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SCHOOL OF SCIENCE

DEPARTMENT OF CHEMISTRY

ASSESSMENT OF THE CAPABILITY OF *EUCALYPTUS MAIDEN* SAWDUST AND ITS MODIFIED CELLULOSIC COMPOUNDS TO REMOVE INORGANIC POLLUTANTS CONTAINED IN LEACHATE FROM NDUBA DUMPING SITE

A dissertation submitted to the Department of Chemistry, School of Science, College of Science and Technology, University of Rwanda, in partial fulfillment of the requirements for the Degree of Masters of Science in Environmental Chemistry.

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ABSTRACT

The presence of toxic metals from the landfill leachates is a global problem on environment. These chemicals contribute to the pollution of ground water, soil, and surface. Through bio-magnification and bio-concentration, they also affect the whole ecosystem and cause different diseases on living organisms including human and animals. To contribute to the research of solutions to these problems, modified cellulose extracted from *Eucalyptus maiden* sawdust materials were used to treat leachate which was produced from Nduba landfill site.

Chemical modification of the extracted cellulose was achieved by using Ethylenediamine tetraacetic acid (EDTA) in the presence of pyridine used as catalyst. Both extracted and modified cellulosic compounds were characterized using Fourier-transform infrared spectroscopy (FTIR). The capacity of modified cellulose to adsorb toxic metals, Cu, Cd, Fe, Mn, and Pb was determined using Microwave plasma Optical Emission Spectrometry (MP-AES) by comparing their concentrations in leachate before and after its treatment by cellulosic compounds. The obtained results showed that the removal capacity of the unmodified cellulose was 47.05%, 40.00%, 38.65%, 36.00%, 37.98% while that of modified cellulose was 94.00%, 89.33%, 95.50%, 77.60% and 76.74%, for Pb, Cd, Fe, Cu, and Mn, respectively. Modified cellulosic compounds indicated higher ability to adsorb heavy metals and thus its higher ability to bind the positive charges of the metal ions.

Keywords: Eucalyptus sawdust, Modified cellulose, Adsorbents, Leachate treatment

DECLARATION AND COPYRIGHT

I, Philibert SEWABEZA hereby declare that, this master dissertation entitled **"assessment of the capability of *eucalyptus maiden* sawdust and its modified cellulosic compounds to remove inorganic pollutants contained in leachate from Nduba dumping site"** is my own original work. It is submitted at the University of Rwanda for partial fulfilment for the award of the Degree of Masters in Environmental Chemistry of the University of Rwanda. This dissertation has never been submitted and will not be submitted elsewhere for any other award of a degree or academic certificate.

Student:

Philibert SEWABEZA **Date: / /2024** **Signature:**

Supervisor(s):

I (We) supervisor(s) of this master dissertation, confirm for its originality and that it has been submitted for examination with our approval.

Prof. Theoneste MUHIZI **Date: / / 2024** **Signature:**

Dr. Nestor UWITONZE **Date: / / 2024** **Signature:**

DEDICATION

To my Almighty God,

My parents,

My brothers and sisters,

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Firstly, I thank to the Almighty God for his abundant blessing, guidance and protection.

My appreciation is addressed to my family members, for their love, encouragement and support during my studies.

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CHAPTER 1 INTRODUCTION

1.1 Background

Leachate is liquid that slowly seeps out from wastes deposited together in landfill sites. These rainwaters that seep into landfills through garbage are contaminated with many pollutants, both organic and inorganic, that come from the decaying wastes. The content of the resulting leachate varies depending on the type of the materials landfilled [1]. These materials may include dyes, pesticides, phenols, pharmaceuticals, heavy metals, fertilizers, paints, oils, greases and so on, which are released from various anthropogenic activities including mining activities, textile industries, agriculture, and household activities. Because of many pollutants it contains, leachate may have a detrimental effect on the ecosystem and environment. In fact, it when not controlled, leachates could contaminate soils, groundwater, and surface waters, thereby harming human health and the environment [2]. Through this contaminated ecosystem, contaminants enter animals and other living things, and cause them mild, severe, acute, chronic, or lethal effects [3]. In Rwanda, various landfills are found elsewhere in the country and the strategy of their control is questionable. Pollutants and microorganisms from these landfill sites are reaching human foods through different ways and both soils and waters have been contaminated. It is the responsibility of both policy makers and Scientifics to find a way of good management of wastes and to protect humanity. Decontamination of the polluted areas is also highly needed. Regarding too many research studies go over, biomaterials have a high potential for environmentally friendly for adsorbing heavy metals from leachate treatment techniques as adsorbed. By-products, with or without modification, obtained from furnishing shops are being widely used for adsorption. It was remarked that the modified bio sorbents offered large numbers of metals recovery than bio sorption without modification [4]. Previous studies indicated that wood sawdust, which contain hemicelluloses (22.3%), cellulose (43.9%), pectin, protein, and lignin (26.2%), can be used for adsorption [5, 6, 7, 8].

Among those compounds, the most prevalent biopolymer in use today is cellulose. It is a tightly packed, highly organized crystalline polysaccharide that is held together by both intermolecular van der Waals forces and intramolecular hydrogen bonds. This substance, which is insoluble in water, is essential for the structural upkeep of plant cell walls. Its structural components are linear glycan chains connected by 1,4-glycosidic linkages, with cellobiose residues serving as the repeating unit at various levels of polymerization [9].

This natural polymer, cellulose, can be easily functionalized and changed utilizing a number of chemical processes due to the availability of OH-groups on its surface structure. As a result, cellulose's physicochemical characteristics can be improved upon and altered, making it a malleable and flexible substance. Cellulose has received interest for the removal of inorganic pollutants due to its low cost, availability, flexibility, secure processing, nontoxic, and biodegradable features. It has also emerged as one of the most promising alternatives to synthetic and fuel-based materials. It is a cellulose. Agricultural wastes like sugarcane bagasse, fruits, grasses, or rice straws are just a few additional sustainable plant sources for the synthesis of cellulose [10].

1.2 Problem Statement

Due to the limited knowledge of the chemical components in wastes and the associated health risks, people are deposing mixed wastes in landfill sites without any care. These landfills are located elsewhere in Rwanda and sometimes are close to the human residences increasing the risk of contamination. Due to the degradation phenomena, leachates contain many chemicals and microorganisms that risk to human and living organisms’ intoxication. Organic and inorganic contaminants are among the toxic elements released in leachates. Heavy metals which are known to cause severe risks to both human and animal health as well as the environment by contaminating water, soils, and air, are released among other inorganic pollutants [11]. These chemical elements are known to cause different problems to human health including, damage of liver, kidney, and increased cancer risk [12, 13].

Therefore, when discharged in the environment without prior treatment, leachate may cause different abnormalities in humans including congenital defects [14]. Considering these mentioned bad effects from untreated landfill leachate, the need of efficient methods for removing inorganic pollutants from the leachate is highly required. To answer to this issue, modified cellulose extracted from sawdust may be one of the proposed solutions. In fact, derivatization of cellulose may increase the adsorption capability of this molecule and transform it into more efficient adsorbent for toxic metal ions [15].

1.2.1 Significance of the Study

The culture of landfilling wastes without control is increasing in the world, mainly in developing countries including Rwanda. This bad culture is leading to the environmental contamination and to human intoxication. Due to the ignorance of people about the effects of toxic elements on human life and to the lack of adequate technologies for the treatment of leachate, this bad culture is discharging many contaminants into the environment and therefore seriously affecting lives. So, this study comes to contribute to the research of affordable methods for removing heavy metals from leachate and thus reducing the chance of their bad effects to the environment. Additionally, the study indicated the way of lowering the number of wastes or by-products generated by woodworking processes including sawing, sanding, milling, planning, and routing.

1.2.2 Research Question

Are modified cellulose extracted from sawdust efficiency for removing inorganic pollutant present in the leachate?

1.2.3 Objectives

1.2.3.1 General Objective

This study aimed to examine the efficiency of modified cellulose from *Eucalyptus maiden* sawdust to remove toxic metals from contaminated leachate.

1.2.3.2 Specific Objectives

- ✓ To Prepare and characterize cellulose from sawdust from *Eucalyptus maiden* plant
- ✓ To modify cellulose by using EDTA
- ✓ To remove heavy metals in leachate from Nduba dumping site by using modified cellulose extracted from sawdust of *Eucalyptus maiden* plant.

1.2.4 Hypothesis

Modified cellulose extracted from sawdust will reduce concentrations of toxic metals present in the leachate.

CHAPTER 2. LITERATURE REVIEW

2.1 Generality on cellulose

Cellulose, is a big molecule composed by oxygen, carbon, and hydrogen with chemical formula $(C_6H_{10}O_5)_n$, with molecular weight/ molar mass of 162.1406 g/mol, density 1.5 g/cm³ and the melting point of 260–270 °C [16, 17]. This product is mainly composing plant materials including wood. Biomass of wood such as sawdust is composed by 70% to 80% of carbohydrates which are divided into three important constituents, such as cellulose, lignin, and hemicelluloses, with cellulose taking 43.9% [5]. In spite of its large quantities, cellulosic waste has been discarded in the wood product industry of the developing countries as shown on figure (Figure 2.1). Wooded biomass, for example, is sustainable in large quantities worldwide due to the fact it cannot exploited as food in the present form. Due to the lack of exploring technologies, the existence of sawdust hills in developing countries is constituting a big concern for the environmental pollution through the release of dusts and gases from its degradation [18].

