HAWASSA UNIVERSITY

COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCES

DEPARTMENT OF CHEMISTRY POSTGRAGUATE PROGRAM

ADSORPTIVE REMOVAL OF LEAD ION FROM AQUEOUS SOLUTION USING CRYSTALINE NANOCELLULOSE PREPARED FROM MAIZE COBS

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MARCH, 2025

HAWASSA, ETHIOPIA

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A MASTER THESIS SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES OF HAWASSA UNIVERSITY, COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCE, DEPARTMENT OF CHEMISTRY, IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE DEGREE OF MASTERS OF SCIENCE IN CHEMISTRY

MARCH, 2025

HAWASSA, ETHIOPIA

DECLARATION

I, the undersigned, declare that this M.Sc. thesis entitled **"Adsorptive Removal of Lead Ion from Aqueous Solution using Crystalline Nano Cellulose Prepared from Maize Cobs"** is my original work has not been presented for a degree or diploma of any other university and that all sources or materials for the thesis has been duly acknowledged.

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This thesis has been submitted for examination with my approval as university advisor.

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HAWASSA UNIVERSITY

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This is to certify that the thesis entitled **"Adsorptive Removal of Lead Ion from Aqueous Solution Using Crystalline Nano Cellulose Prepared from Maize Cobs"** submitted in partial fulfillment of requirements for the degree of Master of Science in Chemistry in Hawassa University. A record of original research carried out by Getahun Esthete, under my supervision, and no part of the thesis has been submitted for any other degree or diploma. The assistance and help received during the course of thesis investigation have been duly acknowledged. Therefore, I recommended that it be accepted as fulfilling the thesis requirements.

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We, the undersigned, member of the board of the examiners of the final defense by Getahun Eshetu, have read and evaluated this thesis entitled **"Adsorptive Removal of Lead Ion from Aqueous Solution Using Crystalline Nano Cellulose Prepared from Maize Cobs"** examined the candidate. This is therefore to certify that the thesis has been accepted partial fulfillment of the requirement for the degree of Master of Science in Chemistry.

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ACRONYMS AND SYMBOLS

AAS	Atomic absorption spectroscopy
Cd	Cadmium
Cu	Copper
Co	Initial metal concentration
Ce	Final metal (or residual/equilibrium) concentration
FTIR	Fourier transforms infrared spectroscopy
MW	Molecular weight
m:	Dry weight of biomass (dose)
SED	Scanning electron deficiency
SEM	Scanning electron microscopy
Pb	Lead
Zn	Zinc
US EPA	United States Environmental Protection Agency

ABSTRACT

*Heavy metals significantly impact the environment due to their non-*biodegradable, toxic, and *carcinogenic behaviors. Lead contaminants impose severe health impacts on humans and the water environment. Therefore, eco-friendly and efficient lead ion removal practices such as nanotechnology are an urgent requirement for the abatement of lead pollution. The aim of this study was to evaluate the removal of lead from an aqueous solution using maize cob cellulose Nano crystals. In the present study, crystal Nano cellulose was synthesized from maize cob. The crystal Nano cellulose synthesized was characterized by using FTIR, XRD and SEM. FTIR analysis reveals presence of functional groups with a high chelating capacity, as identified via FTIR. From SEM analysis the crystal Nano cellulose was noticed to be disordered and irregular in shape. The adsorption capacity of the crystal Nano cellos was 3.85 mg/g. The adsorption process was evaluated by adjusting the pH, dose, initial concentration and temperature. Optimum conditions were dose of 0.16 gram initial concentration of 10 ppm, contact time of 115 minute, pH of 6 and temperature of* 45^0*c. Based on the optimal parameters, the kinetics were evaluated using the pseudo first and pseudo second order models based on that pseudo second order more fit than pseudo first order model. Equilibrium data were represented better by the Freundlich model than the Langmuir model which describes multilayer adsorptions. The adsorbent-formulated from crystalline Nano cellulose presented a good capacity to remove lead from aqueous media.*

Keywords: adsorption kinetics; cellulose Nano crystals; maize cob; metal removal

1. INTRODUCTION

1.1. Background of the Study

An increased use of metals and chemicals in the process industries has resulted in the generation of large quantities of aqueous effluents that contain high levels of heavy metals, thereby creating serious environmental disposal problems (Holan et al.) Also exponential growth of the world's population over the past 20 years has resulted in environmental build up of waste products, of which heavy metals are of particular concern (Volesky et al.). The need of finding alternative inexpensive and effective methods for heavy metals abatement from waters becomes inevitable. Bio sorption is an emerging field in this regard and has great potentials for application in developing economies. It involves the use of living or non-living biological materials for pollutants' removal from aqueous solutions and industrial effluents. Heavy metals such as zinc are micro nutrients though essential in small amounts for plant and animal life ,can however be harmful if taken up by plants or animals in large amounts, like other heavy metals not known to be essential nutrients There are at least 20 metals which cannot be degraded or destroyed. The important toxic metals are Cd, Zn, Pb and Ni. These heavy toxic metals enter into the water bodies through waste water from metal plating industries and industries of Cd- Ni batteries, phosphate fertilizer, mining, pigments, stabilizers, alloys etc. Heavy metals accumulate in the food chain and because of their persistent nature, it is necessary to remove them from wastewater (Holan et al. , Vole sky et al. , Chong & Vole sky).

Removing heavy metals from waste water has therefore resulted in the search for other materials that may be useful in reducing the levels of heavy metals in the environment (Chong &Volesky). In Nigeria, (Spiff (2004) and Horsfall et al. (2003)) have used groundnut husk, fluted pumpkin and wild cocoyam respectively for removal of heavy metals from aqueous solutions. Lead is an industrial pollutant, which enters the ecosystem through soil, air and water. Inorganic lead is an enzyme inhibitor, which also affects the nervous system. It is very toxic in nature Environ. 1995). Lead (Pb) and its compounds are widely used in the industries, hence they are commonly found in air, water, soil and food. Pb may get into the aquatic environment through sources like smelters, industrial effluents from battery, paint, plastic, textiles, microelectronics, Among the various resources of biological wastes, agricultural wastes (e.g., stems, peels, husks, leaves, fruit shells, ...etc) have been demonstrated to remove metal ions in aqueous solutions (Tee & Khan ;

Scott, McKay & Porter , Sun & Shi , Al-Ashes &Duvnjak , Meunieretal. , Sekhar et al. , Özer et al. , Wang & Qin).

Pb is a heavy metal of great environmental concern and poses threat to plants, animal and human health due to its bio accumulative tendency and toxicity. Pb has known beneficial biochemical attribute and it is known to have toxic effect on the nervous system, kidney and liver Pb, being a heavy metal, tends to accumulate in the food chain because of its persistent nature, and it is therefore necessary to remove it from waste water Thus realizing the effectiveness of lead and their toxicity the present work is framed in such a way to develop efficient Nano crystalline material. The Nano crystalline material chosen here is prepared from Maize cob which is an inexpensive source used for the removal of lead. The removal of lead ion is used to reduce our environmental pollution . Acid hydrolysis is one of the common adopted techniques to prepare crystalline Nano cellulose.

1.2. Statement of the Problem

Agricultural Development Led Industrializations (ADLI) is the basic road map for Ethiopian development (GTP-MoFED, 2010; FDRE-CRGE, 2011). Development of the country is currently based on ADLI. So far, industrial development is beginning to be realized in the leather industry and other agriculturally based processing industries, such as beverages and food, textiles, and the sugar industry. During future implementations of the Growth and Transformation Plan (GTP-MoFED, 2010; FDRE-CRGE, 2011) important strategies will be enacted into promote environmentally sustainable, agriculturally based processing industries. Others industries, such as chemical, textile, cement, pharmacologic and metal industries are also rapidly growing. Continued population growth and rapid industrialization are found to be the cause of wastewater discharge into the environment, affecting the environment, human health and compromising the life of future generations.

