REMOVAL OF CHROMIUM (VI), COPPER (II), CADMIUM
LEAD (II) IONS FROM WASTEWATER USING CHEMIC
MODIFIED BANANA PEEL AS A LOW COST ADSORBENT

MSc THESIS

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Removal of Chromium (VI), Copper (II), Cadmium (II) and Lea
From Waste Water Using Chemically Modified Banana Peel As A
Adsorbent

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I hereby certify that I have read and evaluated this Thesis entitled, "**REMOVAL OF CADMIUM (II), COPPER (II), CHROMIUM (VI) AND LEAD (II) IONS FROM WASTE WATER USING CHEMICALLY MODIFIED BANANA PEEL AS A LOW COST ADSORBENT"**, prepared under my guidance by **Gebeyehu Eshete**. I recommend that it be submitted as fulfilling the thesis requirement.

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As members of the board of examiners of the MSc Thesis Open Defense Examination, I certify that I have read and evaluated the Thesis prepared by **Gebeyehu Eshete** and examined the candidate. I recommend that the thesis be accepted as fulfilling the Thesis requirement for the degree Master of Science.

Chairperson	Signature	Date
Internal examiner	Signature	Date
External examiner	Signature	Date

DEDICATION

This thesis manuscript is dedicated to my wife, Tsehay Ewnetu, daughters and son, who encouraged and strengthened me in my study**.**

STATEMENT OF THE AUTHOR

By my signature below, I declare and affirm that this Thesis is my own work. I have followed all ethical and technical principles of scholarship in the preparation, data collection, data analysis, and compilations of this Thesis. Any scholarly matter that is included in the Thesis has been given recognition through citation.

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BIOGRAPHICAL SKETCH

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ACRONYMS AND ABBREVATIONS

AAS	Atomic Absorption Spectrometer
BL	Blue Litmus
EEPA	Ethiopian Environmental Protection Agency
FTIR	Fourier Transform Infrared Spectrometer
MBP	Modified Banana Peel
MoE	Ministry of Education
UNMBP	Unmodified Banana Peel
WHO	World Health Organization

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ABSRACT

Toxic heavy metal ions; cadmium, copper, chromium and lead removal is important from the environment due to the health effect of plants and animals. Among the different approaches such as precipitation, membrane process, ionic exchange, floatation and others, adsorption is one of the promising approaches. For this purpose, Banana peel powders in the modified (MBP) and unmodified (UNMBP) forms were prepared as adsorbents. The effects of different experimental parameters, namely, solution pH, dosage, contact time, and initial metal ions concentrations, on adsorption of metal ions, were investigated. The optimum value of each parameter was determined, respectively, for both MBP and UNMBP. The metal ions adsorption was found to be highly pH dependent. The experimental results showed that the adsorbed amounts of heavy metal ions tend to decrease with increase in pH from 6 up to 8 except for chromium. Chromium showed maximum adsorption at pH 2 but declined from pH 2 to 8. Both Freundlich and Langmuir isotherm models were applied to the experimental data but Langmuir isotherm model was fitted with the experimental data well. The adsorption capacities (q_{max}*, mg/g) of UNMBP were 6.25, 2.56, 4.78 and 1.13 mg/g for cadmium, chromium, copper and lead adsorption, respectively, and adsorption capacities (*q_{max}*, mg/g) of MBP were 20.09, 3.5, 19.23, and 4.65 mg/g for cadmium, chromium, copper and lead adsorption, respectively. With regard to adsorption kinetics, the two common models (ie, Pseudo - first and pseudo-second order models) were applied. The desorption efficiency decreased as number of cycles increased and based on the obtained results the modified banana peel was found to be recyclable and environmentally friendly adsorbent for the removal of heavy metal ions from wastewater.*

Keywords: Adsorption, Banana Peel Powder, Heavy Metals, Isotherm Model, Kinetics Model

1. INTRODUCTION

Water is one of the vital necessities for the survival of human beings. Wastewater reclamation, recycling and reuse are vital to meet the water requirements for irrigation, industry and domestic use due to increasing population and development in many parts of the world. Industrial wastewaters largely possess organic and inorganic materials such as dyes, phenols, aromatic compounds, and heavy metals (Pankaj *et al.,* 2012). Many aquatic environments face metal concentrations that exceed water quality criteria designed to protect the environment, animals and humans (Ushakumary, 2013).

Heavy metal ions are discharged into water system from various industrial activities such as electroplating industries, electronic equipment manufacturing, and chemical processing plants. Due to rapid development of industrial activities, the levels of heavy metals in water systems have substantially increased. Heavy metals can easily enter the food chain because of their high solubility in water (Ushakumary, 2013).

A wide variety of heavy metal species enters the aquatic compartment through atmospheric deposition, lixiviation of mining areas, cultivated fields, and industrial discharges, and these activities follow an upward curve in response to the world's ever growing population and it needs to protect all life forms (Minello *et al*., 2009; Minello *et al.,* 2010). It is therefore essential to remove heavy metals from industrial waste waters. Although several technologies have been proposed to treat waste water, because of their disposal problem, very costly chemicals and poison effect of solvents, there is a need for some alternative methods which can overcome all these problems and treat the waste water in an appropriate way. In this regard, biomaterials are preferable to treat wastewater because they are low cost, nonhazardous and environmentally friendly (Ushakumary, 2013).

Plant materials are mainly comprised of cellulose can adsorb heavy metal cations in aqueous solution. Numerous waste biomass sources are available in nature in which adsorption properties have been reported e.g. rice husk, saw dust, tea and coffee waste, orange peels, banana peels, peanut shells, dry tree leaves and barks (Kishore *et al.,* 2008; Nuria *et al*., 2010; Ferda and Selen, 2012). Dehydration and carbonization methods were used to prepare the adsorbents from these peels (Hossaia *et al*., 2012). The main advantage of biosorption is that it gives the significant amount of energy saving from a more efficient wastewater treatment system operating for fewer hours; it is economically attractive because biowates are inexpensive and widely available (Prabu *et al*., 2012).

Banana peels have good adsorbent properties and might be a successful method in the purification of water due to the compounds in the banana peels that contain atoms of nitrogen, sulfur and organic compounds such as carboxylic acids. These acids are charged such that their negatively charged electron pairs are exposed, meaning they can bind with metals ions found in the water solution that usually have a positive charge (King'ori, 2011). FT-IR analysis revealed that carboxyl and hydroxyl groups were the principal functional sites taking part in the adsorption process (Ushakumary, 2013).

Several works have been reported on the removal of heavy metals from wastewater using raw banana peel (UNMBP). It is unusual to get works on the removal of heavy metals; cadmium (II), chromium (VI), copper (II), and lead (II) ions using modified banana peels (MBP). In this study the adsorption process was evaluated using chemically modified banana peel (MBP) in the removal of heavy metals; chromium (VI), copper (II), cadmium (II) and lead(II) ions, from artificially made wastewater.

1.1. Objective of the Study

1.1.1. General objective

To study the adsorption capacity of chemically modified banana peel for the removal of four heavy metals; chromium, copper, cadmium and lead ions from waste water

1.1.2. Specific objectives

- To chemically modify the banana peel.
- To characterize the modified and unmodified banana peel using FT-IR.
- To optimize the experimental parameters that influence on the adsorption process
- To determine efficiency of the chemically modified banana peel to adsorb the stated heavy metal adsorption process.
- To evaluate the adsorption isotherms of the adsorption process in Langmuir and Freundlich isotherm models.
- To investigate the adsorption kinetics of adsorption process using pseudo-first and second order kinetics models.
- To investigate the tendency of the metals and evaluate the recyclability of the adsorbent.

2. REVIEW OF LITERATURE

Most of the heavy metals are classified as hazardous pollutants due to their toxicity. It has been established beyond any doubt that dissolved heavy metals escaping into the environment pose serious health hazard. They accumulate in living tissues throughout the food chain, which has humans at its top (Volesky, 1999). Removal of heavy metal ions from wastewater is essential due to their extreme toxicity towards aquatic life and humans. The increasing environmental pressures have led to stricter regulations with regard to metal discharges particularly in industrialized countries. Hence, there is a need for controlling the heavy metal emission into the environment (Ushakumary, 2013).

Natural products usually considered as by products such as sugar cane bagasse, peanut shells, banana peel and apple waste, have been employed to extract metals from waste water (Guragel *et al.*, 2009). This is possible due to the presence of acid groups such as carboxylic and phenolic group adsorbent (Min *et al.*, 2004).

The feasibility of using banana peel for removal of the pesticides atrazine and ametryne from river and treated waters has been demonstrated, allowing the design of an efficient, fast, and low-cost strategy for remediation of polluted waters (Claudineia *et., al* 2013).

The adsorptive removal of hexavalent chromium Cr(VI) from aqueous solutions was investigated by acrylonitrile grafted banana peels (GBPs). Banana peels were treated with 10% HCl, followed by alkaline hydrolysis with 10% NaOH, and washed thoroughly. The bleaching of alkali hydrolyzed peels was carried out with sodium chlorate ($NaClO_3$) in the presence of hydrogen peroxide and glacial acetic acid The optimum conditions for adsorption of Cr(VI) were found to be the following: pH 3, adsorbent dose 4 g/L, concentration 400 mg/L and contact time of 120 min. The adsorption of Cr(VI) onto grafted banana peels (GBPs) was recorded to be 96%. The adsorption data were fully fitted with the Freundlich and Langmuir isotherm model and followed a pseudo-second order kinetic model. Owing to high efficiency and low cost, grafted banana peels (GBPs) can be use in wastewater treatment (Ashraf *et., al* 2016).

Banana peels and Pumpkins are used as good adsorbents for removing heavy metals from contaminated water, which have been observed and studied currently. The effects of various parameters such as pH, agitation speed and contact time was studied and good results were obtained at pH 7, 100 rpm and 90 minnutes of contact time. The results indicate that usage of household waste such as these can be used as a good biosorbent for removal of heavy metals on a large scale and create effective, cheap and efficient methods in treating wastewater (Mrinalini and Anuja, 2014).

The use of dried banana peels as an adsorbent for removal of cadmium ions from aqueous solutions has been studied. Batch experiments have been conducted at different concentrations to evaluate the maximum adsorption capacity of dried banana peels. The influence of pH, contact time, adsorbent dose was investigated at room temperature. Langmuir and Freundlich adsorption isotherm models used to test equilibrium of adsorption. The process of adsorption was found to be fast and equilibrium has been reached in within 2 hours. The maximum adsorption capacity of cadmium on dried banana peels is 5.91 mg/g, evaluated by Langmuir adsorption isotherm model. Pseudo-first-order and pseudo-second-order kinetic models applied to evaluate rate constants. FTIR spectra of adsorbent showed the presence of hydroxyl, carboxylic and amine groups in dried banana peels. This study shows that banana peels has great potential for removal of cadmium ions and can be used as a good adsorbent for removal of cadmium from water and wastewater at very low concentration (Prashant *et., al* 2017).

Banana peel, a discarded agricultural waste was used to produce bioadsorbent through easy and environmentally friendly processes. This banana peel based biosorbent was evaluated for adsorptive removal of copper from water and its desorption capability. The characterization results showed this biosorbent had very high specific surface area, potential binding sites and functional groups. The optimal conditions for biosorption were found at pH 6.5, biosorbent size of less than 75 µ, dose of 0.5 g/100 ml and 1 hour contact time. Thermodynamic analysis also indicated that its adsorption was spontaneous. Significant desorption of copper (94%) was obtained when using 0.1N H_2SO_4. The maximum adsorption and desorption capacities were 20.37 and 32.40 mg/g, respectively. The adsorption processes were controlled by chemisorptions. Both adsorption and desorption processes could be described by the pseudo-first order kinetic. The potential applicability of banana peel based bioadsorbent could be further examined in a large-scale (Hossain *et., al* 2012).