Figure 2.1: Sample of sawdust

This sawdust is however known to be useful source of Cellulose which is the most prevalent biodegradable polymer with the potential of being used as an effective adsorbent for a variety of contaminants, including dyes, oil, salt, and heavy metal [20]. This glucosic polymer can also come from other crops, such as flax, cotton, hemp, sisal, corn, as well as wheat, rice, sorghum, barley, sugar cane, pineapple, bananas, and coconut crops [21]. The isolation process of cellulose from sawdust is known as pulping where cellulosic compounds are separated with other sawdust components including lignin, hemicelluloses and obtained as strong and pure fibers [22]. Yet, cellulosic compounds can be used to make paperboard, paper, cellophane, etc. Due to existence of many hydroxyl functional groups, materials containing cellulose are effective to adsorbing substances which are positively charged, such as heavy metals [23, 21]. This wood material is however likely attacked by many microorganisms and other natural events including heat, sun, and humidity and so on. Therefore, scientific studies have been conducted to chemically modify this polymer prior to the improvement of its properties and therefore allowing it to resist to heat, humidity, abrasion, radiation and microbial attacks [24].

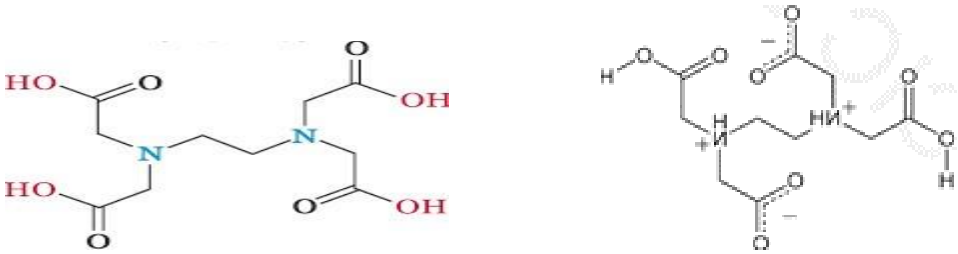
2.2 Chemical treatment of Cellulose

Due to its chemical composition which is likely attracting many living organisms destroying cellulosic materials, due also to its high uses in developed and industrialized countries, cellulose was intensively modified to protect it against any possible enzymatic degradation [25]. This modification is a crucial step in the cellulose conversion process aiming at its durability and applicability in various scientific domains [26].

Modification of cellulose refers to chemical changes of its hydroxyl groups starting with the more reactive C-6 position as the primary hydroxyl group. However, carbon atoms of cellulose can also be to strengthening the modification reactions including nucleophilic displacement reactions [27]. Yet, oxidation reactions to introduce carbonyl- or carboxyl groups was also realized on cellulosic skeleton [28]. Depending on the reacting agent used, modification can increase the adsorption capacity of cellulose. When ethylenediaminetetraacetic acid (EDTA) is used as reactant, it is combined to cellulose making EDTA-Cellulose or Cellulose composites able to complex majority of toxic metals including Cu (II), Zn (II), Cr (VI), Ni (II), and Pb (II) [15]. This capability of Ethylenediamine tetraacetic acid (EDTA) to chelate a few numbers of metal ions resides from the availability of lone-pair electrons which facilitate to its improved reactivity and effectiveness towards metals uptake [29].

2.3 Modification of cellulose with EDTA

Ethylenediaminetetraacetic acid (EDTA) is a polyprotic acid with an anionic ligand made up of two amine groups with lone-pair electrons, two carboxylic acid groups, and four carboxylic acid groups (Figure 2.2).



(a) EDTA **(b) EDTA ion**

Figure 2.2: Chemical Structure of EDTA [30].

Due to its strong ability to bind metal cations, this molecule is considered among the main complexing chemical agents. It can take up metals from both organic and inorganic media, complex them and remove them through precipitation phenomena [31, 32].

During modification with EDTA, cellulose is chelated to produce Cell-EDTA that improve its adsorption capacity to heavy metals [33] had been successfully replaced on the cellulose backbone to boost cellulose's ability to bind complex metal ions during adsorption. The linear glycan chains in cellulose's chemical structure are packed into micro-fibrils and joined by -1,4-glycosidic bonds with cellobiose residues. These micro-fibrils are kept together by both intramolecular hydrogen bonds and intermolecular van der Waals forces [34, 35]. The cellulose backbone had been successfully replaced with an EDTA group throughout the alteration process (Figure: 2.3). The bonds of the CH_2, CH, OH, and C-O in the cellulose backbone overlapped with the vibrations of the C-O and OH of the carboxyl group [35].

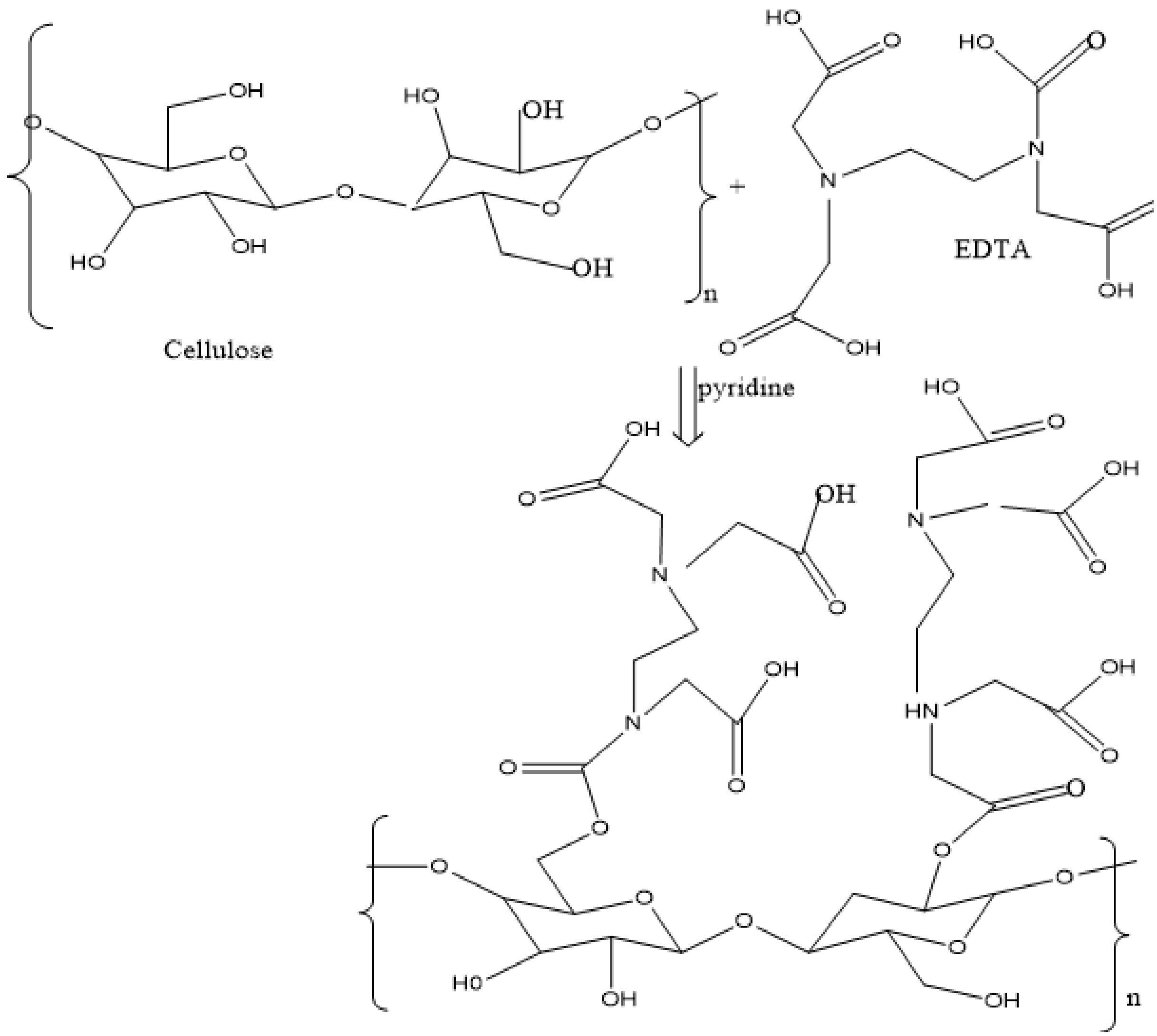


Figure 2.3: Chemical reaction of Cellulose with EDTA

It had been successfully replaced on the cellulose backbone to boost cellulose's ability to bind complex metal ions during adsorption. The linear glycan chains in cellulose's chemical structure are packed into micro-fibrils and joined by -1,4-glycosidic bonds with cellobiose residues. These micro-fibrils are kept together by both intramolecular hydrogen bonds and intermolecular van der Waals forces [34, 35]. The cellulose backbone had been successfully replaced with an EDTA group throughout the alteration process. The bonds of the CH_2, CH, OH, and C-O in the cellulose backbone overlapped with the vibrations of the C-O and OH of the carboxyl group [35].

2.4 Solid waste Management

Solid waste management refers to the entire collection, treatment, and disposal of solid wastes. The waste management procedure involves collecting the rubbish from various sources and disposing of it. This process includes the collection, transportation, treatment, analysis, and disposal of waste. Due to inadequate solid waste management, particularly by waste management organizations, the accumulated wastes begin to pile up and constitute a threat to both the environment and the general public [36].

Massive amounts of trash are dumped, forcing biodegradable materials to decompose and break down in abnormal, uncontrolled, and unclean conditions as shown on the following figure (Figure 2.4 (a) and (b))**.** After a few days of decomposition, it turns into a breeding ground for numerous infectious organisms and disease-causing insects. The place emits a foul stench and loses some of its attractiveness [37].

(a) **(b)**

Figure 2.4: NDUBA Municipal solid waste dumping site

Toxic metals, chemicals, and other dangerous pollutants are among the solid wastes gathered from many industries. When these wastes are released into the environment, they can cause biological and physicochemical issues; the chemicals may seep into the soil and contaminate the groundwater; they may also affect the soil productivity in that specific location [38].

garbage sorting, garbage spreading, soil coverage, compaction, leachate management within landfills, and liquid waste disposal in the ponds dug in the vicinity of the dump make up the bulk of everyday landfill management [39]. As seen on figure 2.5, the most and least preferred are prevention and disposal, respectively.