The techniques are currently being implemented in Ethiopia are conventional treatment methods. However, these conventional treatment processes require large investments making their application unaffordable for developing countries, like Ethiopia (Mandal, 2014). The liquid waste discharged from industries contains heavy metals toxic to living organisms (Barakat, 2011). Heavy metals of urgent environmental concern are lead, chromium, mercury, cadmium, copper, zinc, and iron. Among these heavy metals, Lead (Pb^{2+}) is hazardous and carcinogenic and discharged from most industries above permissible limited set by Ethiopian environmental protection agency. A number of technologies have been developed over the years to remove toxic heavy metals from waste water. One of the most commonly used techniques involves the process of adsorption, which is the physical adhesion of chemicals onto the surface of solid. Adsorption as a process, employed due to its low cost and applicability on large scales. Adsorption is commonly being done using activated carbon, which adsorbs dissolved organic substances in the water treatment and although activated carbon has several advantages, such as its effectiveness in removing high concentrations or organic and inorganic compounds (Agbozu & Emoruwa, 2014).

One of the major issues of the environment is water quality deterioration caused by discharged west water. West water contain serious harmful substances; included heavy metals. Now days heavy metals pollution has become a threat and has a great potential to causes environmental derived cancer because of those metals are non biodegradable. The removal of heavy metals from contaminated water bodies has been attempted by several scientists employing wide variety techniques. However, most of these methods have considerable disadvantages including incomplete metal removal, high capital, operational cost which are not suitable for small scale industries. However, no sufficient research to investigate these issues particularly in Ethiopia from Nan crystalline cellulose prepared from maize cobs as potential adsorbent to remove heavy metal lead from wastewater. Therefore, the research is conducted to remove the lead ion using Nan crystalline cellulose prepared from locally available maize cobs.

1.3. Objectives of the Study

1.3.1. General Objectives

- The main objective of the study was to remove lead ion ($Pb^{2+)}$ from aqueous solution using crystalline nanocellose prepared from maize cob.

1.3.2. Specific Objectives

The specific objectives of the study were:

- To prepare crystalline Nano cellulose from Maize cobs
- To characterize the prepared crystalline Nano cellulose by using FTIR and SEM
- To apply the prepared crystalline Nano cellulose for the removal of Pb^{2+}
- To investigate the effect of different parameters, initial concentration of the adsorbents, pH solutions and Nano crystalline dose by using a batch adsorption technique.

- To study the adsorptive mechanisms by studying adsorption isotherm and adsorption kinetics of crystalline nanocellulose .

1.4. Significance of the Study

This study was expected to have the following significance. The use of Nano crystalline material prepared from maize cob in the remediation of water and soil contaminated with heavy metals and cleans alternative technology for reducing the concentration of heavy metal pollutants in soils. Human and industrial activities produce and discharge wastes containing heavy metals into the water resources making them unavailable and threatening human health and the ecosystem. Conventional methods for the removal of metal ions such as chemical precipitation and membrane filtration are extremely expensive when treating large amounts of water, incompetent at low concentrations of metal (incomplete metal removal) and generate large quantities of sludge and other toxic products that require careful disposal. This study used to compile scattered information on the removal of Pb ions from wasted water by using Nano cellulose prepared from maize cob. The study can also provide fundamental information in the adsorption of lead metal ions, from aqueous solution.

1.5. Limitation of the study

The research study is not free from limitation. Some of the factors that are supposed to hinder my study expected to be the following:-Lack of available materials that are relevant to the study The finance will be allocated to conduct the research work will not sufficient and shortage of time not to assess all aspect of the heavy metals and The sample size will be low due to financial constraints.

2. REVIEW LITERATURE

2.1 Heavy Metals Pollution

Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0 (Srivastava and Majumder, 2008). With the rapid development of industries such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides, etc., heavy metals wastewaters are directly or indirectly discharged into the environment increasingly, especially in developing countries. Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic (Ilhan*et al.,* 2004).

2.2 Heavy Metals Toxicity

Metals can be toxic to microbial population at sufficiently high concentrations. However, some metals such as silver, mercury, cadmium and copper are markedly more toxic even at very low levels (Igwe and Abia, 2006). Metals exert their toxic effects on microorganisms through one or more mechanisms (Nies, 1999). An extensive work is available on the effect of metals on general soil microbiological processes.

2.2.1. Nickel

Nickel is a metallic chemical element with the symbol Ni and atomic number 28, the daily requirement for human was 300 - 700µg, foods naturally high in nickel include chocolate, soybeans, nuts, and oatmeal; it is a silvery-white metal that takes on a high polish. It belongs to the transition metals, and is hard and ductile. It occurs most usually in combination with sulfur and iron in pent landite, with sulfur in mille rite, with arsenic in the mineral nickeling, and with arsenic and sulfur in nickel glance (NPI). Exposure to nickel metal and soluble compounds of nickel should not exceed 0.05 mg/cm³ in nickel equivalents per 40-hour work week. Nickel sulfide fume and dust is believed to be carcinogenic, and various other nickel compounds may be as well. Nickel carbonyl, [Ni (CO)4], is an extremely toxic gas. The toxicity of metal carbonyls is a function of both the toxicity of a metal as well as the carbonyl's ability to give off highly toxic carbon monoxide gas, and this one is no exception (Kasprzak*et al.,* 2003)

2.2.2. Cobalt

Cobalt is a silver or grey ferromagnetic element with the symbol Co and atomic number 27, the daily requirement was 10 - 20µg, naturally occurring cobalt uses are alloys, magnets, Catalysts and Electroplating. Cobalt is a hard, lustrous, silver-grey metal. It is found in various ores, and is used in the preparation of magnetic, wear-resistant, and high strength alloys. Its compounds are used in the production of inks, paints, and varnishes (Flexner, 1993). Cobalt in small amounts is essential to many living organisms, including humans. Having 0.13 to 0.30 mg/kg of cobalt in soils markedly improves the health of grazing animals. Cobalt is a central component of the vitamin coalmine, or vitamin B-12(Herbert, 1988).

2.2.3. Zinc

Zinc is an essential element, with the symbol Zn, the human daily requirement was 10 to 20 mg (Lester, 1987). Zinc is an essential element in all living organisms. Nearly 200 zinc-containing enzymes have been identified, including many dehydrogenases, aldoses, peptidases, polymerases, and phosphatases (WHO). Zinc tends to be less toxic than other heavy metals as shown in table (1). However, some symptoms of zinc toxicity are vomiting, dehydration, electrolyte imbalance, stomach pain, nausea, lethargy, dizziness, and muscular incoordination. Last, the role of zinc as a carcinogen or carcinogen is unclear. Protein-rich foods, such as meat and marine organisms, contain high concentrations of zinc (10–50 mg/kg wet weight), whereas grains, vegetables, and fruit are low in zinc.

2.2.4. Lead

Lead exists in several oxidation states: 0, +1, +2 and +4 with the symbol Pb. However, the divalent form Pb^{2+} is the stable ionic species in most of natural environments (EPA, 1979). Precipitation and sorption are the principal mechanisms controlling the distribution of lead in the aquatic environment. In the presence of inorganic ligands, lead can precipitate as a number of compounds including $PbSO_4$, $PbCO_3$, $Pb(OH)_2$ and PbS.

2.3 Methods for Removing Heavy Metals

Bio sorption can be denied as a simple metabolically passive physicochemical process involved in the binding of metals ions (bio sorbet) to the surface of the bio sorbent which is of biological origin (Mrvčić J, 2012). Biological removal includes the use of microorganisms, plant derived materials, agriculture or industrial wastes, biopolymers, and so on. It is a reversible rapid process involved in binding of ions onto the functional groups present on the surface of the bio sorbent in aqueous solutions by means of various interactions rather than oxidation through aerobic or anaerobic metabolism (Davis TA, 2003).