2.1. Sources and Impacts of Heavy Metals

Heavy metals have been used by humans for thousands of years. Heavy metal cations can be introduced into agricultural soils by application of fertilizers, liming materials, sewage sludge, composts, and other industrial and urban waste materials. Therefore, heavy-metal adsorption reactions, in a competitive system, are important to determine heavy-metal availability to evaluate the selectivity sequence and estimate the competitive adsorption of several heavy metals in seven different soils with different chemical and mineralogical characteristics. The most common sequences were Cr > Pb > Cu > Cd > Zn > Ni and Pb > Cr > Cu > Cd > Ni > Zn. Chromium, lead and copper were the heavy-metal cations most strongly adsorbed by all soils, whereas cadmium, nickel, and zinc were the least adsorbed, in the competitive situation (Ushakumary, 2013).

Chromium is one of the toxic metals often found in effluents discharged from industries involved in paints, pigments, dyes, textiles, leather tanning, electroplating, metal finishing, nuclear power plants and chromate preparation (Wu *et al.*, 2008). Chromium in the form of hexavalent chromium (Cr(VI)) from tannery wastewater is one of the major concerns of environmental contamination.

Although Cr(III) is less toxic and more soluble than hexavalent chromium (Cr (VI)), Cr(III) can be oxidized to Cr(VI) under certain circumstances, resulting in more harm to environment and the public (Bayat, 2002). Chromium in its hexavalent species have become a serious problem as a contaminant because it is a respiratory carcinogen and acutely toxic in high doses. According to (WHO, 2008), chromium is toxic, corrosive and irritant when the concentrations values exceed the threshold limit value of 0.05 mg/L in drinking water. Chromium ingestion beyond permissible quantities causes various chronic disorders in human beings. Strong exposure to chromium causes cancer in digestive tract and lung and may cause nauseas, vomiting, severe diarrhea and hemorrhage (Prakasham *et al.*, 1999).

Lead occurs in mines and smelters as well as welding of lead painted metal, and in battery plants. Low or moderate exposure may take place in the glass industry. Lead can end up in water and soils through corrosion of leaded pipelines in a water transporting system and through corrosion of leaded paints. It cannot be broken down; it can only be converted to other forms. Lead accumulates in the bodies of water and soil organisms. These will experience health effects from lead poisoning. Health effects on shellfish can take place even when only very small concentrations of lead are present. Body functions of phytoplankton can be disturbed when lead interferes (Asma *et al.*, 2005). Lead poisoning causes headache, irritability, abdominal pain and various symptoms related to the nervous system. Lead encephalopathy is characterized by sleeplessness and restlessness. Children may be affected by behavioral disturbances, learning and concentration difficulties. Studies have shown that long-term low level lead exposure in children may also lead to diminished intellectual capacity. Prolonged exposure to heavy metals such as chromium, cadmium, copper, lead, nickel, and zinc can cause deleterious health effects in humans (Larous, 2003).

Copper can be released into the environment by both natural sources and human activities. Examples of natural sources are wind-blown dust, decaying vegetation, forest fires and sea spray. Other examples are mining, metal production, wood production and phosphate fertilizer production. Because copper is released both naturally and through human activity it is very widespread in the environment. Copper is often found near mines, industrial settings, landfills and waste disposals (Asma *et al.*, 2005). Copper is the major available type of heavy metal in the aquatic environment. Copper in the blood system may generate reactive free oxygen species and damage the protein, lipids and DNA (Brewer, 2010). The excess copper compound in the body may also affects on aging, schizophrenia, mental illness, Indian childhood cirrhosis, Wilson's and Alzheimer's diseases (Brewer, 2007; Faller, 2009; Haureau and Falle, 2009). Copper has damaged the marine ecosystem and damaged the gills, liver, kidneys, the nervous system and changing sexual life of fishes (Flemming and Trevors, 1989); Van Genderen *et al.,* 2005).

Cadmium occurs naturally in the environment by the gradual process of erosion and abrasion of rocks and soils, and from singular events such as forest fires and volcanic eruptions. It is therefore naturally present everywhere in air, water, soils and foodstuffs. The best known cadmium mineral is greenockite, cadmium sulfide (77.6% Cd). Other minerals are otavite, cadmium carbonate (61.5% Cd) and pure cadmium oxide (87.5% Cd). Greenockite (CdS) is nearly always associated with sphalerite (ZnS). As a consequence, cadmium is produced mainly as a byproduct from mining, smelting, and refining of sulfide ores of zinc (Rao *et al.,* 2010e). Cadmium is one of the heavy metals, which is highly toxic to human, plants and animals. The metal is of special concern because it is non degradable and therefore persistent. The main anthropogenic pathway through which cadmium enters environment is via wastes from industrial processes such as electroplating, smelting, alloy manufacturing, pigments, plastic, cadmium-nickel batteries, fertilizers, pesticides, mining, pigments and dyes, textile operations and refining (Chen and Wu, 2000; Yua *et al.*, 2000; Chen *et al.,* 2010; Wu, 2010). Cadmium is non-essential and non-beneficial element to plant and animals, it is non biodegradable and it can travel through the food chain. Toxic effects are especially pronounced in humans. It causes kidney damage, bone disease and cancer. Chronic exposure to elevated levels of cadmium known to cause ingestion (renal dysfunction, hypertension and anemia (Mckay, 2000; Polard *et al.*, 2000). Cadmium metal is a serious cause of environmental degradation. Therefore, it is necessary to alleviate cadmium ion from industrial effluents.

2.2. Waste Water Treatment Options for Heavy Metal Removal

Many methods for wastewater treatment have been described include chemical and surface chemistry processes such as precipitation, adsorption, membrane processes, ionic exchange, floatation, and others. However, those techniques have their own inherent limitation such as less efficiency, sensitivity, operating conditions, and production of secondary sludge requiring further costly disposal. These disadvantages, together with the need for more economical and effective methods for recovery of metal from wastewater, have resulted in the development of alternative separation technologies. One of such alternative is adsorption (Ahluwalia and Goyal *et al.*, 2005). Adsorption is by far the most versatile and widely used technique for the removal of heavy metal ions. Activated carbon has been the standard for industrial wastewater treatment for almost three decades. Despite its widespread use, activated carbon still remains an expensive material. In recent years, the research interest in to the low cost locally available biomaterial adsorbent, an alternative to activated carbon has grown. Several technologies have been proposed for the extraction of heavy metal ions using solid materials such as modified silica, alumina, activated carbon, and resins have been extensively investigated (Gehaedi *et al.*, 2005; Gehaedi *et al.*, 2006; Gehaedi *et al.*, 2008; Huang *et al.*, 2008; Gehaedi *et al.*, 2009).

Many researchers have worked on developing efficient treatment technologies. Treatment technologies are mainly based on physicochemical, electrochemical or advanced oxidation processes. Physicochemical processes include membrane filtration, chemical precipitation, ion-exchange, and adsorption. Electrocoagulation, electroflotation, and electrodeposition are categorized under the name of electrochemical methods. Photo catalysis is one of the advanced oxidation processes (Kuniawan *et al.*, 2006). Beside all these, nanotechnology is a practical approach in treating wastewaters, too. Among all these possible methods, those with cost-effective, environmentally friendly and no further pollutants features are the favorites. On the other hand, there are biological processes such as the activated sludge process that are widely used in the treatment of industrial and municipal wastewaters. Biological processes are mostly considered to be cheaper than physical and chemical methods. Biological processes are usually aimed at removing the readily biodegradable chemical oxygen demand (COD), or relatively readily hydrolysable substances, but are not specifically designed to remove heavy metals (Dionisi, *et al*., 2014).

In the last two decades, nanotechnology is becoming a science of nanomaterials. This technology is getting a lot of attention not only in the academic communities but also among investors and industries. It is used extensively in chemistry, biology, engineering, health and medicine, consumer products, and water information technology (Kokini and Sozer, 2012). Numerous studies (Qu *et al*., 2013; Diallo *et al*., 2009; Cloete, 2009; Hotez and Lowry, 2010) have highlighted nanotechnology as a practical developing wastewater treatment system. The treatment systems of this technology overcome old major deficiencies and provide systems with higher removal efficiency, low waste generation, and specific uptake (Kar and Tewari, 2013). .

2.3. Adsorption

Adsorption is the process through which a substance, originally present in one phase, is removed from that phase by accumulation at the interface between that phase and a separate (solid) phase. Adsorption has been described in a wide range of non-living biomass like potato and banana peel wastes (Mohammed and Devi, 2009), untreated Cocos Nucifara (Prasad and Satya, 2010), orange peel, and banana peel (Ferda and Selen, 2012), untreated coffee grounds (Azouaou *et al*., 2010), as well as of living biomass like, microbial cell (moss) (Lee and Low, 1989); fungi (Emilia and Sudha , 2002; Gopal *et al*., 2002), yeast (Can and Jianlong, 2008; Gupta and Rastogi, 2008; Mohammad *et al*., 2011) and algae (Dumitru and Laura, 2012). The metal sequestering ability of microorganism such as yeast, bacteria, fungi and algae have been investigated and reported. Adsorption technology based on the utilization of dead biomass offers certain major advantages such as lack of toxicity constraints, non requirement of nutrient supply, and recovery of bound metal species by desorption (Gadd, 1990).

2.4. Plant wastes as an Adsorbent

Agricultural residue, vegetable wastes, weeds and plant fibers have been used as environmentally friendly adsorbent. In the last few decades, alternative adsorbents for the treatment of heavy metal contamination have been investigated (Bayat, 2002; Amany, 2007; Cetin and Pehlivan, 2007; Hanfiah and Wan, 2008; Mustafa, 2008; Nuria *et al*., 2010). There is a large volume of literature relating to the performance of different biosorbents for the removal of variety of heavy metals (Larous *et al*., 2005; Ar and Uysal, 2007; Aldrich and Qi, 2008; Atalay *et al.,* 2010).The agricultural residue seem to be preferred (Pollard *et al*., 1992; Johnson *et al*., 2002; Nasernejad *et al*., 2005; Horsfall *et al*., 2006). Studies were conducted using banana peel for As(III) (Suantak *et al*., 2012) and watermelon rind for Ni(II) and Co(II) (Lakshmipathy and Sarada, 2013); Azouaou *et al.,* 2010) studied the effect of various parameters on adsorption capacity using untreated coffee grounds as adsorbent. They found that the adsorption process is a function of the adsorbent concentration, pH, metal ion concentration and temperature (Mishra and Pate, 2009) examined the role of low cost adsorbents on lead and zinc ions removal from waste water (Venkateswarlu *et al*., 2007) carried out investigations on *Azadirachta indica* (neem) leaf powder as an adsorbent on chromium removal from aqueous solution. The results indicated that the adsorption capacity is strongly depends on equilibrium pH (Wankasi *et al*., 2006) used the untreated coffee husks as adsorbents for the removal of heavy metal ions such as Cd(II), Cu(II) and Zn(II) from aqueous solution. The results indicated that the highest adsorption capacity occurred at distinct pH values for each metal ion.

2.5. Adsorption Mechanisms

There are two types of adsorption phenomena, physical adsorption and chemical adsorption (Jiaping, 2012).

2.5.1. Physical Adsorption

Physical adsorption mechanism involves Van der waals' forces of attraction between the metal and the cell surface, which is not dependent on the cell metabolism (Tsezos and Volesky, 1982). Thorium and uranium bio-sorption by fungal biomass of *Rhizopus arrhizus* is based on physical adsorption in the cell-wall chitin structure (Kuyucak and Volesky, 1989). Uranium, cadmium, zinc, copper and cobalt bio-sorption by dead biomass of algae, fungi and yeast takes place through electrostatic interaction between ions in solution and cells walls. Physical adsorption is furthermore responsible for copper, nickel, cadmium, zinc and lead bio-sorption by *Rhizopus arrhizus* (Fourest and Roux, 1992).