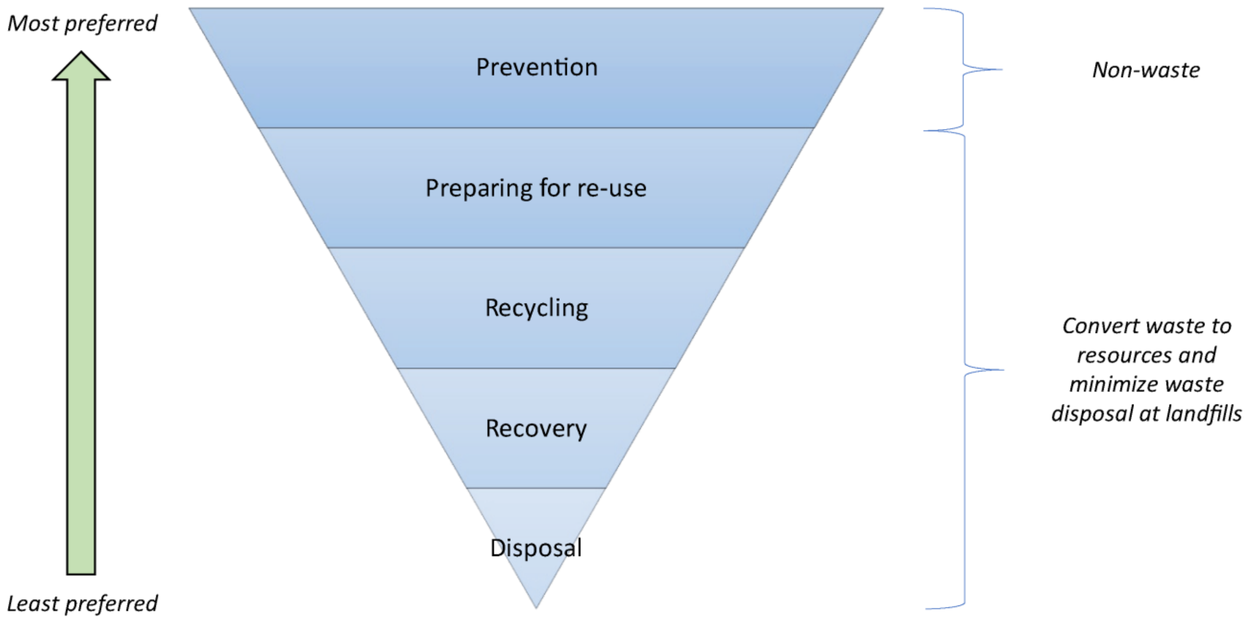


Figure 2.5: Municipal Solid Waste Management [39]

In a few rare instances, hazardous wastes may mix with regular trash and other flammable wastes, making disposal more difficult and dangerous.

Dioxins and other harmful gasses are created and released into the air when hazardous wastes, including paper and other scraps, are burned. These ailments, such as cancer, skin infections, and chronic diseases, are the outcome [40].

2.5 Biological and chemical composition of Leachate

When MSW is dumped in landfills, it undergoes chemical, physical, and biological changes and interactions that release nutrients, elements, and gases [41, 42]. Heavy metals, ammonia nitrogen compounds, hazardous organic and inorganic pollutants, as well as other dissolved and suspended pollutants, are frequently found in leachate. To limit the amount of leachate and avoid the negative outcome of leachate pollution, careful management of landfill leachate is necessary. Depending on the age of the landfill and the sort of waste it contains, a landfill's composition might vary greatly. Both dissolved and suspended particles are typically present [43].

Due to the MSW contain with different waste such as biologically non-degradable and degradable organic substances, nitrogen, chlorinated salt, humic substances, ammonia, and heavy metals (HMs). Also, a leachate characterized by different contaminants, like organic pollutants, inorganic pollutants that has the great effect on human health are heavy metals [44].

The quality and quantity of leachates collected are examined at regular intervals, and directly in the landfill at the inlet into the segregated or separated leachate pond. Total amount and concentration of leachates produced in the open landfill is affected by total rainfall in location by investigation. By considering the frequently and occurrences of higher water rain, the amount of leachates increases and the concentration of pollutants are less, whereas, the leachates in dry season become more concentrated less in volume [44, 45].

2.5.1 Leachate Characterization

Leachate is a by-product fluid produced by liquids in the water and outside pool, including rainwater, filtering through the debris in a landfill or solid waste dumpsite. Due to their physical, chemical, and biological changes that will take place in landfills. General, the commitment of pollutants from leachates in the Municipal dumping site contain higher amount of heavy metal and other types of inorganic pollutant [15, 18].

In developing country and under-developing country is faced with the problem of lack of waste segregation of MSW, landfill or dumping sites are characterized by mixed biodegradable and non-biodegradable waste materials.

Municipal Solid trash at Landfills may include the following examples: food trash, home garbage, plastics, paints, mercury-containing waste, batteries, and other products with excessive metal content or hazardous compounds.

However, because the dissolved organic matter also contains inorganic elements including calcium, magnesium, sulphate, chloride, and ammonia as well as acids, alcohols, aldehydes, and sugars, they are generally present in considerably larger concentrations than in regular aquifers [46].

The leachate intrusion from MSW was distinguished by various contaminants, including heavy metal: Fe, Pb, Ni, Cd, As, Cr, Cu, and Hg are common heavy metals that are introduced into the leachate along with other soluble organic and inorganic components such ammonium, phosphorous, and sulfate. Young leachates are mostly composed of volatile fatty acids, which gradually diminish in older landfills. Humic and fulvic acids, along with suspended particles, are typical characteristics of the leachate percolate in the old landfill. Other harmful pollutants found in landfills include halogenated organic compounds like PCBs and dioxins, phenols, pesticides, polyethylene, and aromatic hydrocarbons including benzene, toluene, ethylene benzene, and xylene, are other types of toxic pollutants present in landfill.

Dependent on landfill location and municipal solid waste composition; landfills also protect against some dangerous germs, primarily bacteria of the coliform kind and some viruses. On the other hand, environmental conditions including pH and temperature fluctuations may render these microbes inactive [47].

The various microorganisms, degrade the various different constituents of waste present in the landfill and producing their metabolic products and also producing other decaying organic matters as by-product. From side to side of the landfill microorganism decomposing all different waste like organic and inorganic constituents in the landfill site through chemical reactions, water is an important factor. Landfill gases released into atmosphere in the form of methane and carbon dioxide, it contributes to the greenhouse gases. The greenhouse gases released have a gradually increasing impact on the people living and working in close proximity to landfill sites, causing threats of environment and safety.

The quality of leachate produced in the landfill depends also on the age of the landfill. For example, in the old landfill, which is characterized by a pH range of 7.0 to 7.6, there is a propensity to develop leachates that are neutral or mildly alkaline in composition. According to research by scientists Slomwcznska and Slomcyznski [48], an extremely ancient landfill produces leachates that are alkaline in character and have a pH between 8.0 and 8.5. On the contrary, pH values range from 3.5 to 6.5 in leachate produced during the first phase of decomposition of waste that has been deposited at a new landfill. These ranges are indicative of the leachate which are acidic in nature, as well as indicate the presence of a cationic acid or phosphate ions in the leachate [48].

2.5.2 Effect of Leachate

Leachate poses serious risks to natural groundwater resources. When it rains, solid trash disposed of outdoors or in landfills is collected, allowing liquid waste and the byproducts of its decomposition to enter the water via waste deposition. Moreover, water may enter through sub-currents in the earth, infiltration from precipitation, or any other means. Numerous organic and inorganic substances are accumulated in leachate that collects at the bottom of landfills, percolates through the soil, and eventually enters groundwater. Moreover, groundwater sub-current or water occurring underneath the earth's surface, from precipitation or any other reasonableness of penetration of water. At the base of the dump, leachate containing a large number of natural and inorganic substances gathers, permeates the soil, and enters the groundwater [49].

Groundwater contamination is more likely to occur near landfills due to the potential polluting source of leachate from the neighboring waste site. Those contamination of groundwater is the important factor that promote a serious risk for users of local water sources as natural resources and the environment.

The impact of leachate on the surface water and ground water has been specifically increased to a number of different studies in recent years and gained significant importance as a result of the extensive increase in population. Experimental determination of the impurities or estimation through mathematical modeling can be used during ground water contamination assessment [50].

Depending on the erosion leachate produced in the dapping landfill site contribute to the contamination of agriculture soil and surface water even the ground water nearby water ways, where it contaminates drinking water supplies and spreads disease, due to soil percolation. Also contains all kinds of harmful chemicals, which are known to cause environmental issues on ecosystem as well as serious harm to animal and human health. In addition, adjacent soil, surface waters and groundwater may be contaminated by leakage of leachate from landfills. It is well known that the flow of leachate into water bodies such as rivers, lakes and groundwater will reduce the water quality, which in turn will disturb the natural ecosystems of the soil contaminated by leachate, which is usually concentrated in terms of chemical characteristics rather than mechanical modification. Depending on the nature of leachate, different chemicals that may contribute to its electrical conductivity and progressively affect soil interaction can react differently in soils compared with ordinary water [51].

2.5.3 Leachate Treatment Method

Due to the effects of inorganic pollutant discharging in environment from untreated leachate in environment, many different methods are proposed by different scientist. Adsorption method is one of the effective methods for leachate treatment due to their low cost of maintenance, use of small time, high efficiency, and no chemical addition. A removal efficiency, increase as operational time increase [52, 53].

