00	0.073
	1.75	8.21	17.9	0.102	8.85	11.50	0.066
	2	8.21	17.9	0.090	8.87	11.30	0.057
	2.25	8.22	17.8	0.079	8.90	11.00	0.049
ES	0.25	9.98	0.20	0.008	9.97	0.30	0.012
	0.5	9.50	5.00	0.100	9.40	6.00	0.120
	0.75	9.15	8.50	0.113	9.05	9.50	0.127
	1	8.01	19.91	0.199	8.61	13.91	0.139
	1.25	7.71	22.91	0.183	7.98	20.21	0.162
	1.5	6.73	32.72	0.218	6.79	32.12	0.214

	1.75	5.65	43.53	0.249	6.66	33.42	0.191
	2	5.66	43.4	0.217	6.65	33.2	0.168
	2.25	5.67	43.3	0.192	6.64	33.1	0.149
CH	0.25	9.96	0.4	0.016	9.98	0.2	0.008
	0.5	9.64	3.6	0.072	9.69	3.1	0.062
	0.75	8.57	14.3	0.191	8.59	14.1	0.188
	1	7.34	26.6	0.266	7.55	24.5	0.245
	1.25	7.01	29.9	0.239	7.21	27.9	0.223
	1.5	6.63	33.7	0.225	6.83	31.7	0.211
	1.75	5.03	49.7	0.284	5.77	42.3	0.242
	2	5.04	49.6	0.248	5.78	42.2	0.211
	2.25	5.06	49.4	0.220	5.78	42.2	0.188
GH	0.25	9.98	0.2	0.008	9.99	0.1	0.004
	0.5	9.74	2.6	0.052	9.78	2.2	0.044
	0.75	9.62	3.8	0.051	9.65	3.5	0.047
	1	9.5	5	0.050	9.55	4.5	0.045
	1.25	8.6	14	0.112	8.72	12.8	0.102
	1.5	7.2	28	0.187	7.40	26	0.173
	1.75	6.12	38.8	0.222	6.90	31	0.177
	2	6.14	38.6	0.193	6.93	30.7	0.154
	2.25	6.17	38.3	0.170	6.94	30.6	0.136
EH	0.25	8.85	11.5	0.460	7.99	9.1	0.804
	0.5	7.4	26.00	0.520	7.8	22	0.440
	0.75	7.24	27.60	0.368	7.34	26.6	0.355
	1	5.25	47.50	0.475	7.25	27.5	0.275
	1.25	4.57	54.30	0.434	5.87	41.3	0.330
	1.5	2.99	70.10	0.467	3.62	63.8	0.425
	1.75	1.7	83.00	0.474	2.77	72.3	0.413
	2	1.8	82	0.410	2.79	72.1	0.361
	2.25	1.9	81	0.360	2.81	71.9	0.320

A2: Effect of pH on lead and cadmium adsorption by using 1.75 g of various adsorbents (CS, GS, ES, CH, GH, and EH) at 25°C, initial concentration of 10 ppm within two hours contact time