2.5.2. Chemisorptions

Chemisorption is the result of chemical interaction between the solid adsorbent and the adsorbed substance. In chemisorptions the bonds may be ionic or covalent depending on the nature of the material. Chemisorption is characterized by the formation of strong chemical bond between adsorbate and chemically active surface sites, often has high activation energy, generally irreversible except at high temperature and due to the high adsorption energy the assumption of monolayer adsorption works well. Chemisorption is of particular importance in catalysis (Ushakumary, 2013).

2.5.2.1. Ion exchange

Ion exchange is an important concept in heavy metal adsorption. (Ozer *et al.*, 2003) found that the bio-sorption capacities of Pb^{2+}, Ni^{2+} and Cr^{3+} onto *S.cerevisiae* increased in the order of Pb^{2+} >Ni^{2+} > Cr^{3+} which increased with the atomic number increasing. (Benguella and Benaissa, 2002) investigated the bio-sorption characters of Cu^{2+}, Zn^{2+} and Cd^{2+}onto chitin, the results indicated that the bio-sorption capacity was correlated with ionic potential and ionic radius. Ion exchange involves interaction between functional groups on the cell surface and the metal ions. Cell wall of microorganism contains polysaccharides as basic building blocks. The ion exchange properties of natural polysaccharides have been studied in detail and are a well established fact that bivalent metal ions exchange with counter ions of the polysaccharides (TseZos and Volesky, 1982).

Alginates of marine algae usually occur as natural salts of K^{+}, Na^{+}, Ca^{+2} and Mg^{2+}. These metallic ions can exchange with the counter ions such as Co^{2+}, Cu^{2+}, $Cd^{2+}$and Zn^{2+} resulting in the biosorptive uptake of the metals (Kuyucak and Volesky, 1989). (Yeneneh *et al.,* 2011) hypothesized that adsorption of Ni(II), Cd(II) and Pb(II) from aqueous solution by shells of hazelnut and almond take place through ion exchange. The major components of the polymeric material in shell are lignin, tannins or other phenolic compounds. Based on the structure of the phenolic compounds a possible mechanism of ion exchange could be considered as a divalent heavy metal ion (M^{2+}) that attaches itself to two adjacent hydroxyl groups and two oxy groups which could donate two pairs of electrons to metal ions forming four coordination number compounds and releasing two hydrogen ions into solution (Ushakumary, 20013).

2.5.2.2. Complexation

The metal removal from solution may also take place through complex formation on the cell surface after interaction between the metal and active groups. Metal ions can bind to unidentate (single) ligands or to chelates (Tsezos and Volesky, 1982; Cabral, 1992). Adsorption by *Rhizopus arrhizus* has a mechanism not only based on physical adsorption , but also on metal complexation with nitrogen of the chitin cell wall network (Cabral, 1992).

2.5.2.3. Precipitation

Precipitation of the metals may take place both in solution and on the cell surface. Furthermore, it may be either dependence on the cellular metabolism if, in the presence of toxic metals, the microorganisms produce compounds which favor the precipitation process. In case where precipitation is not dependent on the cellular metabolism, it may be a consequence of the chemical interaction between the metal and the cell surface. This phenomenon is the terminal step of uranium bio-sorption by *Rhizopus arrhizus.* The formation of the complex uranium–chitin, mentioned above, is followed by the complex hydrolysis and the precipitation of the hydrolysis product uranyl hydroxide in the cell wall (Tsezos and Volesky, 1982). An additional mechanism, such as entrapment of metals in the form of insoluble micro deposits, could greatly contribute to cadmium adsorption by the biomass marine algae (Holan and Volesky, 1994).

2.6. Modification of Biosorbent

The utilization of raw plant materials as biosorbents has been limited due to the leaching of organic compounds such as cellulose lignin, pectin and ligno-cellulose into solution. Chemical modification on solid biomasses has been used as a remedy to improve their physical, chemical and biosorption capacity (Anirudhan *et al.,* 2006; Yeneneh *et al.,* 2011). The application of untreated plant wastes as adsorbents can also bring several problems such as low adsorption capacity, high chemical oxygen demand (COD) and biological oxygen demand (BOD) as well as total organic carbon (TOC) due to release of soluble organic compounds contained in the plant materials (Nakajima and Sakaguchi, 1990; Gaballah *et al*., 1997). The increase of the COD, BOD and TOC can cause depletion of oxygen content in water and can threaten the aquatic life. Therefore, plant wastes need to be modified or treated before being applied for the decontamination of heavy metals.

Pretreatment methods using different kinds of modifying agents such as base solutions (sodium hydroxide, calcium hydroxide, sodium carbonate) mineral and organic acid solutions (hydrochloric acid, nitric acid, sulfuric acid, tartaric acid, citric acid, thioglycollic acid), organic compounds (ethylenediamine, formaldehyde, epichlorohydrin, methanol), oxidizing agent (hydrogen peroxide), dye (Reactive Orange 13), etc. for the purpose of removing soluble organic compounds, eliminating coloration of the aqueous solutions and increasing efficiency of metal adsorption have been performed by many researchers (Lazlo, 1987; Azab and Peterson, 1989; Low *et al*., 1995; Reddy *et al*., 1997; Min *et al*., 2004; Shukla and Pai, 2005a; Abia *et al*., 2006; Acarand and Eren, 2006; Baral *et al.,* 2006; Kumar and Bandyopadhyay, 2006; Rehman *et al*., 2006; Wankasi *et al*., 2006; Gupta *et al*., 2008).

A detail analysis on the ideal concentration of NaOH for modifying juniper fiber for adsorption of cadmium ions was carried out by (Min *et al*., 2004). Sodium hydroxide treatment of lignocellulosic materials can cause swelling which leads to an increase in internal surface area, a decrease in the degree of polymerization, a decrease in crystallinity separation of structural linkages between lignin and carbohydrates and disruption of the lignin structure. Sodium hydroxide is a good reagent for saponification or the conversion of an ester group to carboxylate and alcohol, as shown in the equation below:

$$\mathrm{OH^-}$$

$$\mathrm{RCOOR'} + \mathrm{H_2O} \qquad\qquad \mathrm{RCOO^-} + \mathrm{R'OH}$$

The authors reported that adsorbents contain pectin substances consisting primarily of galacturonic acid and O-methyl esters. Upon treatment with NaOH, the O-methylesters are converted to methanol and additional galacturonic acid. The adsorbent surfaces will have more negative charge sites or greater number of metal adsorption binding sites, hence greater metal adsorption capacity (Kumar and Bandyopadhyay, 2006).

2.7. Factors Affecting Adsorption

2.7.1. Contact Time

The amount adsorbed on to the adsorbent is in a state of dynamic equilibrium with the amount desorbed from the adsorbent. The time required to attain this state of equilibrium is termed as the equilibrium time. The amount adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under the operating conditions. The removal efficiency increased with an increase in contact time before equilibrium is reached (Azouaou *et al*., 2010; Mohammad *et al*., 2011).

2.7.2. pH

The pH value of the metal solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. The pH of the solution would affect both aqueous chemistry and surface binding sites of the adsorbents. The effect of pH in turn depends on the charge on the adsorbent surface. If the adsorbent surface is negatively charged, at lower pH, the large number of H^+, the H^+ ions may compete effectively with the cations of the solution causing a decrease in the amount of metal ions adsorbed. At higher pH, the small number of H^+, the competion of H^+ with the cations of the solution decreases as a result, the amount of metal ions adsorbed increases and a better adsorption is obtained (Jiaping, 2012). The pH of the solution was clearly an important parameter that controlled the adsorption process (Waranusantigul *et al*., 2003; Babu and Gupta, 2008; Azouaou *et al.,* 2010; Hao *et al*., 2010).

2.7.3. Concentration of the Metal ion

Whatever be the mechanism of adsorption from the solution, it is certain that the extent depends mainly on the available surface of the adsorbent. The process of adsorption is almost invariably reversible and a definite equilibrium is reached in a short time dependant on the concentration of the solutions. As the initial metal ion concentration increases, the binding sites becomes more and more saturated, most of the metal ions are unadsorbed and adsorption decreases (Ushakumary, 2013).

2.7.4. Adsorbent Dose

The adsorbent dosage is an important parameter because this determines the capacity of an adsorbent. The removal of metal ions increases with an increase in the adsorbent dosage. The effect of adsorbent dosage on adsorption was studied by varying the amount of adsorbents and keeping the other parameters constant (Saifuddin and Kumaran, 2005; Azouaou *et al*., 2010; EI-Said *et al*., 2010).

2.8. Adsorption Isotherm Model

Among all phenomena governing the mobility of substances in aqueous porous media and aquatic environments, the transfer of substances from a mobile phase (liquid or gaseous) to a solid phase is a universal phenomenon. That is the reason why the ‘‘isotherm’’, a curve describing the retention of a substance on a solid at various concentrations, is a major tool to describe and predict the mobility of this substance in the environment. These retention/ release phenomena are sometimes strongly kinetically controlled, so that time-dependence of the sorption isotherm must be specified. The word ‘‘isotherm’’ was specifically chosen because of the influence of the temperature on adsorption reactions; temperature must be kept constant and specified (Amir *et al.,* 2007).

The need to design low-cost adsorbents for the detoxification of industrial effluents has been a growing concern for most environmental researchers. So modeling of experimental data from adsorption processes is a very important means of predicting the mechanisms of various adsorption systems. A proper understanding and interpretation of adsorption isotherms is critical for the overall improvement of adsorption mechanism pathways and effective design of adsorption system. In recent times, linear regression analysis has been one of the most applied tools for defining the best fitting adsorption models because it quantifies the distribution of adsorbates, analyzes the adsorption system, and verifies the consistency of theoretical assumptions of adsorption isotherm model (Nimibofa *et al.,* 2017).

2.8.1. Langmuir Isotherms

During adsorption a rapid equilibrium is established between adsorbed metal ions and metal ions in the solution. The equilibrium metal uptake q_e is calculated using the following equation:

$$q_e = \qquad (1)$$

Where, V is the volume of the solution, C_i and C_f are initial and equilibrium concentrations, respectively and m is the dry mass of adsorbent (Can and Jianlong, 2007). The most widely used isotherm equation for modeling the equilibrium is the Langmuir equation which is valid for monolayer sorption on to a surface with a finite number of identical sites and is given by equation:

(2)

Where q_{max} is the practical maximum amount of the metal ion per unit weight of the adsorbent to form a complete monolayer on the surface bound at high C_f and b is a constant related to the affinity of the binding sites q_{max} represents a limiting adsorption capacity when the surface is fully covered with metal ions and assists in the comparison of adsorption performance particularly in cases where the sorbent did not reach its full saturation in experiments. q_{max} and b can be determined from the linear plot of C_f/q_e versus C_f (Babu and Gupta, 2008). The linearzed form of this model equation is given as

(3)

The conformity of the adsorption process to Langmuir model is determined using Equation (4), another Langmuir unit less express:

(4)

Table 1. Type of isotherms for various R_L

R_L	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	irreversible

where R_L is the separation factor, C_o is the initial metal concentration (mg/L) and b is the Langmuir adsorption constant (L/mg). $R_L > 1$ indicates an unfavorable monolayer adsorption process, $R_L = 1$ linear, $0 < R_L < 1$ favorable and $R_L = 0$ irreversible (Aysha, 2013).