2.6 Determination of heavy metal by using MP-AES

2.6.1 Mass Plasma Atomic Emission Spectroscopy

Numerous elements, as well as alkaline and earth alkaline metals, transition metals, as well as several metalloids and non-metals, have all been determined using the Mass plasma optical emission spectrometry (MP-AES) instrument. It offers high sensitivity, with superior performance and provide cost efficient and flexible analysis compared to Flame Atomic Absorption Spectroscopy [54]. Atoms were excited to produce an equal emission during the determination using nitrogen-based plasma, and these emissions were then monitored. When compared to a helium plasma that was previously employed, the plasma's greater temperature wasn't high enough to produce enough excited fluorine atoms for their detection. Since the helium plasma has little power, measuring watery samples is challenging, as nitrogen plasmas tend to have [55, 56]. The Agilent 4200 Microwave Plasma Atomic Emission Spectrometer are used for metal analysis [57].

Additionally, the main emission lines of the halogens are in the vacuum-UV region, with fluorine being no exception with a resonance line at 95.5 nm. Because of oxygen interference, it is impossible to detect these elements with standard optical equipment [58, 59, 56].

As an analytical method for figuring out the amount of metal atoms or ions in a sample, MP-AES is defined. Since around 75% of the chemical elements on earth are comprised of metal, an analytical technique is also employed to ascertain how much of each element is present in a sample. Metal presence in a substance is sometimes beneficial, however metals can also be contamination sources, or poisons that contribute to the danger for living organisms [60]. Consequently, during metal measuring the content of metal is critical in many different applications in this study we demonstrate the uses of MP-AES to determine the concentration of metal content in the leachate collected from NDUBA landfill site.

2.6.2 Working Principle of Mass plasma atomic emission spectrophotometer

The basic principle of MP-AES is that after specific element of an atom is providing an external energy by excitation, it characterized by emits the pattern of radiation (light) at wavelengths creating a spectrum emission that reflects it back to the surface. The microwave plasma is the source of the atomic emission in MP-AES. MP-AES an atomic emission spectrophotometer (AES) interfaced with microwave-induced plasma (MIP) enables microwave energy to radiate a plasma release utilizing nitrogen given from a cylinder gas or hauled from outside ambient air, eliminating the need for gas sources at remote locations. In MP-AES measurements, the samples are often nebulized early to interact with the plasma, and the atomized sample completely traverses the plasma, promoting electrons to the excited state [61].

For the energy levels diagram atom is exposed to its own single wavelength, because every electrons within every atom exist at different energy levels. Atoms can absorb the photons or energy by moving electrons from a level of ground state to the level of excited states, and radiation of electron absorbed by energy is directly associated with transition that occurs throughout this process**.** Additionally, every unique element has subsequently electronic structure and absorbed radiation represents a unique property of each individual element also can be measured [60, 62].

2.7 Fourier transform infrared spectroscopy FTIR spectroscopy

An infrared spectrum of interest or emission from a solid, liquid, or gas can be obtained using the Fourier transform infrared spectroscopy (FTIR) technique, which turns raw data or an interferogram into the right spectrum. In addition to measuring how much light a sample absorbs at each wavelength when the plasma and electrons are raised to the excited state, an important FTIR spectrometer also simultaneously captures high resolution spectrum data over a broad spectral range [63, 64].

2.7.1 Fundamental components of an FTIR system

The components of Fourier-transform infrared spectroscopy (FTIR) were grouped into five (5) part: infra-red source, interferometer, gas sample, detector and signal and data processing as shown on (Figure: 2.6).

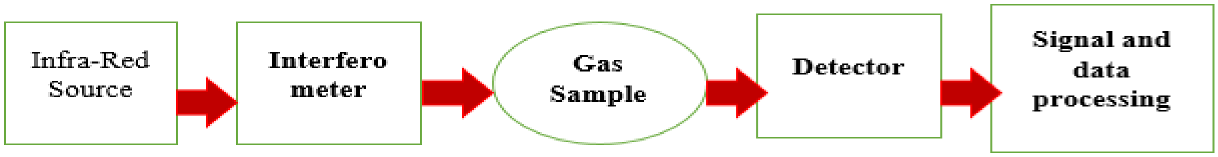


Figure 2.6: Components of an FTIR system

Infrared Radiation Source: For mid- and near-IR measurements, infrared radiation sources are typically utilized in FTIR spectrometers. When heated electrically, a Nernst filament or globar emits infrared radiation between 1000 and 1800 0 F. A golbar is a rod made of silicon carbide, whereas a Nernst filament is an elemental material with high resistance that is mostly made of sintered oxides of zirconium, cerium, and thorium. Globar is more functional at lower frequencies, while near-IR have short wavelengths and require a higher temperature source, typically a tungsten-halogen lamp.

Interferometer or Bean splitter: A beam splitter can be employed alternatively to cover a large spectral range in FTIR and transmits and reflects 50% of the incident beam. While far-IR beam splitters are often made of polymer films with a restricted wavelength range, mid-IR beam splitters are typically made of KBr with a semi-reflective germanium-based coating. One beam travel through the beam splitter twice for Michelson interferometer beam transmission, whereas the second beam only passes once [65, 64]**.**

The Sample: Depending on the type of inquiry being done, beam is also transmitted through or reflected off for the sample surface. Energy at its characteristic frequency is absorbed by that sample. It measures the interferogram signal as the detector. Selective or nonselective detectors are both possible. The thermal radiant energy is converted into electrical energy.

Detector: Selective detectors are those whose reaction is proportionate to incident energy but mostly independent of wavelength, whereas other types of detectors are those whose response is directly proportional to incoming energy. Detectors that are not selective.

Computer: To get the final infrared spectrum for analysis, the computer executes the Fourier transformation [66, 67].

CHAPTER 3. MATERIAL AND METHOD

3.1 Sampling Site

Nduba landfills (Figure:2.1) produce leachate mixtures with various organic and inorganic contaminants (heavy metal) due to the lack of a scientifically sound, sanitary landfill design at this location. Municipal solid waste (MSW) is dampened by decomposing bacteria, which produce inorganic pollutants at landfill sites. When it rains, water washes the pollutants out of the garbage. Leachate samples were collected from Nduba landfill site where all municipal solid wastes collected from different sites of Kigali city were dumped.

Figure 3.1: Nduba dumpsite

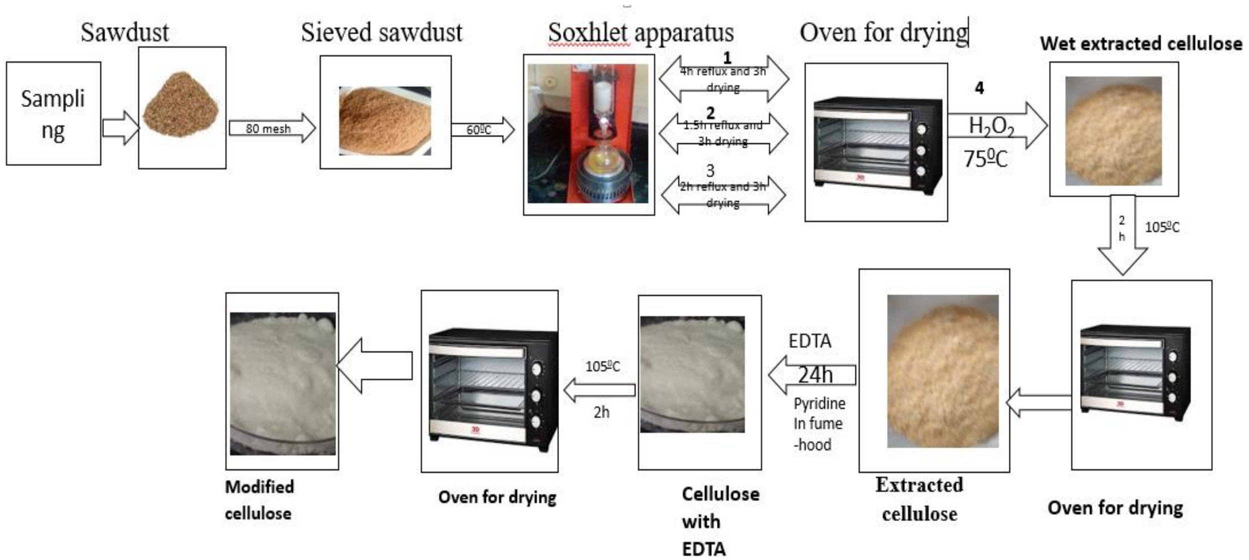
3.2 Sampling method

Pre-cleaned 1 liter of polyethylene plastic bottles container are used to take samples. Liquid detergent and 1% nitric acid were used to wash and soak these containers. As a result, deionized water was used to rinse the sample containers. Leachate samples were taken at two of the margins of the Nduba MSW dumping site, and containers were always washed with the water/leachate sample before full collection. Second leachate sample site was obtained at a distance of 8-9 m from the dumping and depth of 60 cm, whereas the first leachate sample were collected at the edge of the dumping site at a distance of 6-7 m from the dumping site and depth of 50 cm.

In order to preserve the samples prior to the analysis of heavy metals, strong nitric acid was used, and samples were then shipped on ice to the laboratory of the University of Rwanda, College of Sciences and Technology. All samples were stored in the dark place at −4°C until further analysis [68].