2.4. Types of Bio sorbents

Identification of bio sorbents for the process of bio sorption is a major challenge. It is desirable to develop/obtain bio sorbents with the capacity to bind/uptake metal ions with greater anilities (Macek T, 2011). A wide variety of materials available in nature can be used as bio sorbents for the removal of metals from contaminated water resources. Any kind of plant, animal, and microbial biomass and their derivatives; plant, industrial and agriculture wastes; and byproducts discharged from various industries can be employed as bio sorbents. It is important to select a bio sorbent from the large spectrum of available materials. The desired characteristics of an ideal bio sorbent are (Macek T, 2011):

- High affinity for metals (bio sorption capacity)
- Low economic values (low cost)
- Availability in large quantities

2.4.1. Industrial Byproducts

Low-cost materials from different industries have been used for the treatment of wastewater. Many industries, especially food industries, dispose large quantities of waste and byproducts. The cost for disposal is sometimes challenging. Using these zero-cost industrial wastes as effective bio sorbents for treating waste water eluents can solve the dual problem (waste disposal and eluent treatment) (De Gisi S,2016).

2.4.2. Agricultural Waste Materials

A great deal of interest in the removal of pollutants from waste waters has focused on the use of agricultural waste/byproducts as bio sorbents. Agricultural wastes especially those with high percentage of cellulose and lignin contains polar functional groups like amino, carbonyl, alcoholic, phenolic, and ether groups having high potential for metal binding (Hossain M, 2012).

These groups donate a lone pair of electrons and form complexes with metal ions in the solution (Demirbas A.2008).

2.4.3. Microbial Bio sorbents

Microorganisms capable of tolerating unfavorable conditions evolved their use as bio sorbents in the removal of metal ions from wastewaters. They include bacteria, yeast, algae, and fungi. Experiments focused on the use of dead and or living microorganisms offer options for the type of remediation to perform (Hlihor RM,2014).

2.4.3.1 Algae

Algae are divided into two main types: micro-algae and macro-algae. Macro-algae, which are also known as seaweeds, are multi cellular plants that grow in fresh or salt water, they are classified based on their pigmentation, which includes three groups: brown, red and green algae (Anastopoulos&Kyzas, 2015).

2.4.3.2 Yeasts and Fungi

Fungi started to receive more attention as a bio sorbent recently due to the rich cell wall content, which suggests the presence of a wide range functional groups which be involved in metal removal (BenilaSmily&Sumithra, 2017). The fungal cell wall is comprised of chitin, cellulose, b-glucan, a-glucan, chitosans, polyuranides, glucoproteins, lipids, inorganic salts and pigments (Dhankhar&Hooda, 2011). Comparing the usage of fungi as bio sorbents with algae and plants, fungal biomass is easy cultivated in large scales and it is easily grown by simple fermentation techniques with overall low costs (Dhankhar&Hooda, 2011).

2.4.3.3 Bacteria

Bacteria are classified as gram-positive bacteria or gram-negative bacteria, the most significant difference between these two types is in their cell wall composition and thickness (Zyoud et al., 2019). The cell wall of gram-positive bacteria have thicker peptidoglycan layers which are connected by amino acid bridges (Zyoud*et al.*, 2019) (Abdi&Kazemi, 2015) and accumulation of heavy metals. However a dead biomass is preferred to a viable one for the following reasons:

- The bio sorption process is often executed in harsh environmental conditions.

- There is no requirement for maintenance and nutrition, and the bio sorbents can be stored for a long time without affecting their performance.
- There is no toxic effect of metals on dead microorganisms, so their sportive capacity is not affected.
- In many cases, sorption by dead biomass is more efficient than sorption by living biomass (Stenos, 1990).

2.4.3.4 Plants as Bio sorbents

Plants, as agricultural waste materials and food industries discarded material have been used as bio sorbents, it is a form of reusing and recycling those waste materials thus no significant costs are associated with using plant materials. The potential of plant bio sorbents are mainly due to the presence of carboxylic and phenolic functional groups in the cellulosic matrix or components associated with cellulose such as lignin and hemicellulose (Abdi&Kazemi, 2015). Aloe vera wastes were used as bio sorbent for the removal of uranium and cadmium from water, it was found that the carboxyl, carbonyl and hydroxyl groups facilitated metal binding (Noli, Kapashi, &Kapnisti, 2019).

2.5. Parameters Affecting Bio sorption

There are several key characteristics which controls the adsorption ability of adsorbents. The characteristics are the physiochemical characteristics of adsorbents materials. Specific surface area, pore volume, ash content, particle sizes, pH, charge/polarity and surface functional groups are properties of adsorbents. For each bio sorbent, many factors can influence metal uptake onto biomass at different rates determining the overall bio sorption performance (Park *et al*. 2010).

2.5.1. pH

The pH under which bio sorption takes place is very significant and directly affects the bio sorption capacity, and in some cases the mechanism via which bio sorption takes place as mentioned earlier. PH affects both the chemistry of the functional groups of bio sorbent and the chemistry of metal ions (Wei *et al.,* 2016). The bio sorption capacity often increases with the increase of pH until it reaches the optimum pH where the maximum bio sorption capacity is observed, following that, upon further increase in pH, metals begin to precipitate due to formation of metal hydroxides or hydroxide anionic complexes (Abdi&Kazemi, 2015)(Bilal *et al.*, 2018).

2.5.2 Temperature

Temperature is greatly affecting the bio sorption. Decreasing temperature below 24ºC decreased fungal growth and enzymatic activity. Furthermore, increasing the temperature up to about 40º C decreased the fungal growth and consequently the chromium removal extent. NouriSepehr et al., (2005) proved that the maximum biomass growth and chromium removal rate was achieved at 30ºC. The data obtained showed that adsorption of metal ion by the Caladium bicolor biomass increased with increase in temperature which is typical for the bio sorption of most metal ions from their solution (Ho, 2003).

2.5.3 Initial Metal Concentration

Generally, bio sorption capacities of Phanerochaetechry sosporium for Ni and Pb increased with increasing initial metal concentration (Ceribasi and Yetis, 2000). The maximum adsorption was observed for Cr^{6+}, Pb^{2+} and Cu^{2+} , at the initial concentrations of 193.66 mg Cr^{2+} /l; 100 mg Pb^{2+} /l and 105 mg Cu^{2+} /l and under these conditions the bio sorption values were found to be 88.66 mg Cr^{6+}/l; 100 mg Pb^{2+} /l and 44.94 mg Cu^{2+} /l, respectively(Ilhan*et al.*, 2004).

2.5.4 Physiological State

Physiological state is also affect the bio sorption according to Safarikova et al., (2004) who mentioned that yeast cells which are at first magnetically modified and then heated exhibit higher adsorption capacity than yeast cells heated and subsequently magnetically modified. Cabuk et al., (2004) showed that the live biomass of Aspergillums vesicular had the highest bio sorbent activity for lead ions among the species studied such as Metarrhiziumanisopliae var. anisopliae and Penicilliumverrucosum live biomass. Also Cabuk*et al.*, (2004)

2.5.5 Agitation Rate

It was found that copper uptake by Sargassumsp increases with the increase in shaking rate (q = 2.7 mg/g in absence of agitation and 3.8 mg/g at 50 rpm), and that the adsorption capacity of algae remained constant at 4.3 mg/g for agitation rates greater than 100 rpm (Antunes*et al.*, 2003). In order to study the effect of shaking velocity on chromium removal rate by Aspergillusoryzae, this parameter was varied in the range of 50 and 250 rpm. The maximum amount of biomass growth and chromium removal rate occurred at 150 rpm. With increasing shaking velocity, biomass growth was stationary (NouriSepehr*et al.*, 2005).