		Lead adsorption			Cadmium adsorption		
Adsorbent	pH	Ce (mg/L)	Removal (%)	qe (mg/g)	Ce (mg/L)	Removal (%)	qe (mg/g)
CS	2	9.1	9.00	0.051	8.3	17.00	0.097
	5	8.6	14.00	0.080	9.3	7.00	0.040
	6	8.02	19.80	0.113	8.91	10.90	0.062
	7	8.1	19.00	0.109	8.61	13.90	0.079
	9	8.2	18.00	0.103	8.62	13.80	0.079
	12	8.32	16.80	0.096	8.64	13.60	0.078
GS	2	9.3	7.00	0.040	8.66	13.40	0.077
	5	8.8	12.00	0.069	9.12	8.80	0.050
	6	8.21	17.90	0.102	8.9	11.00	0.063
	7	8.24	17.60	0.101	8.85	11.50	0.066
	9	8.26	17.40	0.099	8.87	11.30	0.065
	12	8.3	17.00	0.097	8.9	11.00	0.063
ES	2	9.8	2.00	0.011	8.97	10.30	0.059
	5	8.7	13.00	0.074	9.3	7.00	0.040
	6	4.3	57.00	0.326	5.1	49.00	0.280
	7	4.6	54.00	0.309	5.9	41.00	0.234
	9	6.3	37.00	0.211	8.3	17.00	0.097
	12	9.6	4.00	0.023	9.6	4.00	0.023
CH	2	8.6	14.00	0.080	7.2	28.00	0.160
	5	7.2	28.00	0.160	6.3	37.00	0.211
	6	5.03	49.70	0.284	5.77	42.30	0.242
	7	5.1	49.00	0.280	5.8	42.00	0.240
	9	5.16	48.40	0.277	5.82	41.80	0.239
	12	5.19	48.10	0.275	5.84	41.60	0.238
GH	2	8.7	13.00	0.074	8.1	19.00	0.109
	5	7.3	27.00	0.154	7.4	26.00	0.149
	6	6.12	38.80	0.222	6.9	31.00	0.177

	7	6.15	38.50	0.220	6.92	30.80	0.176
	9	6.21	37.90	0.217	6.94	30.60	0.175
	12	6.28	37.20	0.213	6.7	33.00	0.189
EH	2	9.3	7.00	0.040	9.6	4.00	0.023
	5	8.4	16.00	0.091	8.7	13.00	0.074
	6	2.4	76.00	0.434	3.6	64.00	0.366
	7	3.1	69.00	0.394	4.2	58.00	0.331
	9	5.4	49.00	0.263	7.6	24.00	0.137
	12	7.1	29.00	0.166	8.3	17.00	0.097

A3: Effect of Temperature on lead and cadmium adsorption by using 1.75 g of various adsorbents (CS, GS, ES, CH, GH, EH) at pH 6, initial concentration of 10 ppm with contact time of two hours

		Lead adsorption			Cadmium adsorption		
Adsorbent	Temperature	Ce (mg/L)	Removal (%)	qe (mg/g)	Ce (mg/L)	Removal (%)	qe (mg/g)
CS	20	8.9	11	0.063	8.8	12	0.069
	25	8.02	19.8	0.113	8.61	13.9	0.079
	30	8.04	19.6	0.112	8.64	13.6	0.078
	35	8.06	19.4	0.111	8.7	13	0.074
	40	8.07	19.3	0.110	8.71	12.9	0.074
GS	20	9.1	9.00	0.051	9.23	7.70	0.044
	25	8.21	17.90	0.102	8.85	11.50	0.066
	30	8.23	17.70	0.101	8.87	11.30	0.065
	35	8.25	17.50	0.100	8.89	11.10	0.063
	40	8.27	17.30	0.099	8.9	11.00	0.063
ES	20	7.3	27.00	0.154	8.5	15.00	0.086
	25	5.65	43.50	0.249	6.66	33.42	0.191
	30	6.4	36.00	0.206	6.9	31.00	0.177
	35	7.8	22.00	0.126	8.2	18.00	0.103
	40	9.4	6.00	0.034	9.6	4.00	0.023
CH	20	6.16	38.40	0.219	7.9	21.00	0.120
	25	5.03	49.70	0.284	5.77	42.30	0.242

	30	5.11	48.90	0.279	5.79	42.10	0.241
	35	5.21	47.90	0.274	5.8	42.00	0.240
	40	5.23	47.70	0.273	5.82	41.80	0.239
GH	20	7.4	26.00	0.149	7.37	26.30	0.150
	25	6.12	38.80	0.222	6.9	31.00	0.177
	30	6.14	38.60	0.221	6.94	30.60	0.175
	35	6.21	37.90	0.217	6.97	30.30	0.173
	40	6.25	37.50	0.214	6.99	30.10	0.172
EH	20	6.9	31.00	0.177	7.1	29.00	0.166
	25	1.7	83.00	0.474	2.77	72.30	0.413
	30	5.7	43.00	0.246	6.2	38.00	0.217
	35	6.8	32.00	0.183	7.1	29.00	0.166
	40	8.5	15.00	0.086	9.5	5.00	0.029