3.3 Extraction of cellulose from Sawdust

In extraction of cellulose from the *Eucalyptus maiden* plant (Figure: 3.1), the Kurschner- Hoffer method was used. To proceed, 16 grams of sawdust were placed in a Soxhlet extraction system and using 400 mL of the mixture of a toluene: ethanol (1: 1), a reflux heat of four hours was conducted. At the end of this time, toluene and ethanol were separated from the mixture by filtration and then the compounds soluble in toluene: ethanol were obtained by evaporation of these solvents by a rotary evaporator. The rernnant, consisting of sawdust free of oils, was dried in an oven for three hours and weighed. Thereafter a volume of 400 mL of the mixture of ethanol: nitric acid (4:1) was added to the rernnant and refluxed for 1.5 hours. When the reflux ended, the product was filtered and washed with distilled water. The obtained liquid was evaporated off and the residue obtained was weighed, this residue (residue 1). This residue consists of acid-soluble lignin. Again, the solid obtained from filtering consisting of cellulose and hernicellulose (residue 2), was dried in an oven for three hours and weighed. Finally, the rernnant was returned to reflux in 400 mL distilled water for one hour, 280 mL NaOH 0.4 N was added, and the reflux continued for an additional hour. The rernnant, consisting of pure cellulose, was then filtered, washed and hydrogen peroxide (H_2O_2) 3 % (w/v) was added for bleaching the cellulose, the final product (residue 3) was filtered, washed with distilled water and dried at 105 ºC for three hours. The obtained solid was kept in vials for further studies [25, 24].



- ✓ 1: (1: 1) Toluene: ethanol mixture
- ✓ 2: (4:1) ethanol: nitric acid mixture
- ✓ 3: distilled water and NaOH 0.4 N
- ✓ 4: (H2O2) 3 % w/v for bleaching cellulose

Figure 3.2: Extraction of cellulose from Sawdust

3.4 Chemical modification of cellulose with EDTA

During cellulose modification (Figure: 3.3), 2 grams of cellulose were mixed with 6 g of EDTA and 50 mL of pyridine and then the mixture was heated at 65^{0}C for 24 hours. This experiment was conducted in fume hood. After heating, the obtained solid was washed with distilled water and dried in the oven for two hours at 105^{0}C [69, 70].

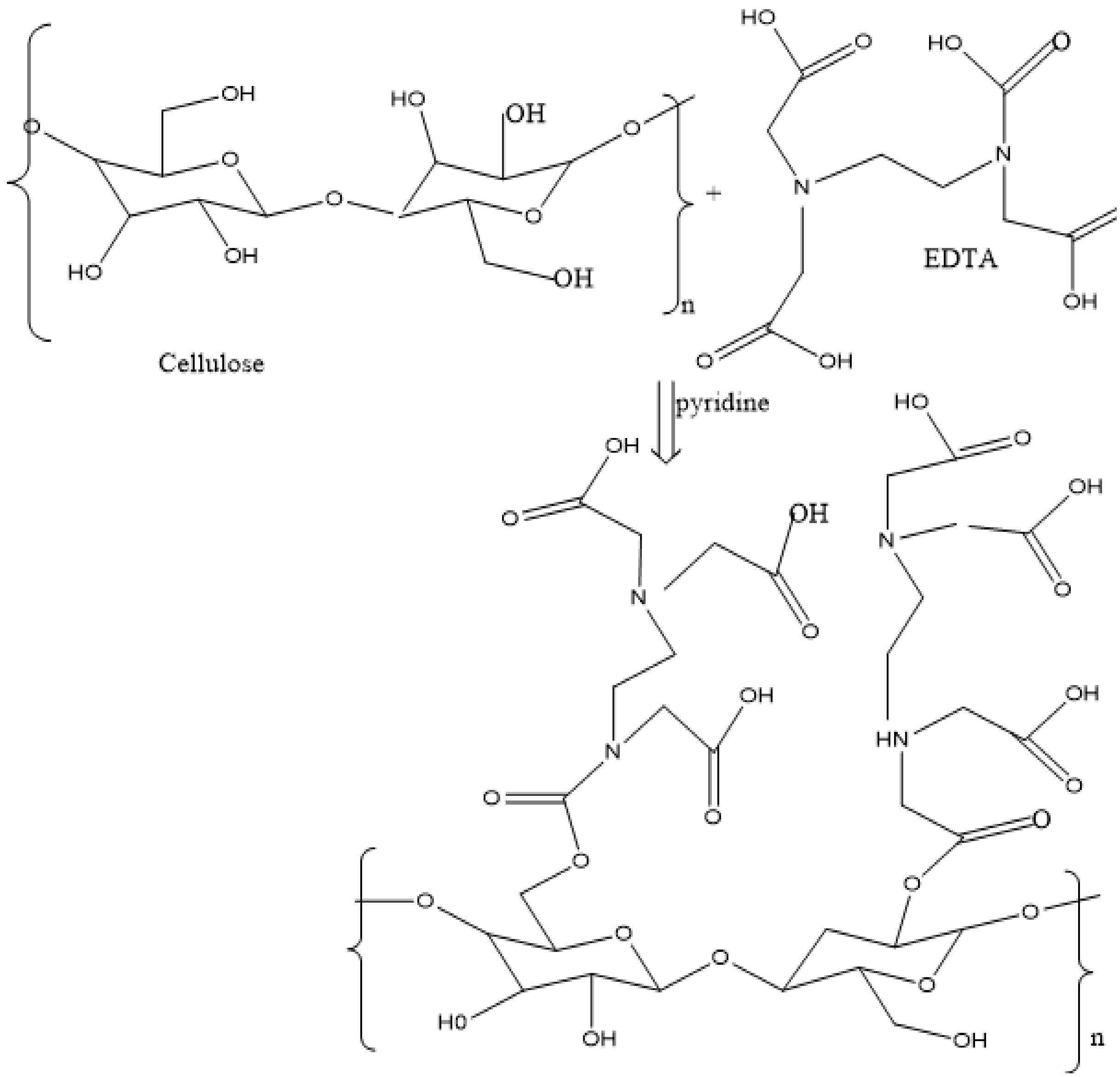


Figure 3.3: Chemical reaction of Cellulose with EDTA

3.5 Chemical characterization of the extracted and modified cellulosic compounds

The remnants obtained after each treatment were weighed and characterized using a Fourier transform infrared (FTIR) with 32 scans per analysis and on the range of frequency varying between 650 to 4000 cm^{-1}. When analyzing cellulose, samples were put on a rotating mirror that came into contact with the Cassegrain condenser of an infrared spectrometer using the Fourier transform. The FTIR light is redirected beginning in the interior of the crystal, but it only travels a short distance before entering the cellulose sample, where it is partially absorbed. Because only a little sample was required to come in close contact with the FTIR spectrometer's surface, sample preparation was necessary. The differential scanning calorimetric (DSC) used was TA instrument MDSC 2920, the conditions used in the analysis were: temperature programed from 25 to 300 ºC, 20ºC/min ramp, 50 mL of N_2 per minute.

3.6 Assessment of the adsorption capability of cellulose and modified cellulose

3.6.1 Samples preparation and digestion

Before analysis, the leachate sample was prepared by digestion; during the digestion, 50 mL of the leachate sample was transferred into a 250 mL volumetric flask, 35 mL of nitric acid, and 1:3 hydrochloric acid was added (a freshly prepared acid mixture of 65% HNO3 was added, and 37% HCl was added). The resultant mixture was cooked for three hours, or until the sample had completely dissolved, using a combination of heating at 1500C and shaking at 2500 rotations per minute. To prevent sample loss during the digestion processes, 2 mL of deionized water was slapped on the inside walls of the beakers [71]. The samples were then filtered using filter paper at the conclusion of the digestion operations. The pH was then adjusted by raising the final volume of acidity to an acceptable level by adding enough deionized water [72, 73].

3.6.2 Determination of the capability of both cellulose and modified cellulose to remove heavy metals from leachate

To assess the capability of both extracted cellulose and the modified cellulose to remove heavy metals from leachate, concentrations of the concerned heavy metals were determined in the sample before and after using cellulose or modified cellulose as adsorbent. Five toxic metals, Cd, Fe, Cu, Pb, and Mn, which were suspected to be present in the leachate were analyzed. The analysis was performed using a Microwaves plasma atomic emission spectrophotometer (MP-AES). Each sample was analyzed three times, with the acquisition parameters of 20, 15 and 20 seconds for sample uptake delay, stabilization time and read time, respectively [74]. Toxic metals were analyzed at different wavelengths of 213.857, 371.993, 324.754, 405.781 and 403.076 nm for Cd, Fe, Cu, Pb and Mn, respectively. The percentage of the removal efficiency was calculated by the following mathematical formula:

$$\text{P R} = \frac{(CBT - CAT)}{CBT} \times 100$$

Where: **PR:** stand for Percentage of Removal

CBT: stand for Concentration Before Treatment

CAT: stand for Concentration After Treatment

CHAPTER 4: RESULT AND DISCUSSION

4.1 Extraction of Cellulose

After mixing sawdust with different reagents and refluxing in soxhlet extraction system, the solution was becoming darker. Thereafter, hydrogen peroxide H_2O_2 3 % w/v was added under magnetic stirrer with speed of 2500 rotation per minute to the filtrating rernnant for bleaching the cellulose. Then the observed increase of the viscosity demonstrated that the dissolution of the *Eucalyptus maiden* sawdust has been achieved. After the cellulose product was obtained, it was further bleached, and washed with distilled water until the pH became neutral [75].

4.2 FTIR characteristics of the extracted cellulose

To confirm the cellulosic nature of the extracted compound, IR spectrophotometer was used. The obtained IR spectrum of the extracted cellulose (Figure 4.1, spectrum in red) indicated different absorption bands which were in close relationship with those from the spectrum of the commercial cellulose (spectrum in black). The wide range of peaks in the spectra which were approximately at 3300-3400 cm^{-1}, indicated the stretching vibrations of the O-H bonds of cellulose molecules which were absorbed onto the matrices of the samples. Bands around 2900 cm^{-1} is for aliphatic C-H symmetric and asymmetric stretches [76]. The presence of cyclic C-C bonds in glucose units can be seen in the appearance of the peaks between the regions from 1500 to 1600 cm^{-1}. These bonds can be comparable to double bonds. In the meantime, it is possible to indicate a stretching vibration from C-O bonds of hydroxyl groups for large peaks which have been observed in this region between 1050-1070 cm^{-1} [77]. The same observations were done by the stretching and bending vibrations of the C-H, O-H, and C-O bonds in the cellulose backbone were attributed to the observed bands at 1584, 1329, 1025, and 896 cm^{-1} [35].