2.5.6 Time of Bio sorption

Ahalya*et al.,* (2006) stated that the sorption of iron by Bengal gram husk biomass was very rapid, in which the equilibrium was achieved with in 15 min. Bishnoi et al (2007) stated that the adsorption equilibrium was reached in 90 min. for Cr (VI) with Trichodermaviride. Park et al. (2005) stated that the concentration of Cr (VI) decreased with increasing contact time. The time required to attain maximum bio sorption depends on the type of bio sorbent, metal ion, and their combination (Abdel-, 2009)

2.6 Mechanisms of Bio sorption

The mechanism of bio sorption is a complex process which involves the binding of sorbet onto the bio sorbent. Many natural materials can be used as bio sorbents which involve the binding of metal ions by physical (electrostatic interaction or van der Waals forces) or chemical (displacement of either bound metal cations (ion exchange) or protons) binding, chelation, reduction, precipitation, and complication. The key factors controlling and characterizing these mechanisms are (NouriSepehr*et al.*, 2005).

2.7 Heavy Metals Sources and Toxicity

Different metals have different toxicity or toxic profiles depending upon their chemical form. The source of heavy metal includes natural source, mining, smelting, agrochemicals and sewage sludge applications, and livestock manure uses. The Table 1 gives the source and impact of most hazardous heavy metals on the human health.

Table 1: Source and impact of most hazardous heavy metals on human health (Jarup. 2003)

Sr. No	Heavy Metal	Source	Impact
1	Mercury (Hg)	Enters the environment through the leaching of soil due to acid rain, coal burning, or industrial, household, and mining wastes	Causes damage to nervous system, kidneys, and vision.
2	Lead (Pb)	Sources include paint, mining wastes, incinerator ash, water from lead pipes and solder, and automobile exhaust	Causes damage to kidneys, nervous system, learning ability, ability to synthesize protein, and nerve and red blood cells.
3	Cadmium (Cd)	Sources include electroplating, mining, and plastic industries, as well as sewage	Causes kidney disease.
4	Arsenic (As)	Enters the environment through herbicides, wood preservatives, and mining industry	Causes damage to skin, eyes, and liver. May also cause cancer.
5	Antimony (Sb)	Enters the environment through mining and ore processing industry	Can irritate eyes, skin, and lungs can also cause heart problems, stomach pain, diarrhea, vomiting, and stomach ulcers.
6	Chromium (Cr)	Source includes cement industry, effluents from chemical plants, tobacco smoke and contaminated land fill.	Can Cause Pulmonary fibrosis, lung cancer.

2.8. Treatment Methods for Heavy Metals

Removal The various industrially used methods for the removal of heavy metals are Ion exchange, Chemical precipitation, floatation, electrochemical deposition, adsorption, etc. All these methods are used in industries are expensive and may even produce a large quantity of sludge which further needs treatment. Adsorption process is currently considered as one of the upcoming process for the treatment of wastewater containing heavy metals (Barakat, 2011).

2.9. Bio sorption of selected heavy metals

2.9.1. Bio sorption of lead

Lead is a heavy transition metal. The approximated concentration ranges of discharged lead(II) ions in the environment from battery industry is 5-66 mg/L, from mining industry is 0.02-2.5 mg/L and that from the oil industry is 125-150 mg/L (Tas¸ar, Kaya, &Ozer, € 2014). Lead is considered lethal to animals and plants (Nadeem, Manzoor, Iqbal, &Nisar, 2016). It causes several illness for humans, such as anemia, brain damage, mental deficiency, kidney damage, encephalopathy, anorexia, cognitive impairment, behavioral issues and vomiting (Nadeem *et al*., 2016)(Morosanu, Teodosiu, Paduraru, Ibanescu, &Tofan, 2017). Lead (II) ions have high affinity to thio, oxo and phosphate groups that are present in some enzymes and biomolecules in living organisms (Morosanu*et al.*, 2017).

2.9.2. Bio sorption of Chromium

Chromium, a toxic, carcinogenic, mutagenic and teratogenicity heavy metal, which usually exists as trivalent and hexavalent forms in aqueous environment (Rezaei, 2016). Chromium is one of the main pollutants in surface water and groundwater, especially its hexavalent form due its high mobility and solubility in aqueous environment, the hexavalent form is also about 500 times more toxic than trivalent form (Mishra, Dubey, &Shinghal, 2015). iron and steel foundries, inorganic chemical plants and tanneries (Mishra *et al.*, 2015)(Netzahuatl-Munoz *et al.*, ~ 2015).

2.10. Importance of Bio sorbents in Water Treatment

The search for new technologies involving the removal of toxic metals from wastewaters has directed attention to bio sorption, based on metal binding capacities of various biological materials. Bio sorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake (Mahvi, 2008).

2.11 Effect of Lead

Generally lead can be accumulated and adsorbed by the body through inhalation, ingestion, skin contact (occupational exposure), or transfer via the placenta. Adults can absorb 10% of ingested lead into their body (Zhang*et al.,* 2013). Young children can absorb from 40% to 53% of lead ingested from food and the adsorbed lead can enters either a "rapid turnover" biological pool with distribution to the soft tissues (blood, liver, lung, spleen, kidney, and bone marrow) or a intelligence ratings (Jortner, 2008; Zhang *et al.,* 2013).

2.12 Effect of cadmium

Cadmium, lead and mercury are the "Big Three" toxic categories of heavy metals because of their acute toxicity to humans and the environment. Stomach irritation, vomiting and diarrhea may happen instantly after taking heavily contaminated food and drinking water (Gallego*et al.*, 2012). The acute oral lethal dose of cadmium for humans has to be several hundred milligrams (Li and Zhou, 2012). Zhang *et al.*, 2012b).

2.13 Effect of zinc

Zinc toxicities is not a common problem for man and animals. Zinc poisoning occurs in humans from acid foods or beverages stored in galvanized containers. Animals may get zinc poisoning from ingesting or exposure to galvanized metal objects, certain paints and fertilizers, zinc-containing coins etc(Zhang*et al.,* 2012b). Several factors such as water hardness, salinity, temperature, and the presence of other contaminants influence zinc toxicity in aquatic environments. The effect of water hardness on zinc toxicity is by far the most studied factor (Giaccio*et al.,* 2012; Holland and White, 1988; Li *et al.,* 2014).

2.14. Advances of Bio sorption over Conventional Methods:

The conventional methods used for the removal of metals or heavy metals are not more efficient, expensive, takes longer time for removal process, incomplete removal, generates toxic compounds and sludge that requires safe disposal and cannot apply for a large scale economical removal process. Bio sorption have following advantages over conventional methods. The process is based on the choice of bio sorbents and which is generally abundant.

3. MATERILAS AND METHODS

3.1. Materials and Chemicals

The maize cob was collected from Hawassa city Sidama, Ethiopia.The analytical grade chemicals and reagents used in this study, were ethanol (97%, India), sodium hydroxide (99%,India), conc. hydrochloric acid (35%, Loba Chemie Pvt. Ltd., India), conc. sulfuric acid (69%, Loba Chemie Pvt. Ltd., India), conc. nitric acid (69%, Loba Chemie Pvt.Ltd., India), and $Pb(NO_3)_2$ (99%, BDH Chemicals Ltd., England).