A4: Effect of initial adsorbate concentration on lead and cadmium adsorption using CS, GS, ES, CH, GH and EH adsorbents at pH 6, adsorbent dose of 1.75 g with contact time of two hours at 25°C

		Lead adsorption			Cadmium adsorption		
Adsorbent	C_o (mg/L)	C_e (mg/L)	Removal (%)	qe (mg/g)	C_e (mg/L)	Removal (%)	q_e (mg/g)
CS	10	8.02	19.8	0.113	8.6	13.9	0.079
	15	8.34	16.6	0.381	8.6	13.7	0.364
	20	8.35	16.5	0.666	8.7	13.5	0.649
	25	8.38	16.2	0.95	8.7	13.4	0.934
	30	8.39	16.1	1.235	8.7	13	1.217
	35	8.41	15.9	1.519	8.7	12.6	1.501
	40	8.43	15.7	1.804	8.8	12.3	1.785
GS	10	8.21	17.90	0.102	8.9	11.50	0.066
	15	8.43	15.70	0.375	8.9	11.30	0.350
	20	8.45	15.50	0.66	8.9	11.10	0.635
	25	8.47	15.30	0.945	8.9	11.00	0.920
	30	8.5	15.00	1.229	8.9	10.70	1.204

	35	8.53	14.70	1.513	9	10.50	1.489
	40	8.6	14.00	1.794	9	10.50	1.774
ES	10	5.65	43.53	0.249	6.66	33.42	0.191
	15	7.3	27.00	0.44	7.9	21.00	0.406
	20	7.9	21.00	0.691	8.3	17.00	0.669
	25	8.4	16.00	0.949	8.7	13.00	0.931
	30	8.9	11.00	1.206	9.2	8.00	1.189
	35	9.1	9.00	1.48	9.4	6.00	1.463
	40	9.3	7.00	1.754	9.7	3.00	1.731
CH	10	5.03	49.70	0.284	5.8	42.20	0.241
	15	5.07	49.30	0.567	5.8	42.00	0.526
	20	5.12	48.80	0.85	5.8	41.90	0.811
	25	5.3	47.00	1.126	5.8	41.60	1.095
	30	5.33	46.70	1.41	5.9	41.20	1.378
	35	5.36	46.40	1.694	5.9	41.00	1.663
	40	5.4	46.00	1.977	5.9	40.90	1.948
GH	10	6.12	38.80	0.222	6.9	31.00	0.177
	15	6.14	38.60	0.506	6.9	30.80	0.462
	20	6.17	38.30	0.79	6.9	30.70	0.747
	25	6.21	37.90	1.074	7	30.50	1.031
	30	6.25	37.50	1.357	7	29.90	1.314
	35	6.27	37.30	1.642	7.1	29.40	1.597
	40	6.3	37.00	1.926	7.1	28.70	1.878
EH	10	1.7	83.00	0.474	2.8	72.30	0.413
	15	2.4	76.00	0.72	3.5	65.00	0.657
	20	3.3	67.00	0.954	4.6	54.00	0.880
	25	4.1	59.00	1.194	5.1	49.00	1.137
	30	4.8	52.00	1.44	6.2	38.00	1.360
	35	5.4	46.00	1.691	7.1	29.00	1.594
	40	6.8	32.00	1.897	7.3	27.00	1.869

A5: Effect of contact time on adsorption of lead and cadmium by using CS, GS, ES, CH, GH and EH adsorbents at room temperature, 25 °C