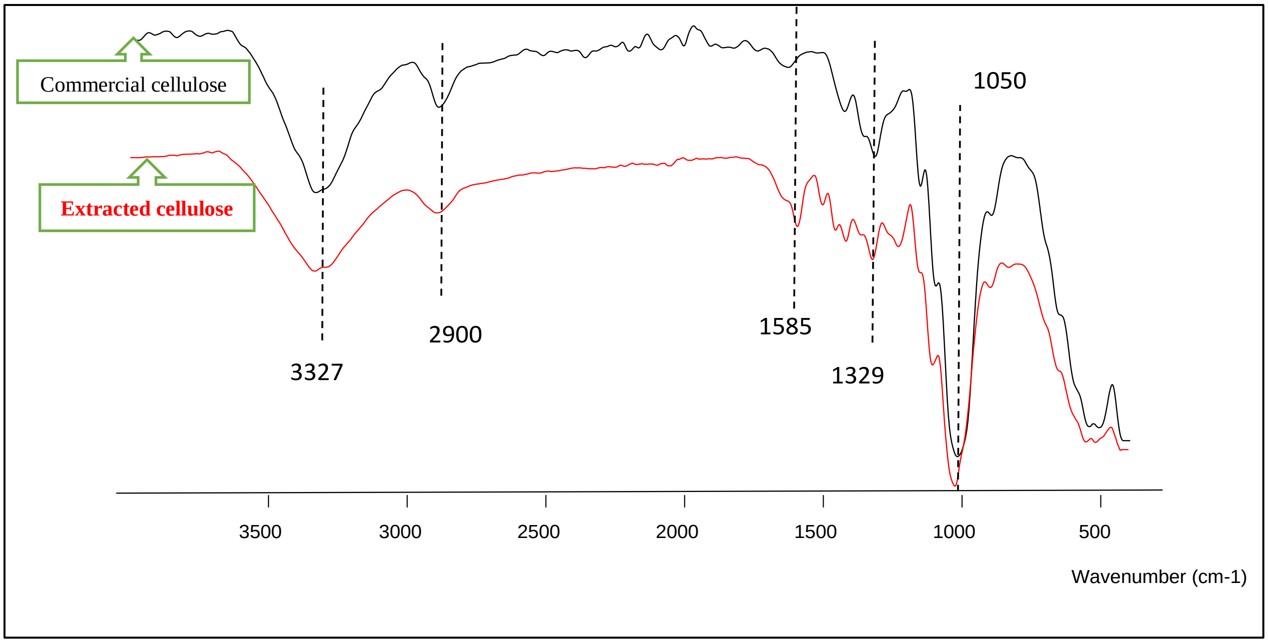


Figure 4.1: Infrared spectrum of the extracted cellulose

4.3 Modifications of the Extracted Cellulose

To confirm that extracted cellulose was successfully modified by EDTA, infrared spectrophotometer was also used. New bands of the robust absorption were emerged at 1604 cm^{-1} and at 1700 cm^{-1} in the modified cellulose (Figure 4.2, blue spectrum), indicating the presence of the carboxyl group (O=C-O- stretching). Additionally, there was a greater adsorption peak at about 1417 cm^{-1}, which indicated the O-H bending vibration of carboxylic groups. Furthermore, absorption bands at 1300 cm^{-1} were attributed to C-O carboxylic groups stretching vibration while bands at around 1220 cm^{-1} indicated C-N stretching vibration. The same observations were done by previous researchers [78]. This indicated that the alteration had successfully swapped an EDTA group onto the cellulose backbone [79].

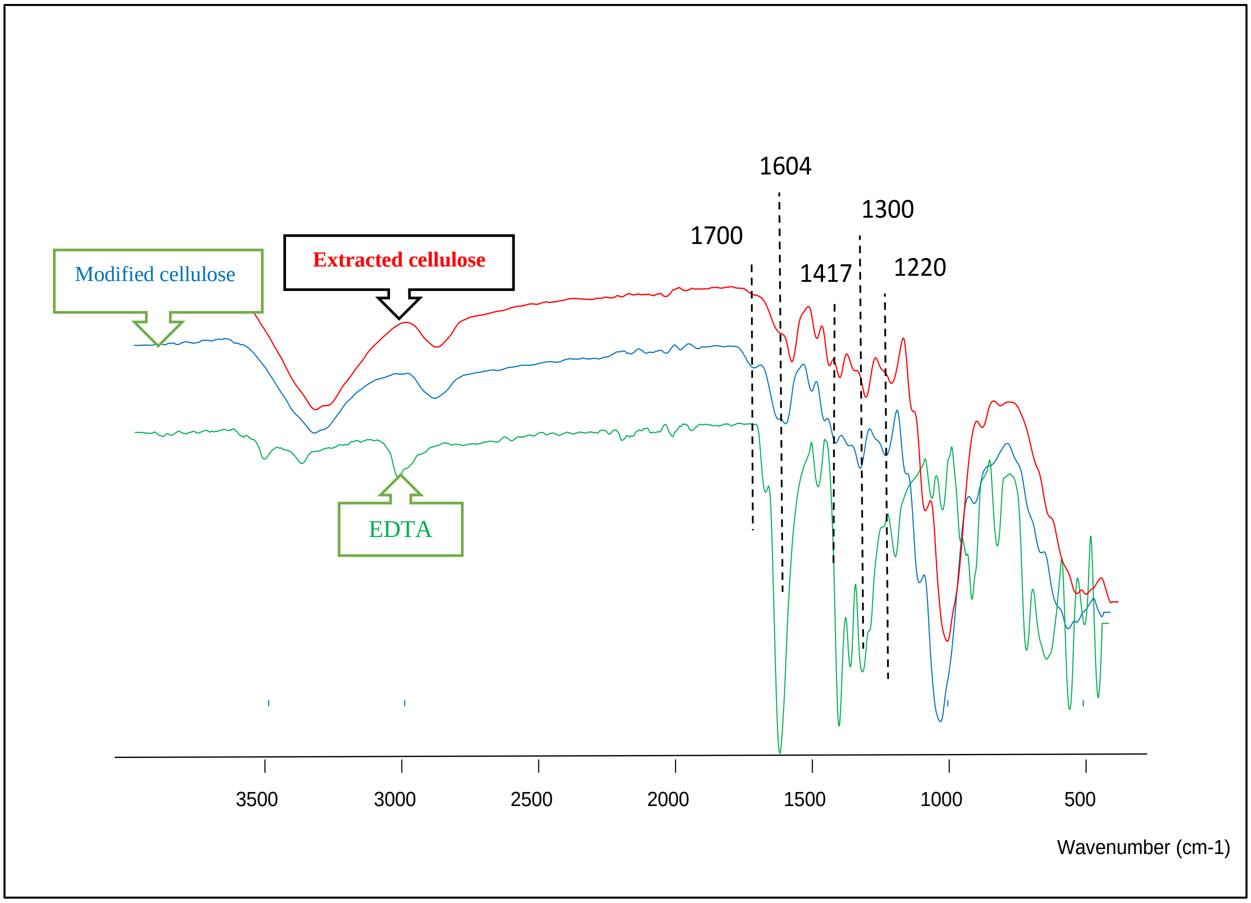


Figure 4.2: IR Spectra of modified cellulose by EDTA (in blue), EDTA spectrum (in green) and extracted cellulose (in red)

4.4 Concentration of heavy mental in the leachates

After analysis heavy metal in the leachate the result showed that the higher amount of heavy metal in the leachate were Zinc (Zn^{2+}), Lead (Pb^{2+}), Copper (Cu^{2+}), Iron (Fe^{2+}), and Manganese (Mn^{2+}). The results showed that among other metals, iron was one which had the highest concentration (Figure 4.3). The higher concentration of iron in Nduba landfill is explaining the type of solid wastes which are dumped there. According to previous reports [80], Nduba landfill is receiving 1% of metallic wastes, and these are judged to be a source of the obtained results in this study.

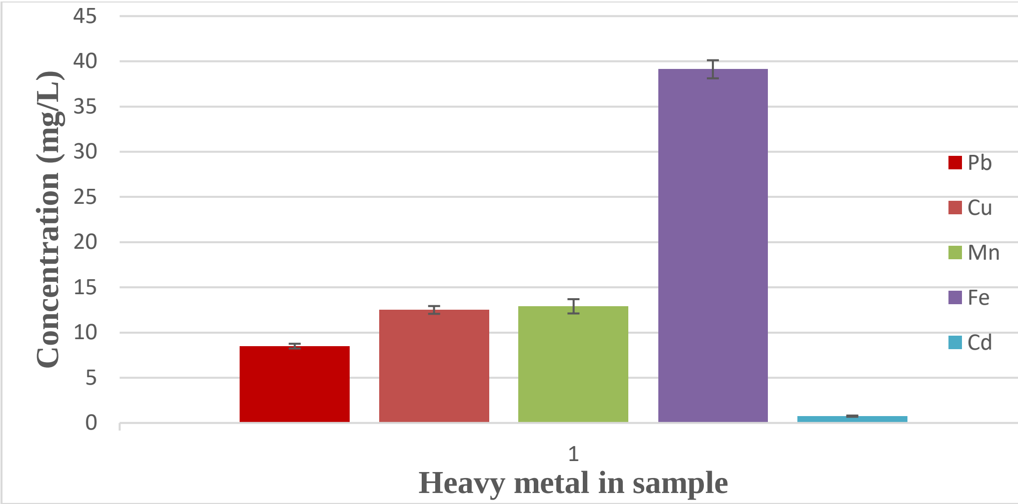


Figure 4.3: Concentration of heavy metal in Nduba leachate

The leachate collected at Nduba dumping site had a pH value ranged between 8 and 9. The value of the pH observed was close to the pH value of 8.45 described for other leachates produced from other different land fill sites studied [81, 82]. In comparison with Nyanza landfill, which was banned in the past years due to its bad management, Nduba landfill, was found to be at the same level of contamination by heavy metals with Nyanza landfill. In fact, in 2012, Nyanza landfill was found to contain 39.2, 8.5, 0.75, and 2.8 mg/L for iron, lead, cadmium, and copper, respectively, which are close to the results found in this study, 39.12, 8.5, 0.75, 12.5 and 12.9 for iron, lead, cadmium, copper and manganese, respectively (Figure 4.4). The only difference was found on copper where its concentration at Nduba was 12.5 mg/L against 2.8 mg/L found at Nyanza at that time [83]. These results indicated that Nduba landfill is highly contaminated by iron which was found to occupy 53.3% of the detected heavy metals. It was followed by both copper and manganese occupying 17.06%, each. Cadmium was the lesser concentrated (Figure 13).