3.2. Instruments.

Digital analytical balance (Explorer, Ohaus, Model E11140, Switzerland), atomic absorption spectrophotometer (AAS, Buck Scientific 210 VGP), X-ray diffraction (XRD) (XRD-7000 X-ray diffract meter, Shimadzu Co., Japan), Fourier transform infrared (FT-IR) spectroscopy (PerkinElmer 65, PerkinElmer, Inc., Waltham, USA), scanning electron microscopy (SEM) (JCM6000Plus, JEOL/EO, USA), and a water deionizer were used throughout the study.

3.3. Preparation of crystalline Nano cellulose from maize cob

The maize cobs , for crystalline nanocellluloses preparation, were Collected from Sidama region Hawassa city Ethiopia.

The collected maize cob sample was washed with distilled water repeatedly, dried with air at room temperature, and ground using a grinder carefully to form a coarse particle. For the extraction of crystalline Nano cellulose 10 g of the ground coarse particle and a 125 mL: 75 mL ratio mixture of toluene: ethanol solvent were added to a beaker and placed in a water bath for 40 hours at 50°C. Subsequently, the extracted mixture was washed with boiling water, filtrated, and dried in an oven at 50°C for 10 hours. The dried fibers were cut into short fibers of approximately 5 mm in length. Next, these short fibers were treated with 100 mL of 3.0 M NaOH solution at 50° C for 2.5 hours to remove the lignin and hemicelluloses present in lignocellulose biomass. Afterward, this mixture was washed well with deionized water repeatedly until it becomes neutral. Thereafter, the neutral mixture was centrifuged, filtered, and dried in an oven at 50°C for 10 hours. Then, the dried mixture was ground into a pulp form and bleached with a 3: 0.75 ratio mixture by volume of sodium chlorite ($NaClO_2$) to glacial acetic acid for 4 hours at 60° C under mechanical stirring. This procedure was repeated with half of the initial amount of bleaching agent. Then after, it was centrifuged, washed repeatedly, and filtered, forming cellulose suspension. Subsequently, it was hydrolyzed by 100 mL of 6 M H_2SO_4 for 2 hours to break up the cell wall and to separate the fibrils present for the production of cellulose nanomaterial suspension through sonication. Then, the prepared crystal Nano cellulose suspension was centrifuged at 1600 rpm to separate the crystal Nano cellulose from Nano cellulosic constituents and homogenized in homogenizer at 12,000 rpm for 2.0 hours. It was then washed, filtered, and dried in an oven at 50°C for 10 hours to form crystalline Nano cellulose. During this proses, number of liquid wastes that are harmful to the working environments are produced. This problem was managed through a scientific and sensible liquid waste management system.

Finally, the prepared crystalline Nano cellulose was kept in a suitable place for characterization purposes.

3.4 Characterization of the synthesized crystalline Nano cellules

The crystallite size, functional groups, surface morphologies, and thermal stability of crystal Nano cellules sorbents were investigated by using XRD with Cu-Kα radiation ($\lambda = 0.154$ nm) at 40 kV and 30 mA in a diffraction angle of 2θ ranging from 10° to 80° at a scan rate of 3° /min, FT-IR and SEM analysis, respectively.

3.5. Adsorption Experiments.

For this experiment, the required amount of adsorbents such and 25 mL of Pb(II) ions solutions were mixed together in 100 mL flasks. The mixture was shaken thoroughly using an orbital shaker. Subsequently, for the concentration measurement of Pb (II) ions solutions, atomic absorption spectrophotometer was used. All the adsorption experiments were performed by measuring various factors that were inducing the Pb (II) ions adsorption ability such as solution pH, adsorbent dose, contact time, and initial Pb (II) ions concentration. The effect of each parameter on the Pb(II) ions uptake ability was examined by keeping all other parameters at constant values. These parameters were determined by ranging the initial concentration of Pb (II) ions from 5 to 35mg/L, adsorbent dosage from 0.05 to 0.3 g, contact time from 20 to 120 min, solution pH from 2 to 10, and temperature from 25 to 65°C.

4. RESULT AND DISCUSSION

4.1 Characterization of Nano cellulose crystal

4.1.1 FIIR Analysis

The identification of functional groups and surface characteristics of the prepared Nano cellules crystal sorbents was carried out by using FT-IR spectroscopy. Their spectrum was presented in Figure 1. The spectra have shown major absorption zones in the ranges of 1057–3403 cm^{-1}. Based on these spectral zones, the Nano crystal sorbents prepared from maize cob have several functional groups which display either stretching vibration or bending vibration. These are (broadband around 3403 cm^{-1}), indicating the presence of O–H free stretching vibration of the CH_2–OH structure on cellulose. The bands found in the region of 2884 cm^{-1} are because of the stretching vibration of C–H in cellulose, and the bandsm situated at 1639 cm^{-1} are attributed to the O–H bending vibrations of cellulose. The peaks detected at 1388 cm^{-1} match the C–C stretching and/ or CH_2 symmetric bending in aromatic groups of cellulose. The peaks located at 1057 cm^{-1} are associated with stretching vibration of C = O groups.

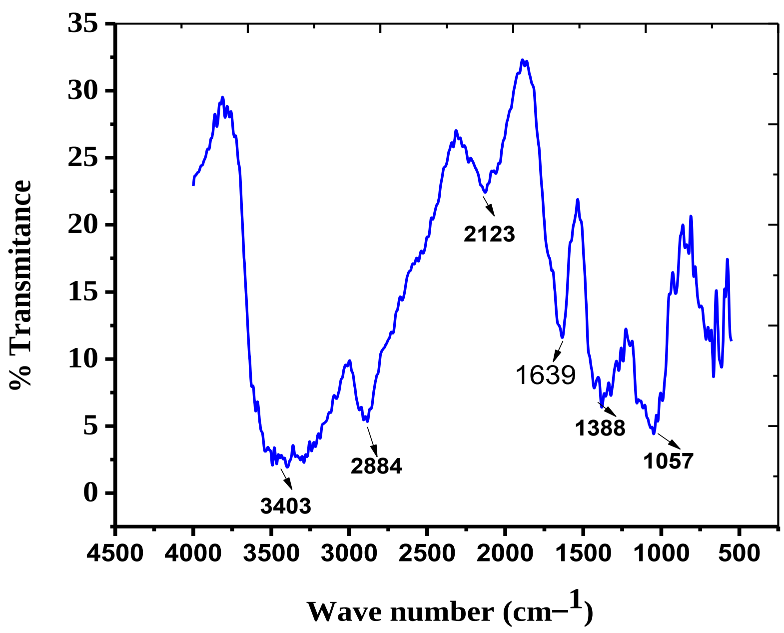

Figure 1 FTIR spectra of Nano cellulose crystal prepared from maize cob

4.1.2 SEM Analysis

SEM characterization was carried out to obtain information about the surface morphology of Nano cellulose crystal prepared from maize cob adsorbents. The SEM images with cylindrical fibrous structure for adsorbent are indicated in Figures 2. These images show that adsorbent was likely to agglomerate.

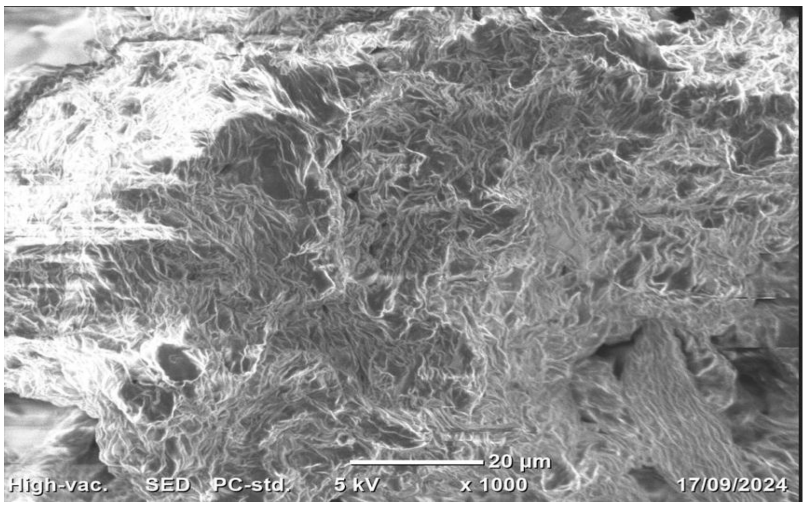

Figure 2 SEM image of crystalline Nano cellulose prepared from maize cob

4.1.3 XRD Analysis

The crystallinity of the sorbent materials was determined with the help of XRD spectrometry (Figure 3). the peaks at 2θ 15.57°, 22.22°, and 34.47° are represented by (110), (110), and (004) crystallographic planes of cellulose , respectively . From the XRD spectra, the crystallite sizes were calculated using Debye Scherer equation.