		Lead adsorption			Cadmium adsorption		
Adsorbent	contact time (min)	C_e (mg/L)	Removal (%)	q_e (mg/g)	C_e (mg/L)	Removal (%)	q_e (mg/g)
CS	0	10	0.00	0.000	10.00	0.00	0.000
	30	9.7	3.00	0.017	9.80	2.00	0.011
	60	9.3	7.00	0.040	9.30	7.00	0.040
	90	8.9	11.00	0.063	9.10	9.00	0.051
	120	8.02	19.80	0.113	8.60	14.00	0.080
	150	8.01	19.90	0.114	8.59	14.10	0.081
	180	8	20.00	0.114	8.57	14.30	0.082
GS	0	10	0.00	0.000	10.00	0.00	0.000
	30	9.9	1.00	0.006	9.90	1.00	0.006
	60	9.5	5.00	0.029	9.50	5.00	0.029
	90	9.1	9.00	0.051	9.30	7.00	0.040
	120	8.21	17.90	0.102	8.85	11.50	0.066
	150	8.2	18.00	0.103	8.83	11.70	0.067
	180	8.19	18.10	0.103	8.81	11.90	0.068
ES	0	10	0	0.000	10	0	0.000
	30	9.5	5	0.029	9.7	3	0.017
	60	8.8	12	0.069	9.1	9	0.051
	90	7.3	27	0.154	7.6	24	0.137
	120	5.6	44	0.251	6.7	33	0.189
	150	5.5	45	0.257	6.6	34	0.194
	180	5.4	46	0.263	6.5	35	0.200
CH	0	10	0.00	0.000	10.00	0.00	0.000
	30	8.3	17.00	0.097	9.40	6.00	0.034
	60	7.1	29.00	0.166	8.70	13.00	0.074
	90	6.2	38.00	0.217	8.10	19.00	0.109
	120	5.03	49.70	0.284	5.77	42.30	0.242
	150	5.02	49.80	0.285	5.74	42.60	0.243

	180	5	50.00	0.286	5.70	43.00	0.246
GH	0	10	0.00	0.000	10.00	0.00	0.000
	30	8.8	12.00	0.069	9.60	4.00	0.023
	60	7.5	25.00	0.143	8.90	11.00	0.063
	90	6.9	31.00	0.177	8.40	16.00	0.091
	120	6.12	38.80	0.222	6.90	31.00	0.177
	150	6.1	39.00	0.223	6.87	31.30	0.179
	180	6.07	39.30	0.225	6.85	31.50	0.180
EH	0	10	0	0.000	10	0	0.000
	30	9.2	8	0.046	9.3	7	0.040
	60	4.1	59	0.337	6.8	32	0.183
	90	2.4	76	0.434	3.9	61	0.349
	120	1.7	83	0.474	2.7	73	0.417
	150	1.7	83	0.474	2.7	73	0.417
	180	1.6	84	0.480	2.7	73	0.417

Appendix B: Toxic metal removal efficiency on batch and column flow adsorption technologies from polluted water.

Technology	Adsorbent	Lead adsorption			Cadmium adsorption		
		C_e (mg/L)	Removal (%)	q_e (mg/g)	C_e (mg/L)	Removal (%)	q_e (mg/g)
Batch	ES	5.65	43.00	0.249	6.66	33.42	0.191
	EH	1.70	83.00	0.474	2.77	72.30	0.413
	CS	8.02	19.80	0.113	8.61	13.90	0.079
	CH	5.03	49.70	0.284	5.77	42.30	0.242
	GS	8.21	17.90	0.102	8.85	11.50	0.066
	GH	6.12	38.80	0.222	6.90	31.00	0.177
Column	ES	4.50	55.00	0.314	5.70	43.00	0.246
	EH	0.60	94.00	0.537	1.80	82.00	0.469
	CS	6.10	39.00	0.223	5.10	49.00	0.280

	CH	3.20	68.00	0.389	2.10	79.00	0.451
	GS	6.70	33.00	0.189	5.90	41.00	0.234
	GH	4.40	56.00	0.320	3.00	70.00	0.400

Appendix C: Toxic metal removal efficiency on batch and column flow adsorption technologies from car garage and car washes wastewater.