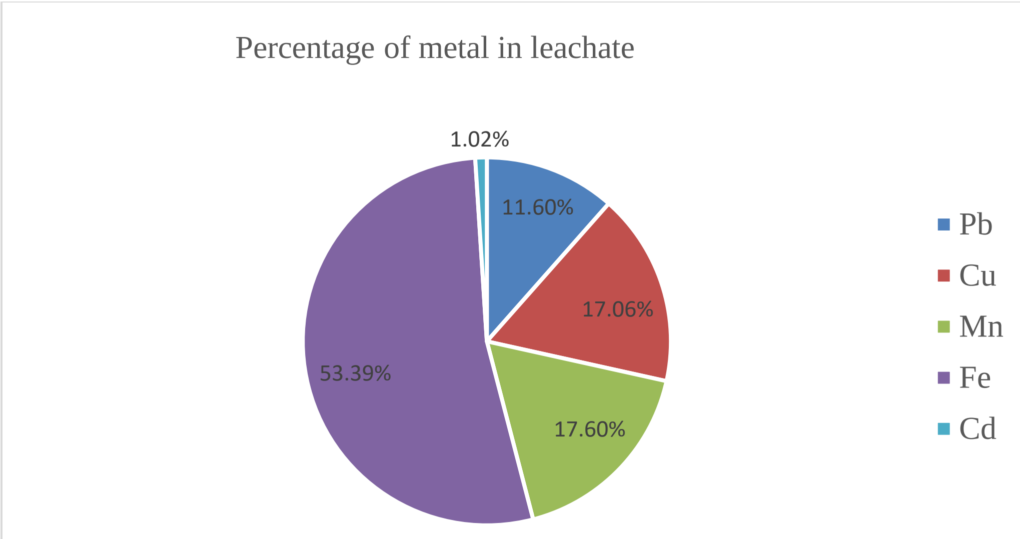


Figure 4.4: Percentage of heavy metal in leachate

4.5 Removal of heavy metal in leachate

Concentrations of heavy metals were measured in the original sample, after treatment of samples with both cellulose and modified cellulose by EDTA. The efficiency of both cellulose and treated cellulose was found (Table: 3)

Table 1: Decreasing concentration during leachate treatment by using cellulose and modified cellulose

	Concentration of heavy metal in Leachate		
Toxic metal	Original sample	Sample treated with extracted cellulose	Sample treated with modified cellulose by EDTA
Lead (Pb) (mg/L)	8.50 ± 0.26	4.50 ± 0.43	0.50 ± 0.20
Copper (Cu) (mg/L)	12.50 ± 0.43	1.60 ± 0.26	0.56 ± 0.02
Mangamese (Mn) (mg/L)	12.90 ± 0.76	8.00 ± 0.36	3.00 ± 0.36
Iron (Fe) (mg/L)	39.12 ± 1.02	24.00 ±0.55	4.00 ± 0.40
Cadimium (Cd) (mg/L)	0.75 ± 0.07	0.45 ± 0.04	0.08 ± 0.01

4. 5.1 Removal of heavy metal in leachate by using cellulose

Lead was detected in the leachate of Nduba landfill at the concentration of 8.5 mg/L. The presence of this chemical may be due to the disposal of Pb batteries, chemicals for photograph processing, Pb-based paints and pipes at the landfill site [84]. After treatment of the leachate by cellulose, the concentration of lead in leachate decreased from 8.5 mg/L to 4.5mg/L. the efficiency of removal was calculated by this equation.

Equation (1) $Percentage\ of\ removol = \frac{(8.5-4.5)}{8.5} \times 100 = 47.05\ \%$

Regarding to the research conducted by Birkinshaw et. al. [85] hitch show that the percentage of removal equal to 44% at pH between 4-5, it show that it near to the percentage equal to 47.05% [85, 86].

Besides, during the removal of cadmium, the concentration of cadmium which was 0.75 mg/L in leachate was suspected to be from livestock manure, from atmospheric deposition, from mineral fertilizers and from sludge's and composts [87, 46, 48] . After treatment of the leachate by cellulose, concentration of cadmium decreased from 0.75 mg/L to 0.45 mg/L. The efficiency of removal was estimated to:

Equation (2) $\text{Percentage of Removal} = \frac{(0.75-0.45)}{0.75} \times 100 = 40.00\%$

Regarding to the research conducted by Konstantinou [88] which reported the percentage of removal of cadmium is immediate to that result [88, 89].

Furthermore, the leachate sample indicated an average content of 39.2 mg/L of iron, which implies that iron, steel, and household items composed of iron are deposited there. After treatment with cellulose the concentration was decreased from 39.2 mg/L to 24 mg/L, indicating a removal efficiency of:

Equation (3) $Percentage\ of\ Removal = \frac{(39.12-24)}{39.12} \times 100 = 38.65\ \%$

The average concentration of copper in leachate samples collected at Nduba MSW dumping site was estimated to 2.5 mg/L. The deposition of electroplating materials, paints and dyes, petroleum refining, fertilizers, mining and metallurgy, pesticides, and iron and steel from industries are major causes of the observed copper contamination in leachate [90]. Since the pH of the Nduba landfill was in the range of 8 to 9, copper may have been eliminated through precipitation and complexation. Few of the solid wastes that were discharged there did not include bioavailable copper forms, which was suspected to be the cause for the low observed copper concentration. After treatment by cellulose the concentration was decreased from 2.50 mg/L to 1.50 mg/L and thus adsorption efficient is determined as:

Equation (4) $Percentage\ of\ Removal = \frac{(2.5-1.60)}{2.5} \times 100\ = 36.00\ \%$

Finally, manganese was suspected to be from degradation of steel and ferromanganese alloy, metallic manganese material in dumping site. Cellulose indicated its efficacy to remove that toxic metal in leachate. It led to the decrease of manganese concentration from 12.90 mg/L to 8.00 mg/L. This indicated the adsorption efficient of:

Equation (5) $Percentage\ of\ Removal = \frac{(12.9-8)}{12.9} \times 100\ = 37.98\ \%$

4.5.2 Removal of heavy metal in the leachate by using modified cellulose

Modified cellulose was found to have higher adsorption capacity than cellulose due to the increasing of the site of adsorbing heavy metals. During adsorption of heavy metal on Cellulose-EDTA, by covalent coordination bonding (a shared pair of electrons), a metal with a higher electronegativity can share electrons with the EDTA group more effectively than a metal with a lower electronegativity (Cd) in which both electrons come from the same atom [91, 92].

The concentration of lead in leachate was decreased during treatment process with modified cellulose (cellulose with EDTA), the concentration is decreasing from 8.5 mg/L to 0.5 mg/L indicating an efficiency of removal of 94.00% as indicated by this mathematical expression

Equation (6) $\text{Percentage of Removol} = \frac{(8.5-0.5)}{8.5} \times 100\ = 94.00\ \%$

This study indicated that Lead had higher affinity to modified cellulose than other heavy metal. The higher affinity of lead to modified cellulose was previously reported [93, 35, 94]. Yet, for cadmium, treated modified cellulose decreased its concentration 0.75 mg/L to 0.08 mg/L equivalent to the efficiency of removal of 89.33%:

Equation (7) $\text{Percentage of Removal} = \frac{(0.75-0.08)}{0.75} \times 100 = 89.33\ \%$

Other reports indicated a removal efficiency varying from 88 to 94% [95]. Iron was removed by a percentage of 89.77. It decreased from 39.2 mg/L to 8.00 mg/L.

Equation (8) $Percentage\ of\ Removal = \frac{(39.12-4)}{39.12} \times 100 = 89.77\ \%$

Previous report from [96] indicated that iron may be removed at the rate varying from 90% to 99.34% and result from this study was close to this reported data [96, 97]. The study indicated that both copper and manganese were removed at the percentage of 77.60 and 76.74, respectively. Copper decreased from 2.5 mg/L to 0.4 mg/L while manganese decreased from 12.9 mg/L to 3.00 mg/L. These percentages were calculated as follow:

For copper

Equation (9) $Percentage\ of\ Removal = \frac{(2.5-0.56)}{2.5} \times 100 = 77.60\ \%$

For Manganese:

Equation (10) $Percentage\ of\ Removal = \frac{(12.9-3.00)}{12.9} \times 100 = 76.74\ \%$

The results of this study corroborated with that observed by Mehmet et.al [97] where at pH 4, Cu was removed at 93% [97, 98, 99].