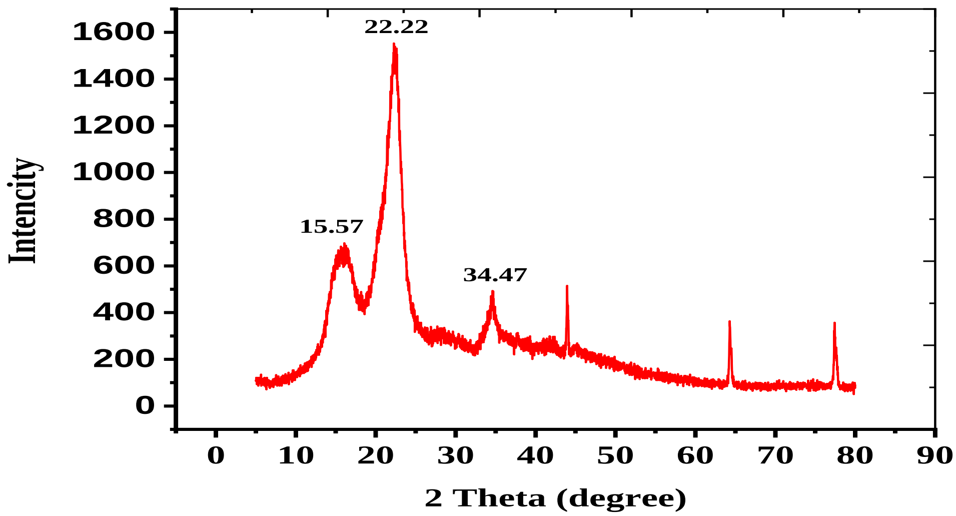

Figure 3 XRD analysis of crystalline Nano cellulose prepared from maize cob

4.2. Optimization adsorption parameters

4.2.1 Effect of Adsorbent Dose.

Investigations for the removal of Pb^{2+} ions from aqueous solution using sorbents mass from 0.05 to 0.3 g, at the optimum initial concentration of 10 mg L^{-1}solution pH of 6, and contact time of 105 minutes. Figures 4 exhibited increased trends of Pb^{2+} ions % removal the results indicated that 90.9 % of Pb^{2+} ions can be removed from aqueous solution using crystalline Nano cellulose sorbent with an optimum sorbent dosage of 0.2 g at 25° C. The increased specific surface area of resulting from the surface modification reactions. The increased specific surface area with smaller particle size resulted in a higher Pb^{2+} ions uptake ability since the oxidation ability of the hydroxyl groups was weaker than that of the aldehyde groups.

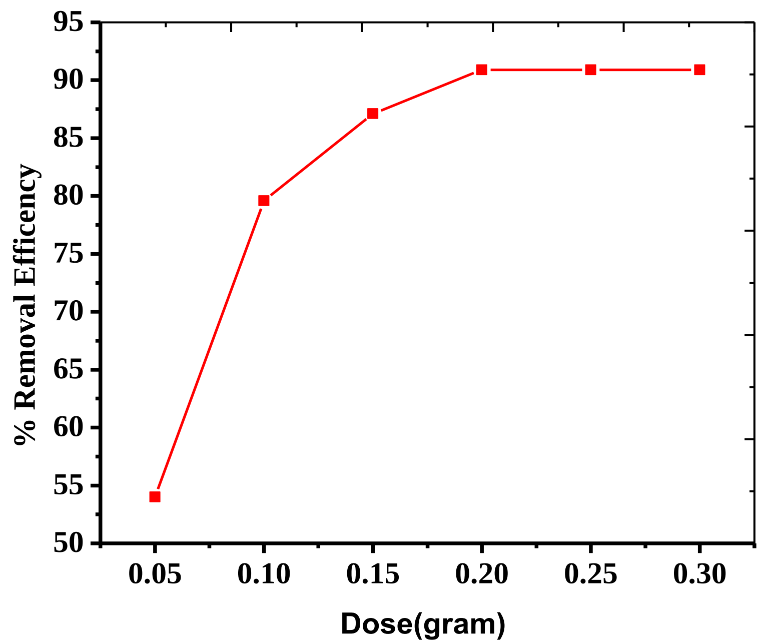

Figure 4 effect of adsorbent dose

4.2.2 Effect of Initial Concentration.

The effect of initial Pb^{2+} ions concentrations for the removal of Pb^{2+} ions from aqeous solution using crystalline Nano cellulose sorbent is given in Figure 5. At the starting point, the removal process was very fast, due to the presence of a large vacant surface area of the sorbents. At increased initial concentrations the removal ability gradually increased, moved toward the optimum value, and reached the optimum amount of 10 mg/L. At this amount, sorbents evidently displayed maximum Pb^{2+} ions uptake ability of 90.1 %.

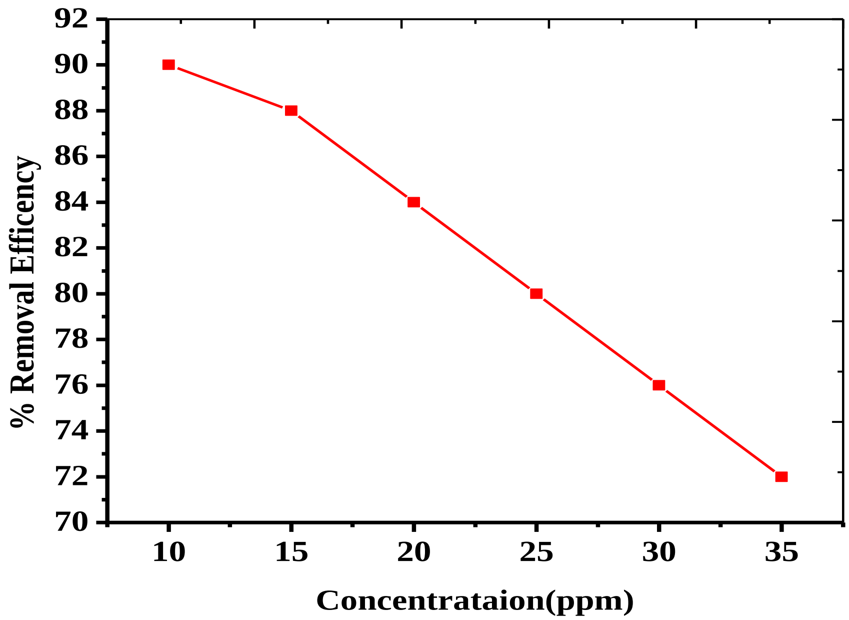

Figure 5 effect of initial concentration

4.2.3 Effect of Contact Times.

The effect of contact time on the Pb^{2+} ions removal was examined by using experiments at an optimum dose of 0.2 g, temperature (T) of 25°C, and initial concentration of Pb^{2+} ions of 10 mg L^{-1} (Figure 6). The % removal ofPb^{2+} ions design with rising the time up to the optimum contact time of 105 min, due to the presence of highly active sites on the surfaces of the adsorbent. The maximum % removal values of 90.1 % were observed Nano cellulose crystal sorbents, at the optimum time of 105 min. After this time, the % removal processes became at equilibrium and proceeded in a fixed manner.