2.8. 2. Freundlich Isotherms

The empirical Freundlich model also considers mono molecular layer coverage of solute on the adsorbent. However, it assumes the adsorbent has a heterogeneous surface so that binding sites are not identical. This model takes the following form for a single component adsorption (Azouaou *et al.*, 2010).

$$q = KC_f^{1/n} \quad (5)$$

where K and n are the Freundlich constants characteristic of the system. K and n are indicators of adsorption capacity and adsorption intensity respectively. Though the Freundlich isotherm is more widely used, it provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model (Yua *et al*., 2000; Ferda *et al*., 2012).

$$\log q = \log K + \log C_f \qquad (6)$$

Langmuir and Freundlich isotherms are insufficient to explain the physical and chemical characteristics of adsorption. The Langmuir isotherm constants do not explain the chemical or physical properties of the adsorption process. However, the mean adsorption energy (E) calculated from the D-R isotherm provides important information about these properties. Dubinin – Radushkevich (D-R) isotherm is commonly used to describe the adsorption isotherms of single solute systems (Azouaou *et al*., 2010). The D-R isotherm is expressed as

$$q = q_{max}\exp(-B[\ RT\ln(1+\ )\ ) \qquad (7)$$

$$\ln q = \ln q_{max} - Be^2 \qquad (8)$$

Where B is a constant related to the adsorption energy, R is the gas constant ($8.314 x 10^{-3}$kJ/mol. K) and T is the absolute temperature.

$$e\ RT\ln) \qquad (9)$$

$$E \qquad (10)$$

This parameter gives information about the physical and chemical adsorption. With the magnitude of E between 8 and 16 $kJmol^{-1}$ the adsorption process follows chemical ion exchange, while for the values of $E < 8$ $kJmol^{-1}$, the adsorption process is of a physical nature. (Kumar *et al.* 2011) studied the adsorption behavior of nickel (II) from aqueous solution onto agricultural waste such as cashew nut shell. They found that the adsorption process is a function of the parameters such as solution pH, adsorbent dose, contact time, initial metal ion concentration and temperature. The Langmuir and Freundlich models were applied to describe the equilibrium isotherms.

2.9. Adsorption Kinetics Models

The prediction of adsorption rate gives important information for designing batch adsorption systems. The kinetics of adsorption described by using two kinetic models, pseudo-first order and pseudo-second order models. These models take into account the adsorbed quantities that will enable us in determining the reactor volume (Gupta and Rastogi, 2007; Azouaou, 2010).

2.9.1. Pseudo-First Order Kinetic

The kinetics in most cases follows the first order rate equation.

$$= k_1 \qquad (11)$$

Where qe and q_t are the adsorption capacity at equilibrium and at time t respectively, and k_1 is the rate constant of the pseudo first order adsorption process. The integrated linear form of the above eqn. can be expressed as follows:

$$\log(q_e - q_t) = \log q_e \ \_ \ t \qquad (12)$$

Plot of log (q_e-q_t) versus time (t) gives a straight line for pseudo-first order adsorption kinetics and the rate constant k_1 was computed from the plot.

2.9.2. Pseudo-Second Order Kinetics

The adsorption data was also studied by pseudo-second order kinetics

$$dq\ /dt = k_2(q_e - q_t)^2 \qquad (13)$$

Where k_2 is the second order rate constant. After integration,

$$t \qquad (14)$$

This can be written in the linear form on further simplification

$$= \qquad (15)$$

The applicability of this equation studied by a plot of t/q_t versus time (t). Plot of t/q_t versus time (t) gives a straight line equation with slope $1/q_e$ and y-intercept $1/k_2q_e^2$ for pseudo-second order adsorption kinetics and second order rate constant, k_2 and q_e were computed from the y - intercept and the slope of straight line equation, respectively.

2.10. Desorption Studies

Desorption efficiency is defined as the percent extraction of heavy metal ions initially loaded onto the biomass. Recovery of metal ions from the loaded adsorbents is necessary for disposal as well as for reuse of adsorbate (Chen *et al.*, 2007). Desorption of metals or regeneration of adsorbents from used-adsorbents are crucial to repeat the use of adsorbents, recover of precious metals and reduce the cost of operation in any water treatment system. The adsorbed metals on adsorbents cannot be completely reversible as reported by several observations on literature (Asima *et al.*, 2005). Desorption and reuse experiments were carried out to determine desorption ratio and reusability of raw materials. These experiments were carried out as described by (Liang *et al*., 2012). For the desorption experiments, several solvents desorbing agents have been known such as HCl, H_2SO_4, HNO_3 ,$H_2C_2O_4$, NaOH and Na_2CO_3 of known concentration of 0.1 N with the metal loaded adsorbent. But the studies were carried out using HCl and NaOH as desorbing agent.

Desorption studies were conducted using 1.0 g of MBP using each of the following desorbing agent 0.1 M NaOH, and 0.1 M HCl. 1.0 g of MBP were placed in 100 mL of (10 mg/L) Cu^{2+}, $Pb^{2+}$and Cd^{2+} and Cr(VI) ions, and the mixtures were shaked on a shaker for three hours. The solutions were filtered and the amount of metal adsorbed was determined. After adsorption, the metal-loaded were filtered then the metal ion concentration was determined. The same process was repeated with 0.1 M HCl. The regenerated material was washed three times in distilled water and the metal ion added again for another adsorption-desorption cycle. This was repeated three times using the above mentioned desorbing agent (Hossain *et al*., 2012a).

3. MATERIALS AND METHODS

3.1. Experimental Sites

Preparation of raw banana peel, chemical modification of banana peel, preparation of metal ion solutions, batch study of parameters, evaluation of adsorption isotherm and kinetics models desorption and recyclability of adsorbent were studied at Haramaya University. On the other hand, characterization of banana peel using FT-IR was determined at Addis Ababa University.

3.2. Instruments and Apparatus

The concentration of the metal ion remained in the solution (filtrate) was determined using Atomic absorption spectrometer (AAS) (AS-210VGP). pH meter (pH-016) was used to measure pH of solution. Whatmaan filter paper No 42 was used to separate metal loaded adsorbent from filtrate. Mechanical shaker (Orbital shaker S01-STUART), oven (Hot Box Oven size-1, Gallen Kamp), Spectrum 65 FT- IR (PerkinElmer), analytical balance (Denver Xs-410) and grinding mill (M-20 kiku werre) were used. Glassware such as beakers, measuring cylinders, flasks, and test tubes were used.

3.3. Chemicals

All reagents used in this study were of analytical reagent grade. Stock solutions of $Pb(NO_3)_2$, $CuSO_4.5H_2O$, $Cd(NO_3)_2.4H_2O$ and $K_2Cr_2O_7$ were prepared from their respective metal salts with distilled water. For biosorption experiments, Cr(VI), Pb(II), Cu(II) and Cd(II) solutions (each working solutions with concentrations of 10, 20, 30, 50, and 100 mg/L were prepared by diluting the stock solution). 0.1 M NaOH and 0.1 M HCl solutions were used for adjustment of the pH of the solution.

3.4. Preparation of the Adsorbent

3.4.1. Preparation of Raw Banana Peel

The experiments were carried out using unmodified Banana Peel (UMBP) and chemically Modified Banana Peel (MBP) adsorbents. The adsorbent sample was collected from Bate (small town near Haramaya University) and was washed several times with distilled water to remove dust and other impurities.

Figure 1. Raw banana peel

The banana peel was allowed to dry in an oven at 80^0C to constant mass for 24 hr.

Figure 2. Crushed dried banana peel Figure 3.

Powdered banana peel

The dried mass was ground using grinding mill and sieved with mesh cut size of 200 µm.The powdered sample was washed with distilled water to remove impurities and dried in an oven for 48 hours. The dried sample was then stored in airtight bottles for further use of FT-IR analysis, batch experiment and chemical modification (Shadreck *et al*., 2013).

3.4.2. Chemical Modification of Banana Peel

The ground banana peel was treated with NaOH to improve the efficiency of the metal uptake. In this study 100 g of dried banana peel was treated with 1 L of 0.1M NaOH solution and was shaken for 48 hours with shaking speed of 120 rpm. After repeated decantation and filtration, the modified banana peel was washed with distilled water until the pH of solutions become neutral. The modified banana peel was then oven dried at 80^0C for 24 hours (Shadreck *et al.*, 2013).

3.5. Characterization of Banana peel

FT- IR spectroscopy before and after adsorption was used to identify the functional groups in the unmodified, modified and chromium loaded forms of banana peel.

3.6. Preparation of Metal Ions Stock Solutions

All reagents used in this study were of analytical reagent grade. Stock solutions of $Pb(NO_3)_2$, $K_2Cr_2O_7$, $CuSO_4$ and $Cd(NO_3)_2$ were prepared from their respective metal salts with distilled water. To prepare standard stock solutions (1000 ppm or 1000 mg/L) of each metal, 1.598 g of $Pb(NO_3)_2$, 2.70 g of $K_2Cr_2O_7$, 2.75 g $Cd(NO_3)_2.4H_2O$ and 3.93 g $CuSO_4.5H_2O$ of each metal salt was dissolved in 1L of distilled water. A 0.1M NaOH and 0.1M HCl were used for adjustment of the pH of solution (Shadreck *et al.*, 2013). For all experiments, Cr(VI), Cu(II), Pb(II) and Cd(II) solutions with concentrations 10, 20, 50 and 100 mg/l were prepared as working solutions by diluting the stock solution. (Working) diluted solution of 10, 20, 50 and 100 mg/L were used to prepare calibration curve which was used to determine the final concentrations after recording the absorbance from AAS experiment.

3.7. Batch Adsorption Studies

3.7.1. The Effect of pH

100 mL of each metal solution (100 mg/L) under controlled pH were mixed in a 250 mL conical flask with a fixed dosage 2.0 g of UNMBP and agitated on a shaker at a speed of 120 rpm at room temperature for 1:30 hours contact time. After determining the final concentration from AAS, and using calibration curve, the optimum pH for chromium (VI) was 2 and for the rest of the metal ions was 6 and the same procedure was repeated for MBP (Shadreck *et al.*, 2013).

3.7.2. The Effect of Adsorbent Dose

The effect of the adsorbent dose was studied using 100 mL of each metal ion solution(100 mg/L) at the optimum pH 2 for chromium and for the rest of metal ions 6 were mixed in a 250 mL conical flask by varying the mass of UNMBP (0.6, 0.8, 1.0, and 2.0 g). The mixtures were agitated on a shaker at a speed of 120 rpm at room temperature for 1: 30 hours contact time. After determining the final concentration of the metal ion from AAS, using calibration curve was determined and then the dose with the maximum percentage removal was selected as 1.0 g for consecutive experiments and the same procedure was repeated for MBP (Shadreck *et al*., 2013).

3.7.3. The Effect of Initial Metal Ion Concentration

With 1.0 g of UNMBP and with each initial metal ion concentrations (10, 20, 50 and 100 mg/L) at pH 2 for chromium (VI) ion and pH 6 for the rest metal ions were mixed in a 250 mL conical flask and agitated on a shaker at a speed of 120 rpm at room temperature for contact time of 1:30 hours. After determining the final concentration of the metal ion from AAS, using calibration curve, the concentration with the highest percent of removal of each metal ion was chosen as 10 mg/L initial concentration of each metal ion for the next experiment and the same procedure was repeated for MBP (Shadreck *et al*., 2013).

3.7.4. The Effect of Contact Time

With 1.0 g of UNMBP, with each 100 mL of 10 mg/L metal ion concentration and at pH 2 for chromium (VI) ion and pH 6 for the rest metal ions were mixed in a 250 mL conical flask and the mixtures were agitated on a shaker at a speed of 120 rpm at room temperature for 30, 60, 90 and 120 minutes contact times. After determining the final concentration of the metal ion from AAS, using calibration curve, the optimum time was found to be 60 minutes and the same procedure was repeated for MBP (Shadreck *et al*., 2013). All the experiments were performed in triplicates. The amount of metal ion adsorbed mg per gram of adsorbent (q) and the adsorption efficiency (%) was calculated according to the following expressions, respectively.

$$q \qquad (16)$$

$$\%\ \text{removal}\ \ 100 \qquad (17)$$

where, V is the volume of solution (L), m is the amount of adsorbent (g), and C_i and C_e (mg/L) are the initial and equilibrium metal ion concentrations in the solution respectively, and q is the amount of metal ion adsorbed mg per gram of adsorbent.