		Lead adsorption				**Cadmium adsorption**			
Technology	Adsorbent	C_o (mg/L)	C_e (mg/L)	Re (%)	q_e (mg/g)	C_o (mg/L)	Ce (mg/L)	Re %	q_e (mg/g)
Batch	ES	2.01	1.15	42.79	0.049	3.77	2.51	33.42	0.072
	EH	2.01	0.33	83.58	0.096	3.77	1.04	72.41	0.156
	CS	2.01	1.61	19.90	0.023	3.77	3.25	13.79	0.030
	CH	2.01	1.00	50.25	0.058	3.77	2.17	42.44	0.091
	GS	2.01	1.65	17.91	0.021	3.77	3.34	11.41	0.025
	GH	2.01	1.23	38.81	0.045	3.77	2.59	31.30	0.067
Column	ES	2.01	0.9	55.22	0.063	3.77	2.15	42.97	0.093
	EH	2.01	0.12	94.03	0.108	3.77	0.68	81.96	0.177
	CS	2.01	1.22	39.30	0.045	3.77	1.92	49.07	0.106
	CH	2.01	0.64	68.16	0.078	3.77	0.80	78.78	0.170
	GS	2.01	1.34	33.33	0.038	3.77	2.20	41.64	0.090
	GH	2.01	0.88	56.22	0.065	3.77	1.13	70.03	0.151

Re: Removal

Appendix D: Comparison of obtained results with published data

Adsorbent	Metal ion	Removal efficiency (%)	Experimental conditions					Ref
			Conc (mg/L)	pH	T (°C)	Adsorbent dose (g)	Contact time	
Tea waste	Cd^{2+}	99.5%	10	5	25	_	90 min	[54]
Araucaria heterophylla biomass	Cd^{2+}	90.02%	-	5.5	25	-	-	[49]
Biomass of sago stem waste	Pb^{2+}	73.97%	10	5	25	_	60 min	[55]
	Cd^{2+}	52%	10	5	25	-	60 min	[55]
Ficus religiosa leaves	Pb^{2+}	16.95	10-1000	4	25	10	1 hour	[21]
Activated Teff straw agricultural waste	Pb^{2+}	68.9	0.12	6.5	25	-	1 hour	[56]
	Cd^{2+}	82.9	1.23	6.5	25	-	1 hour	[56]
Treated pineapple sterm waste by NaOH	Pb^{2+}	97.08	5	4	60	1	30 min	[40]
	Cd^{2+}	94.62	5	4	60	1	30 min	[40]

Treated pineapple fruit waste by NaOH	Pb^{2+}	78.50	78.50	5	4	60	30 min	[40]
	Cd^{2+}	83.75	83.75	5	4	60	60 min	[40]
Treated pineapple leaf waste by NaOH	Pb^{2+}	100.00	100.00	5	4	60	30 min	[40]
	Cd^{2+}	91.06	91.06	5	4	60	60 min	[40]
Treated pineapple mixed waste by NaOH	Pb^{2+}	98.60	98.60	5	4	60	30 min	[40]
	Cd^{2+}	91.5	91.50	5	4	60	60 min	[40]
CS	Pb^{2+}	19.8	10	6	25	1.75	120 min	This work
	Cd^{2+}	13.9	10	6	25	1.75	120 min	This work
GS	Pb^{2+}	17.90	10	6	25	1.75	120 min	This work
	Cd^{2+}	11.50	10	6	25	1.75	120 min	This work
ES	Pb^{2+}	43.50	10	6	25	1.75	120 min	This work
	Cd^{2+}	33.42	10	6	25	1.75	120 min	This work
CH	Pb^{2+}	49.70%	10	6	25	1.75	120 min	This work
	Cd^{2+}	42.30%	10	6	25	1.75	120 min	This work

GH	Pb^{2+}	38.80%	10	6	25	1.75	120 min	This work
	Cd^{2+}	31%	10	6	25	1.75	120 min	This work
EH	Pb^{2+}	83%	10	6	25	1.75	120 min	This work
	Cd^{2+}	72.30%	10	6	25	1.75	120 min	This work