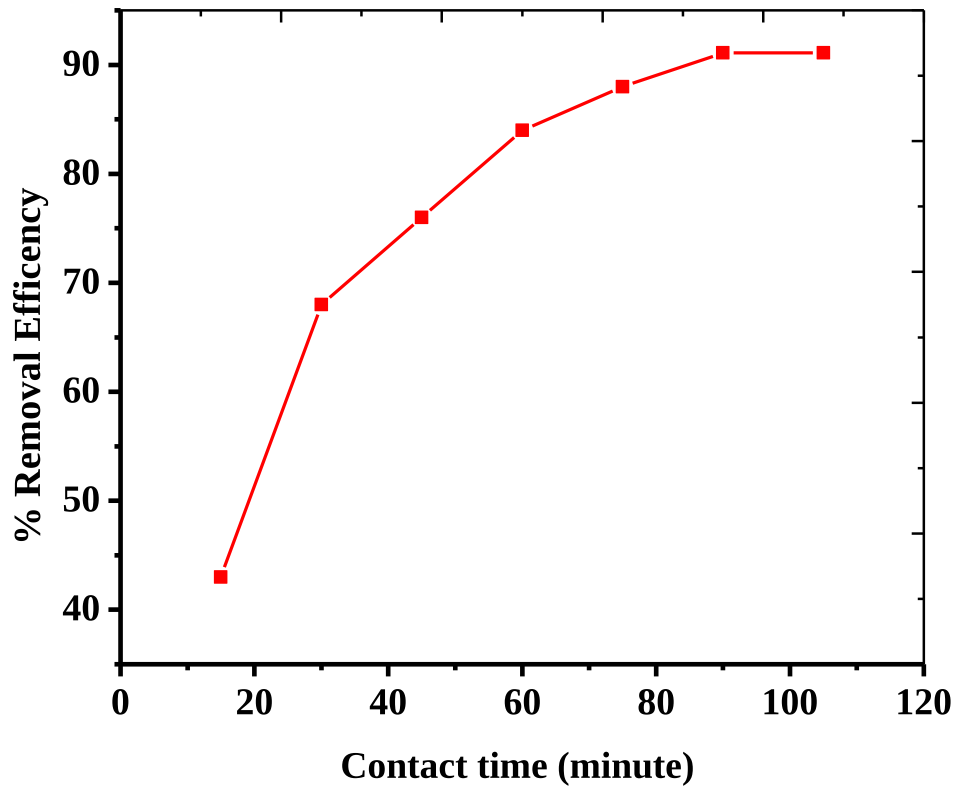

Figure 6 Effect of contact time

4.2.4 Effect of Solution pH.

At low pH values, the interaction of Pb^{2+} ions with sorbents is decreased because of the competition of H^{+} ions and other matrices for the surfaces of Nano crystalline cellulose. In the other words, as the of aqueous lead solution pH raises (less H^{+} ions), the attachment of Pb^{2+} ions to the adsorbents leads to the increased % removal at the pH value of 6. Conversely, if the pH is greater than 6, then the level of OH^{-} ions in the aqueous lead solution increases. Accordingly, the optimum pH for Pb^{2+} ions removal by adsorbents was found to be 6.

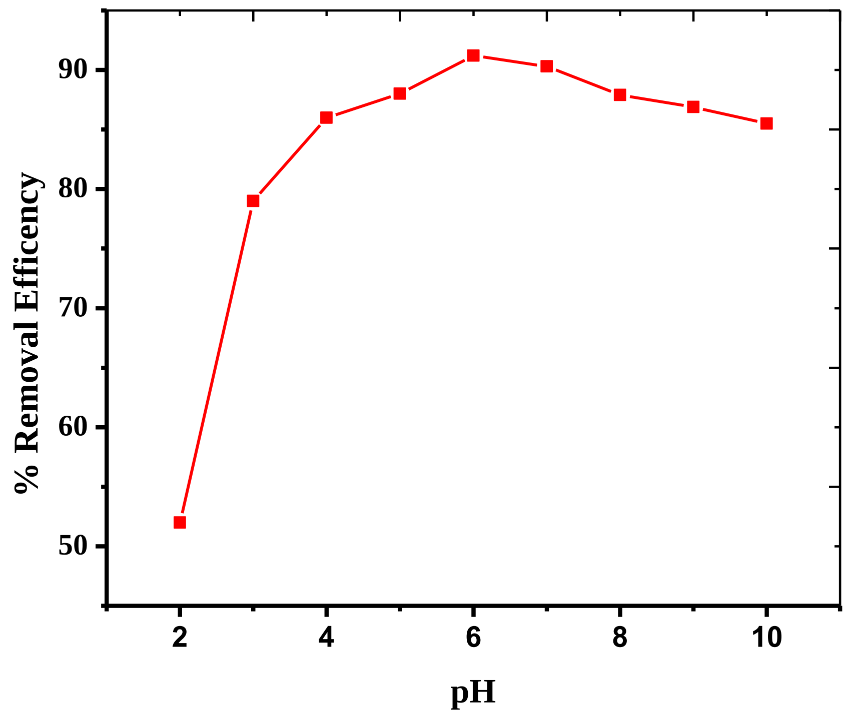

Figure 7 effect of pH

4.2.5 Effect of Temperature.

Figures 8 indicated the effect of temperature on % removal of Pb^{2+} ions from aqueous solution by using Nano crystal cellulose adsorbents. Results have shown that increasing the temperature from 25 to 40°C increase the % removal of Pb^{2+} ions from aqueous solution. The adsorbent have shown the maximum % removal efficiency of 91.3%of Pb^{2+}ions at the optimum dosage of 0.2 g and the optimum temperature of 45°C.

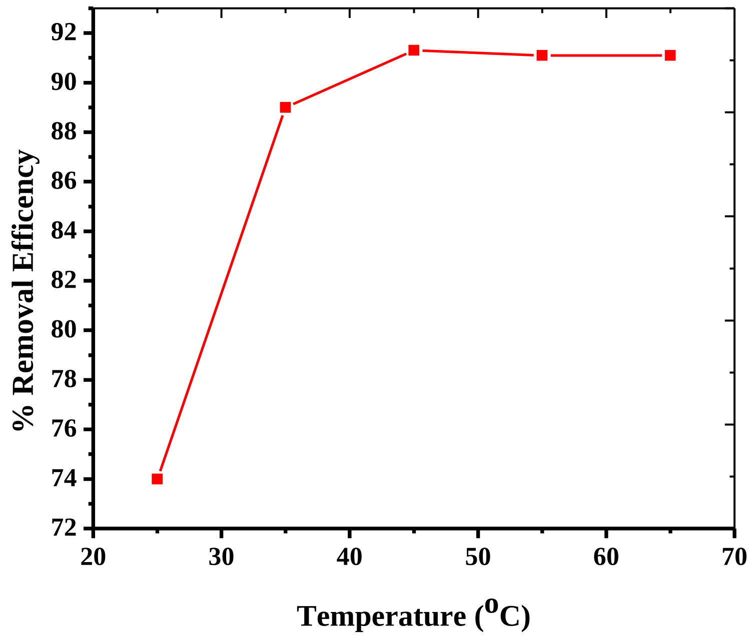

Figure 8 Effect of temperature

4.3. Adsorption Isotherms.

To know the mechanism of Pb^{2+} ions uptake by crystalline Nano cellulose adsorbents, Langmuir and Freundlich, adsorption isotherms were investigated and presented in Figures 9 and 10 respectively. Table 2 illustrates the corresponding parameter values and the correlation coefficient (R^2) values, obtained from each plot. Higher R^2 values for both Langmuir and Freundlich isotherms have shown that the Langmuir and Freundlich isotherm models better fit the isothermal uptake. This suggested that the surfaces of Nano crystalline cellules adsorbents were heterogeneous and physically compatible with monolayer adsorption and the adsorption process was favorable. The favorability of the uptake process was due to n value that lies between 1 and 10, and the strong interactions between the adsorbents and surfaces of the adsorbents were because $1/n < 1$. The fundamental nature of the Langmuir model could be also determined by a dimensionless equilibrium parameter (R_L), the values (0.20) of $R_L < 1$ suggested that the uptake process of Pb^{2+} ions crystal Nano cellulose