3.8. Equilibrium Study (Adsorption Isotherms)

Copper, chromium, lead and cadmium adsorption isotherm studies were carried out to determine the adsorption capacity of UMBP and MBP using optimum metal ion concentration. Langmuir and Freundlich parameters were determined (Hossain *et al.*, 2012).

3.9. Kinetics Study

In order to define the adsorption kinetics of heavy metals, the kinetic parameters for the adsorption processes were studied for the contact times intervals 30, 60, 90 and120 minutes and pseudo- first order and pseudo- second order models were applied to the experimental data. The kinetics data were evaluated with pseudo- first order, and pseudo-second order kinetics models and parameters of each order were determined (Hossain *et al.*, 2012).

3.10. Desorption Study and Recyclability of the Adsorbent

The 1.0 g of the adsorbent was mixed with 100 mL of 10 mg/L of each metal ion solution at adjusted pH for each metal ion. The mixtures were agitated at 60 minutes contact time of each metal ion, at agitation speed of 120 rpm and at room temperature. The mixtures were filtered using a Whatman filter paper No.42 and the filtrate was analyzed using AAS to determine the amount of total heavy metal ion adsorbed onto adsorbent. For desorption process, the metal ion loaded adsorbent was then mixed with 100 mL of 0.1 M HCl solution (desorbing agent) and agitated at 60 minutes contact time of each metal ion, at agitation speed of 120 rpm and under at room temperature. The mixtures were filtered using a Whatman filter paper No.42 and the filtrate was analyzed using AAS to determine the final concentration of the metal ion and to evaluate the amount of total heavy metal ion removed from adsorbent. The recovered adsorbent again mixed with 100 mL of each optimum metal ion solution for the second cycle adsorption and was agitated at optimum contact time, at agitation speed of 120 rpm and under at room temperature and filtered. The filtrate was then analyzed using AAS to determine the amount of total heavy metal ion adsorbed onto adsorbent. The metal ion loaded adsorbent was mixed again with 100 mL of 0.1 M HCl solution (desorbing agent) and agitated at optimum contact time, at agitation speed of 120 rpm and under at room temperature. The mixture was filtered using a Whatman filter paper No.42 and the filtrate was analyzed using AAS to determine the final concentration the metal ion and to evaluate the amount of total heavy metal ion removed from adsorbent. These procedures were repeated for the second and third cycle (Cecilia, 2015). The adsorption - desorption procedure was repeated using 0.1 M NaOH solution as desorbing agent (Ushakumary, 2013).

4. RESULTS AND DISCUSSION

4.1. Characterization of the adsorbent

Fourier transform infrared spectral analysis was carried out to identify the different functional groups present in the given samples. In order to determine which functional groups were responsible for metal uptake, FT-IR spectra of the adsorbent before and after Cr(VI) binding were recorded in the range of 4000-400 cm^{-1} as shown in table 1. stretching vibrational modes were observed in the given samples; OH stretching, C-H stretching, C=C stretching, C-O stretching and –C=O (carbonyl group) stretching. Broad and intense peaks were observed from FT-IR spectrium of UNMBP sample. The peak observed at 2927cm^{-1} was associated with the stretching vibrations of C-H bond of methyl or methylene groups. The peak at 1625cm^{-1}corresponded to the C=C stretching which might be attributed to the presence of aromatic or olefinic groups. The peak observed at 1747 cm^{-1} is the stretching vibration due to non-ionic carboxyl groups (-COOH, -COOCH$_3$), and might be due to carboxylic acids or their esters. The intense peak at 1039 cm^{-1} corresponds to the C-O stretching of alcohol or carboxylic acid. FT-IR spectra of the unmodified banana powder and chromium metal loaded banana powder showed that the peaks at 3406, 2927, 1625 and 1039 cm^{-1}(before adsorption) had shifted slightly after (adsorption) binding with chromium metals as shown in the Table 1. This was due to the participation of these functional groups in the binding of chromium ions. It was also noted that shifting of wave number depends on the concentration of the metal ion present in the given sample agreed by literature survey (Azouaou, 2010; Chen *et al*., 2010; Hao, 2010; Abuzer and Huseyin, 2011). The FT-IR spectrum of modified banana peel with NaOH indicated that weak intensity of the peak at 1747 cm^{-1} showed that the methyl esters were hydrolyzed with NaOH and the ester group was converted to the carboxylate ion as reported by (Feng *et al*., 2009).

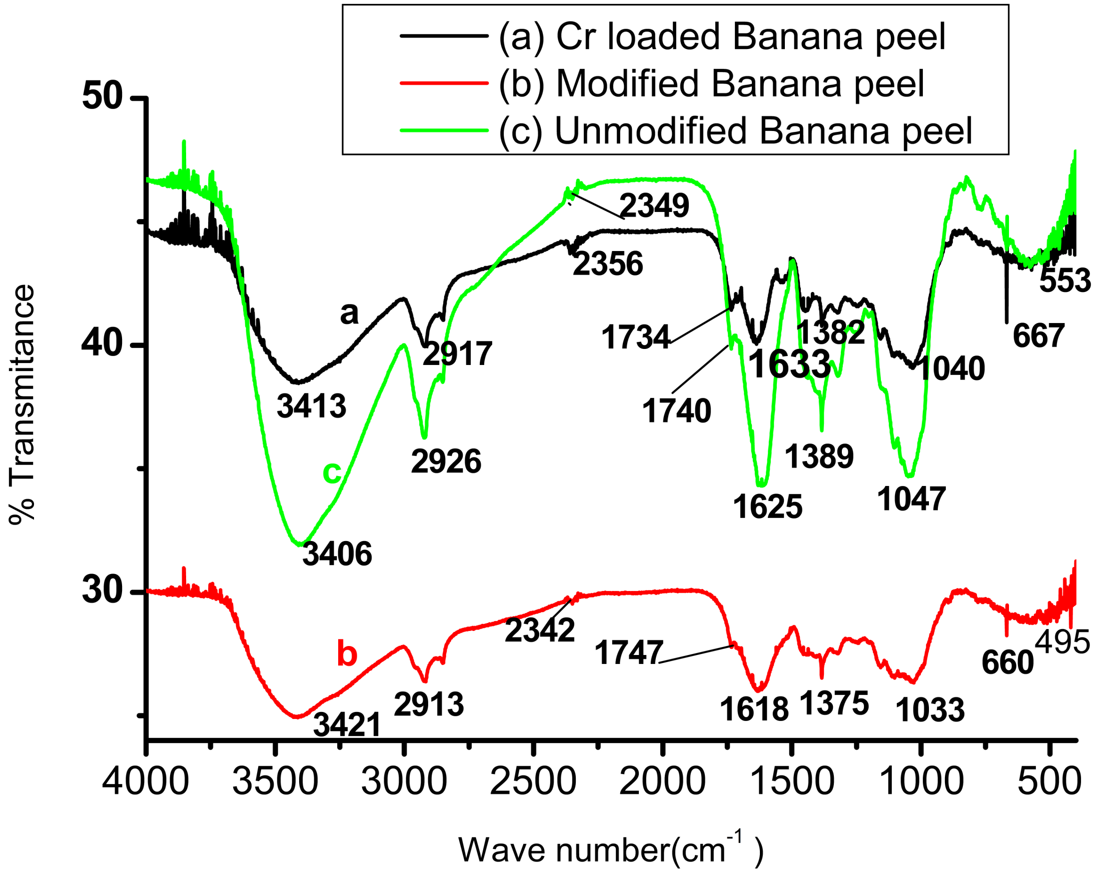

Figure 4. FTIR spectra of UNMBP, MPB and chromium loaded banana peel

Table 2. Comparison of FT-IR band positions of UNMBP, MBP and before and after metal ions adsorption in wave number (cm^{-1})

Assignment	Wave number (cm^{-1})		
	UNMBP (before adsorption)	After adsorption (chromium loaded)	MBP
O-H stretching	3406	3413	3421
C-H stretching	2927	2920	2913
C=C stretching	1625	1633	1618
C-O stretching -COOH or	1039	1032	1025

$COOCH_3$,carboxylic acid and their esters	1740	1734	1747

4.2. Effect of pH on Uptake of Cd(II), Cu(II), Cr(VI) and Pb(II) Ions

The pH of the solution affects the protonation of the functional groups on the biomass as well as the metal chemistry. Figure 5 showed the removal of Cr(VI) at varying pH for initial Cr(VI) concentration of 100 mg/L, biosorbent concentration of 2.0 g/L and contact time of 90 minutes. As illustrated in Figure 5, the maximum adsorption of Cr(VI) ions was observed at pH 2.0 for both adsorbents (UNMBP and MBP) and significantly decreased by increasing the pH values up to 8. This observation may be attributed to the fact that by decreasing pH, hydroxyl groups in ligno cellulosic wastes tend to diffuse into the solution, so, it would be more probable for $Cr_2O_7^{2-}$ ions to be adsorbed on available adsorption sites. At lower pH, the adsorbent is positively charged due to protonation resulting in electrostatic attraction with the dichromate (Boddu *et al.*, 2003). A sharp decrease in adsorption above pH 2 may be due to occupation of the adsorption sites by anionic species like $HCrO_4^-$, $Cr_2O_7^{2-}$ or CrO_4^{2-} which retards the approach of such ions further towards the sorbent surface (Das *et al.*, 2000; Aksu and Dnemz, 2002). Uptake of Cr(VI) increased markedly with decreasing pH. At pH 2 and 8 corresponding uptake yield values were found to be 65.0% and 41.0% for unmodified Banana peel, 72.0% and 46.0% for chemically modified banana peel, respectively. The decrease in adsorption at high pH values may be due to the competitiveness of the oxyanion of chromium and OH^- ions in the bulk. From figure 5, it was concluded that the optimum pH of Cr(VI) ion adsorption was 2.

At low pH values the H_3O^+ concentration is high and therefore protons can compete with the Cd^{2+} ions for surface sites. At low pH values the metal exists in the solution as Cd^{2+} free cations. When pH increases, there is a decrease in positive surface charge due to the deprotonation of the adsorbent functional groups, which results in a lower electrostatic repulsion between the positively charged metal ion and the surface of the adsorbent (Gupta, 2007; Babu and Gupta, 2008; Azouaou *et al.*, 2010). As pH value is higher, more exchangeable cations contained in the adsorbent can be exchanged with metal ions due to weak competitive adsorption of H_3O^+ ions. The results obtained were illustrated in Figure 6 and 7. For both adsorbents, as the pH of the solution increased from 2 to 8, the adsorption capacity of each of MBP and UMBP was changed. The removal efficiency of UNMBP increased from 51.0% to 90.0% when the pH value was raised from 2 to 6 and the removal efficiency of MBP were increased from 59.3% to 96.0 % for the same pH range. Afterwards, the removal efficiency has drastically decreased from 89.0% to 60.0% and 96.0% to 70.7% for UNMBP and MBP, respectively. These results are similar with those reported by (Azouaou *et al*., 2010) on the biosorption of Cd, Cr, Pb, and Zn ions by the biomass of *Medicagi Satiya* (Alfalfa) as well as with those reported by (Reen *et al*., 2011) on the removal of heavy metals using activated biocarbon. The adsorption capacity of both adsorbents increased with increase pH value up to 6 and then began to decrease until pH 8. In the latter case, the removal of Cd(II) ions would take place by both adsorption as well as precipitation of the Cd(II) ions in the form of $Cd(OH)_2$. From the figure it was concluded that the optimum pH at which the maximum percentage removal of cadmium observed was 6.