For manganese, it was reported that maize husk adsorbent removed this chemical at the percentage of 88% [100]. Furthermore, EDTA, itself indicated a removal efficiency of manganese which was estimated at 99%. The obtained results in this study were not far from these reported reports [101, 102, 103]. The observed difference may be due to different working conditions

From this study it was found that modified cellulose has a higher adsorption capacity of heavy metals compared to unmodified cellulose which in turn indicated its efficacy to decrease concentration of heavy metals from the leachate of Nduba landfill (Figure 4.5).

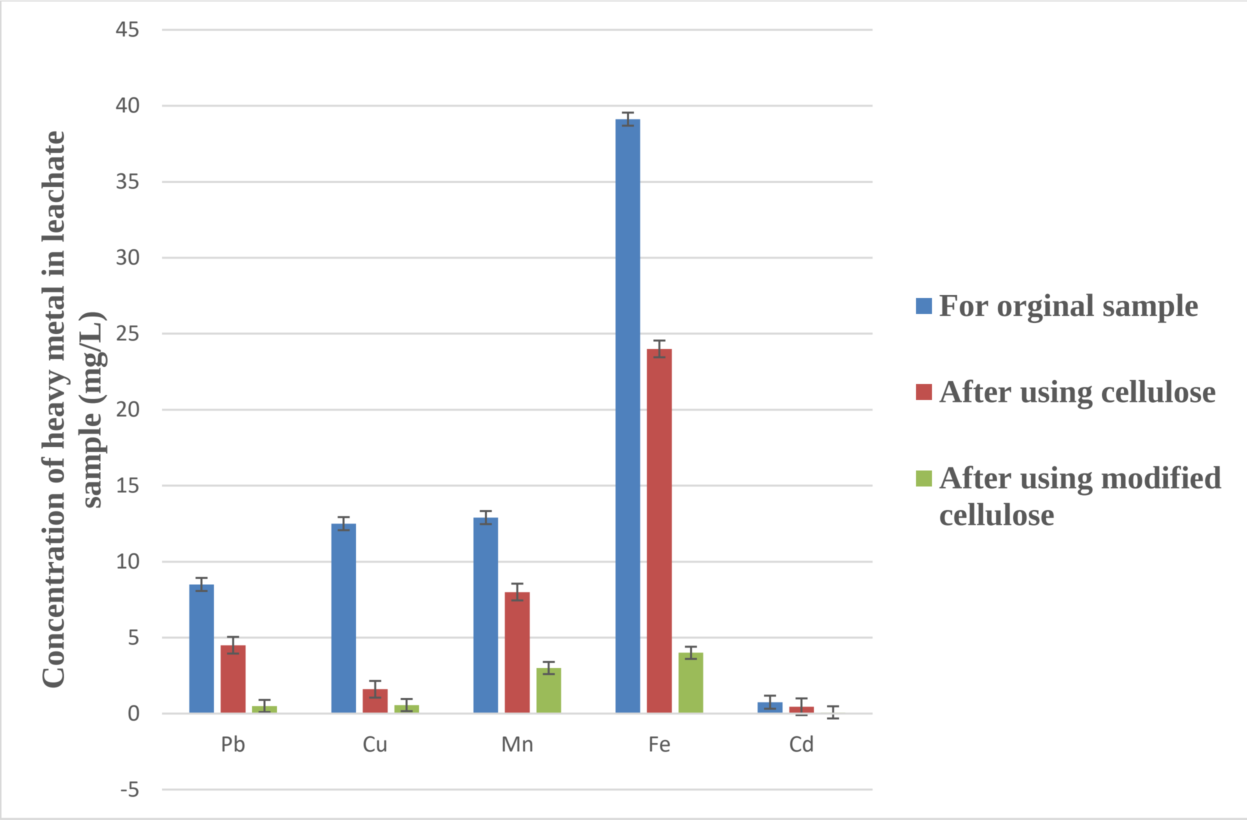


Figure 7.5: Variation concentration of heavy metal in leachate

The above results (Figure: 14), demonstrated the big variation in heavy metal concentrations. Results showed that modified cellulose was more efficient adsorbant used to remove heavy metal in the leachate. Using treated cellulose, concentrations of heavy metals were reduced from as: Pb: from 8.50 to 0.50 mg/L, Cd: from 0.75 to 0.08 mg/L, Mn: from 12.90 to 3.00 mg/L, Cu: from 2.50 to 0.56 mg/L, Fe: from 39.20 to 8.00 mg/L. These obtained concentrations after treating leachate seemed to be accepted by environmental protection agencies including United States Environmental Protection Agency (US EPA) guidelines, and EU standards for discharged leachate in the environment [104, 105] and this indicated the efficacy of the treated celluose in wastewater treatment This study also indicated that there was not any interest in increasing time of adsorption from 6 hours to 8 hours. The optimum adsorption time was found to be six hours. The increasing reaction time could not affect the teatment rate. These are close to other reported results by Wuana et. al. [106].

This study indicated that modified cellulose had the higher percentage of removal than unmodified one (Figure 4.6).

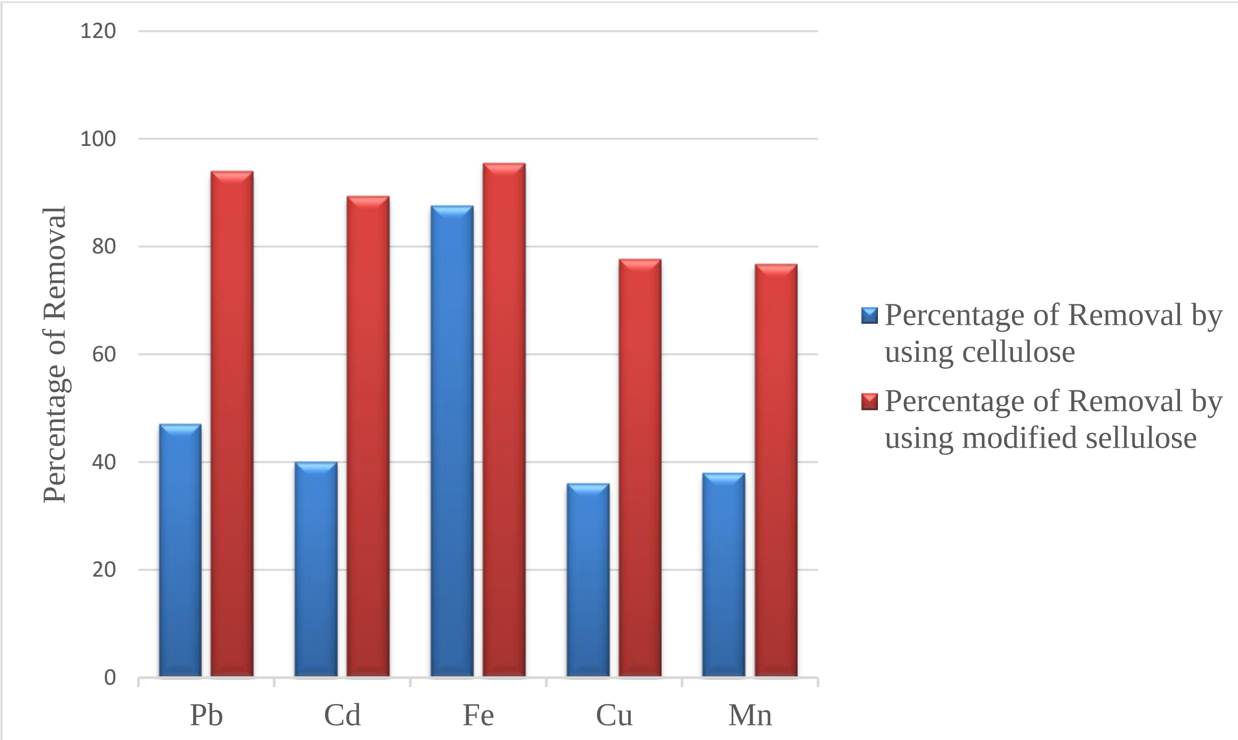


Figure 4.6: Percentage of removal by using cellulose and modified cellulose as adsorbent

The efficacy of modified cellulose can indicate its excellent properties as adsorbents for heavy metals. This may be due to its high selectivity and adsorption capacity brought by EDTA during modification, and this to increase the sites which were associated with heavy metals.

4.6.4 Conclusions and recommendation

4.6.4.1 Conclusion

Regarding to the conducted research, Modified cellulose has higher affinity to heavy metal like: Cadmium (Cd), Copper (Cu), Lead (Pb), Iron (Fe), and Manganeze (Mn), that have been concerned as one that pose threats to human being and environment, and also be dangerous to the ecological balance, public health, and environment.

The purpose of this study is to use biodegradable, eco-friendly materials modified cellulose (cellulose with EDTA) for adsorption of heavy metal ions from contaminated leachate collected from Nduba landfill such as: Cd, Pb, Cu, Fe, and Mn. To increase the adsorption capacity of

Cellulose, cellulose was treated with EDTA in the presence of Pyridine to have better adsorption properties. Among other things, adsorption experiments were carried out by measuring the different concentration of metal ion from initial concentration to the final concentration of metal ions in the solution. Maximum percentage of removal of Cd, Pb, Cu, Fe, and Mn by composites was 89.33, 94.00, 77.60, 89.77 and 76.74%, respectively.

4.6.4.2 Recommendation

In the different area of the country there are higher amount of sawdust which produced from different wood processing industries that cause the problem for its management. For solving the problem of discharging leachate with pollution of heavy metal the institution who is charged to protect environment can start to establish the way, that sawdust can be prepared in order to be used as the way to removal heavy metal in the leachate from different duping site. As the search show that the modified cellulose is able to removal heavy metal in leachate, those leachates can be used in other purpose in the field of agriculture.

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