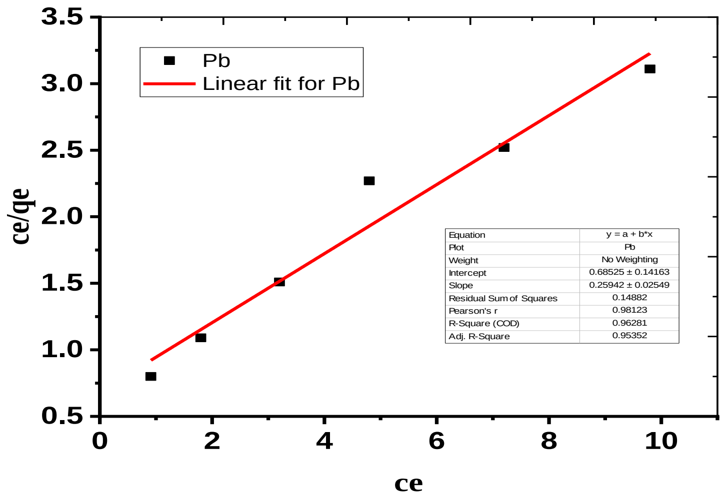

Figure 9 Langmuir adsorption isotherms for the removal of Pb2+ i

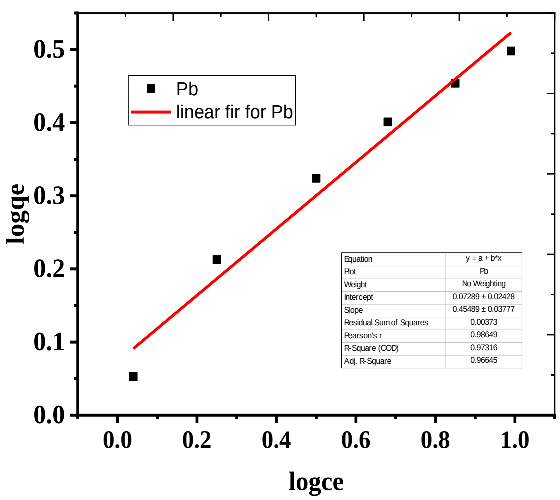

Figure 10 Freundlich adsorption isotherms for the removal of Pb^{2+} ions

Table 2: Langmuir and Freundlich Adsorption isotherm constant for Adsorption Pb^{2+}

Metals	Langmuir constant				Freundlich constants		
Pb	Qe (mg/g	bL (L/mg	R_L	R^2	K_F L/mg	1/n	R^2
	3.85	0.38	0.20	0.95	1.18	2.19	0.94

4.4 Adsorption Kinetics.

In order to investigate the rates of uptake mechanism, pseudo-first-order and pseudo-second-order kinetic models were tested**.** For these, the rates of Pb^{2+} ions uptake crystal Nano cellules sorbents were estimated using linearized pseudo-first-order and pseudo-second order respectively the kinetics data are presented in Table 3 with maximum correlation coefficient values (R^2= 0.99) for pseudo second order kinetic model by crystal Nano cellules sorbents for Pb^{2+} ions uptake. Thus, R^2 values (R^2= 0.96) indicated that pseudo first order kinetic model models were not suitable for Pb^{2+} ions adsorption. Therefore, Figures 11 and 12 indicate representative plot **of** the data for kinetic models for Pb^{2+} ions uptake by crystal Nano cellules sorbents and suggest that the uptake process is chemisorption.

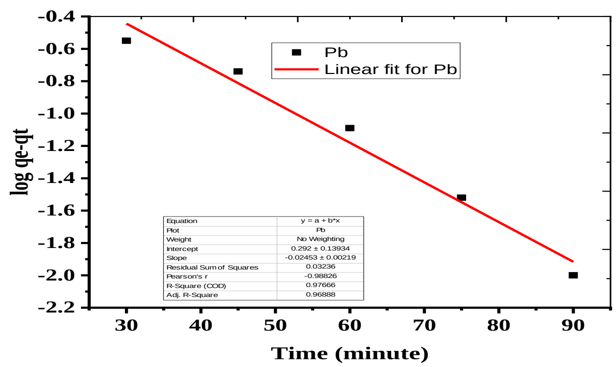

Figure 11 Pseudo first order kinetic model for the adsorption of Pb2+

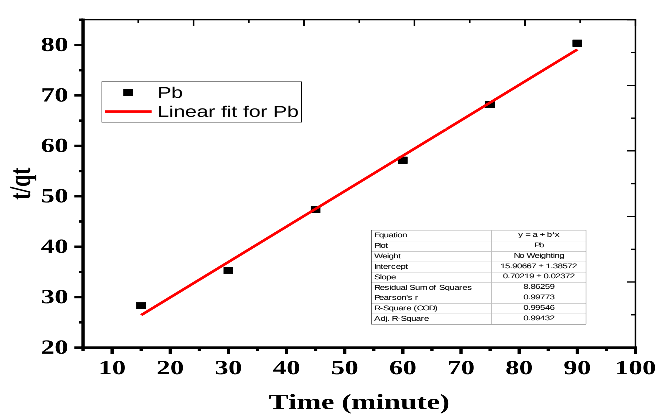

Figure 12 Pseudo second order kinetic model for the adsorption of Pb^{2+}

Table 3: Kinetics parameters for the adsorption of Pb

Metal ion	Pseudo first order			Pseudo second order			
	qe(mg/g)	k_1	R^2		qe(mg/g)	k_2	R^2
Pb	1.95	0.024	0.96	Pb	1.42	0.030	0.99

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

Decomposable and biocompatible cellulose nanomaterial's were prepared by sulfuric acid hydrolysis methods. The prepared adsorbent materials were employed as cost-effective, easily recyclable, and nontoxic materials, with high adsorption abilities, for the removal of Pb^{2+} ions from aqueous solution. The proposed mechanisms for the uptake process under the optimum condition of crystal Nano cellules adsorbent mainly involve the interaction of carboxyl, and hydroxyl groups of cellulose with Pb(II) ions that resulted in higher Pb^{2+} ions uptake ability for adsorbent. The adsorption process was evaluated by adjusting the pH, dose, initial concentration and temperature. Optimum conditions were dose of 0.16 gram initial concentration of 10 ppm, contact time of 115 minute, pH of 6 and temperature of 45 ^{0}c. The uptake mechanism fits with Langmuir and Freundlich uptake isotherm models, and the kinetics of Pb^{2+} ions uptake by crystal Nana cellulose adsorbents were described with the help of the pseudo kinetics model. From this point, one can conclude that crystal Nano cellules adsorbent proved to be a cost-effective and environmentally friendly adsorbent for the uptake of Pb^{2+} ions aqueous solution wastewater.

5.2 Recommendation

Base on the above result the following points were forwarded

Synthesis of functionalized Nano cellules material

.Application of the synthesized nanomaterial for the removal of other toxic heavy metals

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