The effect of pH on the adsorption of copper (II) ions is shown in Figure 6 and 7. The removal efficiencies were increased from 55.0% to 87.0% and 64.7% to 92.3% for UNMBP and MBP, respectively, as the pH increases from pH 2 to pH 6. Copper adsorption was significantly increased between pH 4 and 6. This can be explained as Cu^{2+}, $Cu(OH)^+$ and $Cu(OH)_2$ species are available for adsorption at below pH 6 (Wang and Qin, 2005). The removal efficiency has drastically decreased from 87.0% to 55.0% and 93.3% to 65.0% for UNMBP and MBP, respectively. The adsorption efficiency decreased after pH 6 and continued to decreases till pH 8. Low adsorption efficiencies were observed at both low and high pH for both adsorbents. At a low pH, H_3O^+ ion concentration is high and competes with Cu^{2+} for binding sites on the adsorbents and surrounded H_3O^+ preventing the copper ions from approaching the binding sites and it could be responsible for low adsorption capacities (Karthikeyan *et al*., 2007). At higher pH, low H_3O^+ concentration, the competition of H_3O^+ for the binding sites decreased. Only Cu(II) approached to the negative binding site as a result adsorption efficiency increased (Demirbas, 2009). Above pH 6, the copper started precipitating as $Cu(OH)_2$, so the removal was not completely by adsorption (Murugan *et al*., 2010). From figures 6 and 7 it was concluded that the optimum pH of Cu(II) adsorption was 6.

The effect of pH on the adsorption of lead(II) ion is shown in Figure 6 and 7. The uptake and equilibrium adsorption capacity of metal removal from aqueous solution are strongly affected by the pH (Zvinowanda *et al.,* 2009). At the same time, the state of chemically active sites is changed by the solution pH (Qaiser *et al.,* 2009). The maximum adsorption of lead(II) ion was achieved at pH 6, hence the optimum pH was 6. At pH values higher than 6 the Pb(II) ions were precipitated. Therefore the removal of Pb(II) ion at higher pH values is due to the formation of precipitates, $Pb(OH)_2$ rather than adsorption (Bayat, 2002). The removal efficiency increased from 57.6% to 86.8% and 66.5% to 95.1% for UMBP and MBP, respectively, with increase in pH from 2 up to pH 6. The removal efficiency has drastically decreased from 86.8% to 60.0% and 95.1% to 65.0% for UNMBP and MBP, respectively. The increased in lead ion adsorption with increase in pH is due to a decrease in competition between H_3O^+ ions and lead ions for the surface sites and also due to decrease in positive surface charge, protonated adsorption sites were incapable of binding metal ions due to electrostatic repulsion between positively charged metal ions and positive charged site.

Figure 5. Effect of pH on lead, copper and cadmium adsorption using UNMBP (initial concentration = 100 mg/L, dose = 2.0 g, at room temperature, orbital shaking speed = 120 rpm and contact time = 90 minutes)

Figure 6. Effect of pH on lead, copper and cadmium adsorption using MBP (initial concentration = 100 mg/L, dose = 2.0 g, at room temperature, orbital shaking speed = 120 rpm and contact time = 90 minutes)

4.3. Effect of Initial Metal Ions Concentration

The rate of adsorption is a function of initial concentration of metal ions. Figures 8 and 9 indicated that higher adsorption was found at lower concentrations. This may be due to the interaction of all metal ions present in the solution with binding sites. At higher concentrations, more metal ions are left unadsorbed in solution due to saturation of adsorption sites (Mausumi *et al*., 2006; Azouaou *et al*., 2010; Mohammad Mehdi *et al*., 2011). According to (SenthilKumar *et al*., 2010), at lower metal ions concentration, the percentage uptake was higher due to larger surface area of adsorbent being available for adsorption. High metal ion concentration saturates the adsorbent sites more quickly thereby decreasing the overall percentage metal removal, resulting in lower adsorption percentage.

The adsorption of Pb(II), Cd(II), Cu(II) and Cr(VI) ions were treated in the same way for both adsorbents. The above explanation was compatible with the figures shown below. The removal efficiencies were decreased from 88.0% to 79.0%, 90.0% to 55.0%, 88.0% to 69.0% and 88.0% to71.0% for Pb(II), Cr(VI), Cu(II) and Cd(II) ions, respectively, for adsorption on UNMBP. In addition to this, the removal efficiencies of the MBP were studied. The removal efficiencies were also decreased from 92.0% to 81.0%, 98.0% to 63.0%, 97.0% to 77.0% and 93.0% to 75.0% for

Pb(II), Cr(VI), Cu(II) and Cd(II) ions, respectively, for adsorption on MBP. As a result of this, the optimum initial metal ion concentration for each metal ion adsorption was found to be 10 mg/L.

Figure 7. Effect of initial metal ion concentration on adsorption of heavy metal ion (cadmium, (pH = 6), copper (pH = 6), lead (pH = 6) and chromium (pH = 2), adsorbent dose = 1.0 g, contact time = 90 minutes, at room temperature and orbital shaking speed = 120 rpm) using UNMBP.

Figure 8. Effect of initial metal ion concentration on adsorption of heavy metal ions (cadmium, (pH = 6), copper (pH = 6), lead (pH = 6) and chromium (pH = 2), adsorbent dose = 1.0 g, contact time = 90 minutes, at room temperature and orbital shaking speed =120 rpm) using MBP.

4.4. Effect of Contact Time

The purpose of the experiment was to determine the contact time required to reach the equilibrium between the solid phase (metal ion adsorbed) and liquid phase (metal ion in the solution). Figures 10 and 11 showed that the percentage uptake increased with time and after some time, it reached a constant value where no more metal ion can be removed from the solution (Azouaou *et al.*, 2010;

Maria Martinez *et al*., 2006; Mohammad Mehdi *et al*., 2011). At this point, the amount of metal ions being adsorbed by the adsorbent was in a state of dynamic equilibrium with the amount of metal ions desorbed from the adsorbent. The time required to attain this state of equilibrium is termed as the equilibrium time. The amount of metal ion adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under these particular conditions. The result showed that the adsorption of metal ion increased with time up to 60 minutes and then it becomes almost constant at the end of the experiment. It can be concluded that the rate of metal binding with adsorbent is more predominant during initial stages, which gradually decreased and remained almost constant after 60 minutes. The active adsorption sites of the adsorbent get involved in metal adsorption as soon as the adsorbent is introduced into the system. The figures 10 and 11 showed that the removal efficiencies were increased from 75.0% to 84.6%, 75.0% to 87.0%, 85.0% to 95.0%, and 75.0% to 86.0% for Pb(II), Cr(VI), Cu(II) and Cd(II) ions, respectively, for adsorption on UNMBP. Similarly, the removal efficiencies were increased when MBP was used as adsorbent. The increment was observed from 80.3% to 94.5%, 80.0% to 94.0%, 88.0% to 98.7% and 81.0% to 93.0% for Pb(II), Cr(VI), Cu(II) and Cd(II) ions, respectively, for adsorption on MBP. The optimum time required for the highest adsorption efficiency of adsorbents was found to be 60 minutes.

Figure 9. Effect of contact time on adsorption of heavy metal ions (cadmium (pH = 6), chromium (pH = 2), copper (pH = 6) and lead (pH = 6)), adsorption (adsorbent dose = 1.0 g, initial metal ion concentration = 10 mg/L, orbital shaking speed = 120 rpm and at room temperature) using UNMBP adsorbent.

Figure 10. Effect of contact time on adsorption of heavy metal ions (cadmium (pH = 6), chromium (pH = 2), copper (pH = 6) and lead (pH = 6), (adsorbent dose = 1.0 g, initial metal ion concentration = 10 mg/L, orbital shaking speed = 120 rpm and at room temperature) using MBP adsorbent.

4.5. Effect of Adsorbent Dose

The effect of adsorbent dosage is an important parameter on the removal percentage of toxic metal ions from aqueous solutions, because it determines the capacity of an adsorbent for a given concentration (Khazaei *et al*., 2011). The effect of biomass dosage on metal adsorption is shown in Figures 12 and 13. The adsorption of metal ions increased with the adsorbent dosage and at adsorbent dosage above 1.0 g/100 mL reached equilibrium. The percentage of metal removal increased with the increasing amount of adsorbent (Azouaou *et al*., 2010; EI-Said *et al*., 2010; Saifuddin and Kumaran, 2005). The percent removal efficiency of both adsorbents increased rapidly from 0.6 g to 1.0 g and then little variation was observed with further increment. This may be attributed to the availability of more and more binding sites for adsorption of metal ions. Further increment in adsorbent dose did not cause significant improvement in adsorption. This seems to be the aggregation/agglomeration of adsorbent particles at higher dosages which would lead to a decrease in the total surface area of the adsorbent particles available to the metal ions. As a result the adsorption capacity of the adsorbent was not fully utilized (Andal and sakthi, 2010). Finally, the equilibrium is reached between the ions bound to the adsorbent and those remaining unadsorbed in the solution. The figures 12 and 13 showed that the removal efficiencies were increased from 70.0% to 83.7%, 63.5% to 83.6%, 63.67% to 84.0%, and 75.8% to 81.2% for Pb(II), Cr(VI), Cu(II) and Cd(II) ions, respectively for adsorption on UNMBP. Similarly, the removal efficiencies were increased when MBP was used as adsorbent. The increment was observed from 75.0% to 95.5%, 69.5% to 90.4%, 73.3% to 90.3% and 82.7% to 90.7% for Pb(II), Cr(VI), Cu(II) and Cd(II) ions, respectively for adsorption on MBP. The optimum adsorbent dose required for the highest adsorption efficiency of each metal was found to be 1.0 g.

Figure 11. Effect of adsorbent dose on adsorption of heavy metal ions (cadmium (pH = 6), chromium (pH = 2), copper (pH = 6) and lead (pH = 6), (adsorbent dose = 2 g, initial metal ion concentration =10 mg/L, orbital shaking speed = 120 rpm, contact time = 60 minutes and at room temperature) using UNMBP adsorbent.

Figure 12. Effect of adsorbent dose on adsorption of heavy metal ions (cadmium (pH = 6), chromium (pH = 2), copper (pH = 6) and lead (pH = 6), (adsorbent dose = 1.0 g, initial metal ion concentration = 10 mg/L, orbital shaking speed = 120 rpm, contact time = 60 minutes and at room temperature) using MBP adsorbent

4.6. Adsorption Isotherm Studies

Two well-known equilibrium adsorption isotherm models were employed to facilitate the estimation of adsorption capacities at various concentrations of metal ions. These models are Langmuir and Freundlich (Acar and Malkov, 2004).

4.6.1. Langmuir Adsorption Isotherm

$$1/q_e = 1/q_{max}bC_e + 1/q_{max} \tag{18}$$

$$C_e/q_e = 1/q_{max}b + C_e/q_{max} \tag{19}$$

Adsorption isotherms show the distribution of solute between the liquid and solid phases and can be described by several mathematical relationships such as the standard Langmuir, Freundlich and Dubinin-Radushkevich models were known. The linearized Langmuir adsorption isotherms parameters obtained are shown in Table 2 with the values of linear regression coefficients. In view of the values of the linear regression coefficients, Langmuir model fitted very well to the adsorption data in the studied concentration range in both types of adsorbents. It was observed that the Langmuir adsorption isotherm satisfactorily described the adsorption of copper, cadmium, chromium and lead ions from aqueous solutions using UNMBP and MBP as indicated by the high correlation coefficients. The applicability of the Langmuir isotherm indicates good monolayer coverage of lead (II), copper (II), chromium (VI) and cadmium (II) ions on the surface of banana peel which consequently suggests the formation of a mono layer on the adsorbent surface in the given concentration range (Mohammed *et al.*, 2011). The fact that the Langmuir isotherm fitted the experimental data very well may be due to the homogenous distribution of active sites on the adsorbent since the Langmuir model assumes that the surface is homogenous. The calculated model parameters with correlation coefficients are shown in Table 2. The adsorption capacity, q_{max}, (mg/g) of cadmium is higher than that of lead, copper and chromium.

Table 3. Parameters of Langmuir isotherm on adsorption of metal ions using UNMBP and MBP adsorbents.

Type of adsorbent	Parameter	Metal ions			
		Cadmium	Chromium	Copper	Lead
UNMBP	R^2	0.980	0.998	0.991	0.979
	b	0.345	0.275	0.271	0.175
	q_{max}	6.25	2.56	4.78	1.13
	slope	0.160	0.391	0.209	0.885
MBP	R^2	0.992	0.986	0.996	0.981
	b	0.089	0.264	0.08	0.0532
	q_{max}	20.08	13.51	19.23	15.65
	slope	0.0324	0.206	0.052	0.215

The higher the b, the higher is the affinity of the adsorbent for metal ions. q_{max} can also be interpreted as the total number of binding sites that are available for adsorption and q_{max} as the number of binding sites that are in fact occupied by the metal ions at the concentration C_f (Volesky, 1995). According to the above Table, the adsorption capacities are in the order Cd > Cu

> Cr > Pb UNMBP. But this trend was disordered for MBP adsorbent that is Cd > Cu > Pb >Cr. From the above table, all values of the Langmuir isotherm parameters were increased in magnitude when the adsorption process was taken place using MBP rather than UNMBP. Thus adsorption capacity of the adsorbent was enhanced for Modified Banana Peel (MBP).

Figure 13. Langmuir plot of chromium adsorption using UNMBP (pH = 2, adsorbent dose = 1 g, contact time = 60 minutes, at room temperature and orbital shaking speed = 120 rpm)

Figure 14. Langmuir plot of copper adsorption using MBP (pH = 6, adsorbent dose = 1 g, contact time = 60 minutes, at room temperature and orbital shaking speed = 120 rpm)

4.6.2. Freundlich Adsorption Isotherms

The Freundlich model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites accompanied by interactions between adsorbed molecules. This can be linearized as;

$$\text{Log } q_e = \log C_e + \log k \qquad (20)$$

where qe is the amount of metal ions adsorbed on the adsorbent (mg/g), C_e is equilibrium adsorbate concentration in mg/L, k_f is the adsorbent capacity measure and n is the adsorption intensity. Table 3 showed the Freundlich model metal ions adsorption using UNMBP and MBP. In the Freundlich model a linear plot of log q_e versus log C_e gives a straight line for both adsorbents. The constant k and 1/n were determined from the plot of logq_e against log C_f. Small value of k indicated there is more adsorption (Horsfall *et al.*, 2006) while 1/n is used as an indication of whether adsorption remains constant (at 1/n=1) or decreases or increases with increasing metal ions concentrations.

Table 4. Parameters of Freundlich isotherm on adsorption of metal ions using UNMBP and MBP adsorbents.

Adsorbent	parameters	Metal ions			
		Lead	Chromium	Copper	Cadmium
UNMBP	K	1.75	1.412	1.854	1.914
	R^2	0.975	0.997	0.985	0.976
	1/n	1.849	4.198	2.382	2.256
	n	0.541	0.238	0.420	0.443
MBP	K	0.039	0.153	0.133	0.082
	R^2	0.990	0.994	0.996	0.999
	1/n	1.558	0.775	1.058	1.146
	n	0.641	1.324	0.963	0.872

It was concluded from the above Table, Freundlich model for each metal ion, the values of n and 1/n were highly deviated from the values in the range ($0 < 1/n < 1$) and for n in the range ($1 < n < 10$). Thus Freundlich model failed to fit with the experimental data which implies that the adsorption surface coverage were heterogeneous and not identical.

Figure 15. Freundlich plot of chromium adsorption using UNMBP (pH = 2, adsorbent dose = 1 g, contact time = 60 minutes, at room temperature and orbital shaking speed = 120 rpm)

Figure 16. Freundlich plot of cadmium adsorption using MBP (pH = 6, adsorbent dose = 1 g, contact time = 60 minutes, at room temperature and orbital shaking speed = 120 rpm)

4.6.3. Comparison of Adsorption Capacity of MBP and UNMBP with Other Adsorbents Using Langmuir parameter (q_{max})

Table 5. Comparison of adsorption capacity of UNMBP for cadmium ions removal from aqueous solution with other adsorbents.

Unmodified Adsorbents	q_{max}(mg/g)	Reference
Exhausted coffee	1.48	(Orhan and Buyukgungor,1993)
Perlitle	0.64	(Mathialagan and viravahavan, 2002)
Wheat bran	0.7	(Singh *et al.*, 2006)
UNMBP	6.25	Present study

Table 6. Comparison of adsorption capacity of MBP for cadmium ions removal from aqueous solution with other adsorbents

Modified Adsorbents (NaOH as modifying agent)	q_{max}(mg/g)	Reference
Rice husk	20.24	(Kumar and Bandyopadhyay, 2006b)
Spent grain	17.3	(Low *et al.*, 2000)
Neam leaf powder	29.41	(Aysha, 2013)
Modified Banana Powder (MBP)	21.43	Present study

From the above table, it was concluded that the UNMBP has higher adsorption capacity than those adsorbents listed in Table 4. Similarly, MBP has also better adsorption capacity than those adsorbents mentioned in Table 5.

Table 7. Comparison of adsorption efficiency of UNMBP for cadmium (II) chromium (VI), copper (II) and lead (II) ions removal from aqueous solution with other studies.

Heavy metal ions	% removal of the previous study	Reference	% removal of the present study
Cadmium (II)	88.9	Abdulfatai *et al.,* 2013	65.0
Chromium (VI)	94.0	Hossain *et al.,* 2012	87.0
Copper (II)	74.0	Ashraf *et al*., 2011	86.9
Lead (II)	87.0	Prashant, 2017	90.0

From the above Table, it was concluded that the UNMBP showed higher adsorption efficiency for copper (II) and lead (II) ions adsorption in present study than those cadmium (II) and chromium (VI) ions in the previous study.

4.7. Adsorption Kinetics

In order to define the adsorption kinetics of heavy metals ions, the kinetic parameters for the adsorption processes were studied for the contact times in the intervals 30, 60, 90 and 120 minutes and pseudo-first order, and pseudo-second order models were applied to adsorption experimental data.

4.7.1. Pseudo - First Order Kinetic Model

The pseudo-first order kinetic equation is

$$\log(q_e-q_t) = \log q_e \ - \ t \qquad (21)$$

Where q_e and q_t are the adsorption capacity at equilibrium and at time t respectively and K_{ads} is the rate constant of the pseudo-first order adsorption process. Plot of $\log(q_e-q_t)$ versus t gives a straight line for first order adsorption kinetics and the rate constant, $K_{ads,}$ was computed from the plot.

Figure 17. Pseudo-first order adsorption kinetics plot of lead using UNMBP (pH = 6, dose = 1.0 g, Initial concentration = 10 mg/L, orbital shaker speed = 120 rpm and at room temperature)

Figure 18. Pseudo-first order adsorption kinetics plot of chromium using MBP (pH = 2, dose = 1.0 g, initial concentration = 10 mg/L, orbital shaker speed = 120 rpm, and at room temperature).

Table 8. Parameters of pseudo-first order kinetics model

Adsorbent	Parameter	Metal ions			
		Lead	Copper	Chromium	cadmium
UNMBP	R^2	0.990	0.984	0.980	0.982
	$k_1(min^{-1})$	0.032	0.021	0.035	0.023
	q_{calc}	7.76	3.16	8.51	7.76
MBP	R^2	0.994	0.995	0.988	0.986
	k_1	0.0392	0.037	0.0161	0.044
	(q_{calc})	2.09	1.38	0.126	2.04

From the parameters depicted in Table 6, the regression coefficients, R^2, were much closed to 1.

Thus the adsorption experimental data fitted with pseudo 1^{st} order kinetics model using MBP.

4.7.2. Pseudo - Second Order Kinetic Model

The adsorption modeling data were also studied by pseudo second order kinetics using the following equation,

$$= + \qquad (22)$$

The applicability of this equation can be studied by a plot of t/q_t versus time(t) where k_2 [g/(mg min)] is the rate constant of the pseudo-second order adsorption process, and q_e and q_t are the amounts of heavy metal ions adsorbed at equilibrium and at any time t, respectively.

Figure 19. Pseudo-second order adsorption kinetics plot of chromium using UNMBP (pH = 2, dose = 1.0 g, concentration = 10 mg/L, orbital shaker speed = 120 rpm and at room temperature)

Figure 20. Pseudo-second order adsorption kinetics plot of copper using MBP (pH = 6, dose = 1.0 g, initial concentration = 10 mg/L, orbital shaker speed = 120 rpm and at room temperature)

Table 9. Parameters of pseudo-second order kinetics model

Adsorbent	Parameter	Metal ions			
		Lead	Copper	Chromium	Cadmium
UNMBP	R^2	0.973	0.990	0.981	0.982
	$K_2(min^{-1})$	0.002	0.0007	0.004	0.0009
	q_{calc}	7.35	5.68	6.49	8.85

MBP	R^2	0.989	0.996	0.991	0.987
	K_2	0.00004	0.00002	0.00005	0.00004
	(q_{calc})	83.3	125	71.4	83.3

Table 10. Pseudo-first order and pseudo-second order kinetics parameters for the adsorption of Cd(II), Pb(II), Cr(VI) and Cu(II) ions onto UNMBP

Heavy metal ions	Pseudo-first order			Pseudo-second order			
	q_{expt}	R^2	q_{calc}	k_1	R^2	q_{calc}	K_2
Cd (II)	4.45	0.985	5.76	0.023	0.982	8.85	0.0009
Pb (II)	4.7	0.990	5.76	0.032	0.973	8.43	0.002
Cr (VI)	4.7	0.980	3.51	0.035	0.981	8.94	0.004
Cu (II)	4.8	0.994	3.16	0.021	0.990	5.68	0.0007

The comparison of experimental adsorption capacities (q_{exp}) and the predicted values (q_{cal}, k_1, k_2, and R^2) from pseudo-first order and pseudo-second order kinetics parameters were given in Table 9. The pseudo-second order kinetics was not satisfactorily explained the experimental data, because the calculated, q_{calc} values obtained from pseudo-second order kinetics model were much higher than the experimental q_{exp} value. The k_2 values of pseudo-second order kinetics were much lower than that of the pseudo-first order kinetics model which implies that the extent of the reaction to proceed through pseudo-second order reaction is very small. Thus pseudo-first order kinetics appeared to be better fitted model than pseudo second order (Azouaou, 2010; Gupta and Rastogi, 2007).

4.8. Desorption Study and Recycling of the Adsorbent

Recovery of metal ions from the loaded adsorbents is necessary for disposal as well as for reuse of (Chen *et al.*, 2007). For the desorption experiments, several solvents desorbing agent have been used. The studies were carried out using 0.1M HCl and NaOH with the metal loaded adsorbent. Batch desorption experiments were carried out and the desorption efficiencies were compared in Table 10. It can be concluded from the table that desorption efficiency decreases with increasing cycle number due to the decreasing of adsorption capacity. For each adsorption – desorption cycle, new active sites generated by dilute HCl treatment was decreased, resulting in a decrease in adsorption capacity with the increase in cycle number. Hydrochloric acid showed the maximum desorption efficiency for Pb(II) and Cu(II).

Table 11. Percentage desorption efficiency using 0.1M HCl for three cycles

Cycle	I		II		III	
Heay metal	Adsorption %	Desorption %	Adsorption %	Desorption %	Adsorption %	Desorption %
Pb(II)	89	79	74	71	68	59
Cr(V)	86	77	43	34	31	24
Cu(II)	86	75	71	67	59	47
Cd(II)	74	63	55	52	49	35

5. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

5.1. Summary and Conclusions

This research work dealt with the removal of Pb(II), Cu(II), Cr(II) and Cd(II) ions from aqueous solution using MBP and UNMBP. The banana peel was characterized using FT-IR and hydroxyl, carboxylic, carbonyl and ester functional groups were found as the principal binding sites in the adsorption process.

Optimum adsorption conditions were determined as a function of pH, contact time, initial metal concentration and adsorbent doses. Along with the increase of adsorbent dosage from 0.6 g to 1.0 g, the percentage removals of the metal ions were increased. This might be due to the increase of active sites for adsorption with increasing the dosage. The results indicated that optimum conditions for Cd(II), Cu(II), Cr(VI) and Pb(II) ions adsorption onto MBP and UNMBP were achieved at contact time of 60 minutes. The percentage removals of metal ions were found to decrease with increase in metal ions concentrations, the optimum concentration of each metal ion was determined to be 10 mg/L. The adsorption of Cd(II), Cu(II), Cr(VI) and Pb(II) ions onto MBP and UNMBP was also pH dependent and the maximum adsorption of the metal ion onto both adsorbent were attained at pH 6 except for chromium adsorption. Chromium showed maximum adsorption at pH = 2.

Both Langmuir and Freundlich models treated adsorption data for a given adsorbent doses. The experimental data were analyzed using the Langmuir and Freundlich models and the calculated equilibrium data were well fitted with Langmuir model. The equilibrium data of adsorption of ions were simply described by the Langmuir isotherm model. The higher correlation coefficients of Langmuir isotherm indicated that this model fitted the adsorption data better than the Freundlich model.

The adsorption data were evaluated using pseudo-first and pseudo-second order kinetics model. The adsorption data were well fitted with pseudo-first order kinetics model because the regression coefficients, R^2, were very close to 1 for all metal ions. The experimental adsorption capacities (q_{expt}) and predicted adsorption capacity (q_{calc}) were compared. The q_{calc} values of pseudo-second order values were much greater than the experimental value (q_{expt}). But q_{calc} values of pseudo - first order kinetic model were much closer to q_{expt}. Because of the reasons given above the adsorption data were well fitted with pseudo-first order kinetics.

Comparison of adsorption capacity of MBP and UNMBP with other adsorbents reported in the literature showed that relatively both MBP and UNMBP have higher capacity for the removal of lead, chromium, copper and cadmium ions from aqueous solution and it was found that MBP showed a higher adsorption capacity than UNMBP. This is due to mainly that the chemical modification might have improved the adsorption capacity of the adsorbent in the modified form, which could probably because of formation of higher number of active binding sites after modification, better ion-exchange properties and appearance of new functional groups that favored metal uptake.

For the desorption experiments, 0.1 M HCl and 0.1 M NaOH with the metal loaded adsorbent were used. Batch desorption experiments were carried out and the desorption efficiencies were compared. It was noted that desorption efficiency decreased with increasing cycle number due to the decreasing of adsorption capacity. For each adsorption – desorption cycle, new active sites generated by dilute HCl treatment was decreased, resulting in a decrease in adsorption capacity with the increase in cycle number. The desorption experiment showed that banana peel had high potential to be used up to three cycles for desorption process.

From the whole experimental study it was concluded that banana peel, especially in its modified form, was found to be more available, efficient recyclable and environmental friendly adsorbent to remove heavy metal ions from wastewater than the conventional adsorbents.

5.2. Recommendations

The following recommendations are made for further study

- Studies should be carried out on the characterization of the surface area, and pore size responsible for adsorption by using SEM and XRD and investigate the effect of temperature on adsorption.
- Langmuir and Freundlich isotherms are insufficient to explain the physical and chemical characteristics of adsorption. So it was impossible to decide what kind of chemisorptions that have been taken place in the adsorption process except for the favorability of the processes.

- The study reported here was conducted using synthetic waste metal ions solutions, further investigation should be carried out on wastewater (real effluent), real samples taken from industry discharge which clicks for environmental protection.

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7. APPENDICES

Appendix Tables

App. Table 1. Comparison of FTIR band positions of raw banana peel before and after metal ions adsorption in wave number (cm-1)

Assignment	Wave number (cm^{-1})		
	Unmodified banana peel (before adsorption)	After adsorption (chromium loaded)	Modified banana peel
O-H stretching	3406	3413	3421
C-H stretching	2927	2920	2913
C=C stretching	1625	1633	1618
C-O stretching	1039	1032	1025
-COOH or COOCH$_3$,carboxylic acid and their esters	1740		1747

App. Table 2. Effect of pH on Lead up take with UNMBP

pH	Absorbance	C$_o$(ppm)	C$_f$(ppm)	%	q	Stand.solution

	After adsorption					absorbance.
2	0.368	100	42.375	57.625	2.88	0.09
4	0.260	100	15.25	84.75	4.24	0.2
6	0.195	100	19.875	80.125	4.00	0.47
8	0.180	100	40	60	3.00	0.79

App. Table 3. Effect of pH on Lead up take (MBP)

pH	Absorbance After adsorption	C_o(ppm)	C_f(ppm)	% removal	q
2	0.385	100	33.5	66.5	3.325
4	0.196	100	9.875	90.125	4.5
6	0.156	100	4.875	95.125	4.76
8	0.357	100	30	70	3.5

App. Table 4. Effect of pH on chromium up take with UNMBP

pH	Absorbance After adsorption	C_0(ppm)	C_f(ppm)	%	q_e	Absorbance of stand.solution
2	0.135	100	35	65	3.25	0.082
4	0.204	100	54.825	45.125	2.26	0.357
6	0.315	100	36.5	63.5	3.175	0.437
8	0.397	100	48.75	51.25	2.56	0.880

App. Table 5. Effect of pH on chromium up take with MBP

pH	Absorbance After adsorption	C_o	C_f	%removal	q_e
2	0.255	100	28	72	3.6
4	0.391	100	45	55	2.75
6	0.439	100	51	49	2.45
8	0.463	100	54	46	2.3

App. Table 6. Effect of pH on Copper up take with UNMBP

pH	Absorbance After adsorption	C_0(ppm)	C_f(ppm)	%	q_e	Absorbance standard sol

2	0.750	100	45	55	2.75	0.559
4	0.615	100	23.67	76.33	3.82	0.630
6	0.584	100	13	87	4.35	0.750
8	0.674	100	35	65	3.25	0.90

App. Table 7. Effect of pH on Copper up take with MBP

pH	Absorbance After adsorption	C_0(ppm)	C_f(ppm)	%	q_e	Absorbance standard sol
2	0.651	100	35.33	64.67	3.23	0.559
4	0.594	100	16.33	83.67	4.18	0.630
6	0.568	100	7.67	92.33	4.61	0.750
8	0.624	100	26.33	73.67	3.68	0.90

App. Table 8. Effect of pH on cadmium with UNMBP

pH	Absorbance After adsorption	C_0(ppm)	C_f(ppm)	%	q_e	Absorbance of stand. Soln.
2	0.978	100	49	51	2.55	0.957
4	0.967	100	23	77	3.85	0.993
6	0.964	100	10	90	4.50	1.230
8	1.102	100	40	60	3.00	1.451

App. Table 9. Effect of pH on cadmium up take with MBP adsorbent

pH	Absorbance After adsorption	C_0(ppm)	C_f(ppm)	%removal	q_e	Absorbance of sta Soln.
2	1.075	100	40.67	59.33	2.97	0.957
4	0.921	100	15	85	4.25	0.993
6	0.855	100	4	96	4.8	1.230
8	1.01	100	29.33	70.67	3.53	1.451

App. Table 10. Percentage removal of heavy metal ions at different pH values using UNMBP and MBP

Type of adsorbent	pH	% removal of Pb(II) ion	% removal of Cr(VI) ion	% removal of Cu(II ion
UNMBP	2	57.625	65	55
	4	90.125	48	76.33
	6	95.125	43	87

	8	86.875	41	65
MBP	2	66.5	72	64.67
	4	90.125	55	83.67
	6	95.125	49	92.33
	8	70	46	73.67

App. Table 11. Effect of Adsorbent Dose on lead up take with UNMB

Adsorbent dose(g)	Absorbance After adsorption	C_0(ppm)	C_f(ppm)	%	q_e(mg/g)	Absorbance of standard solution
0.6	0.365	100	30	70	11.67	0.09
0.8	0.334	100	20	80	10.00	0.2
1.0	0.252	100	17	83	8.30	0.47
2.0	0.265	100	16.3	83.7	4.185	0.79

App. Table 12. Effect of Adsorbent dose on lead up take with MBP

Adsorbent dose	Absorbance After adsorption	C_o(ppm)	C_f	% removal
0.6	0.317	100	25	75
0.8	0.205	100	11	89
1.0	0.157	100	5	95
2.0	0.867	100	4.5	95.5

App. Table 13.Effect of adsorbent dose on chromium up take with UNMBP

Adsorbent dose(g)	Absorbance After adsorption	C_0(ppm)	C_f(ppm)	%	q_e(mg/g)	Absorbance of standard solution
0.6	0.245	100	36.75	63.25	10.54	0.082
0.8	0.204	100	21.625	78.375	9.80	0.357
1.0	0.189	100	19.75	84.25	8.4	0.437
2.0	0.194	100	16.5	83.5	8.35	0.880

App. Table 14. Effect of adsorbent dose on chromium up take with MBP

Adsorbent dose(g)	Absorbance After adsorption	C_0(ppm)	C_f(ppm)	%removal	q_e(mg/g)	Absorbance of standard solution
0.6	0.274	100	30.5	69.5	11.58	0.082
0.8	0.161	100	16.25	83.75	10.47	0.357

1.0	0.105	100	9.25	90.75	9.075	0.437
2.0	0.108	100	9.6	90.4	4.52	0.880

App. Table 15. Effect of adsorbent dose on Copper up take with UNMBP

Adsorbent dose(g)	Absorbance After adsorption	C_0(ppm)	C_f(ppm)	%	q_e(mg/g)	Absorbance of standard solution
0.6	0.654	100	36.33	63.67	10.61	0.559
0.8	0.615	100	23.33	76.67	9.58	0.630
1.0	0.589	100	14.67	85.33	8.53	0.750
2.0	0.593	100	16	84.0	4.2	0.900

App. Table 16. Effect of adsorbent dose on Copper up take with MBP

Adsorbent dose(g)	Absorbance After adsorption	C_0(ppm)	C_f(ppm)	%removal	q_e(mg/g)	Absorbance of standard solution
0.6	0.625	100	26.67	73.33	12.22	0.559
0.8	0.589	100	14.67	85.33	10.67	0.630
1.0	0.573	100	9.33	90.67	9.07	0.750
2.0	0.574	100	9.67	90.33	4.52	0.900

App. Table 17. Effect of adsorbent dose on Cadmium up take with UNMBP

Adsorbent dose(g)	Absorbance After adsorption	C_0(ppm)	C_f(ppm)	%	q_e(mg/g)	Absorbance of standard solutio
0.6	1.122	100	24.17	75.83	12.64	0.957
0.8	0.991	100	19.33	80.67	10.084	0.993
1.0	0.981	100	17.67	82.33	8.233	1.230
2.0	0.984	100	18.17	81.2	4.092	1.451

App. Table 18. Effect of adsorbent dose on Cadmium up take with MBP

Adsorbent dose(g)	Absorbance After adsorption	C_0(ppm)	C_f(ppm)	%removal	q_e(mg/g)	Absorbanc standard solution
0.6	0.995	100	27.33	82.67	13.78	0.957

0.8	0.893	100	10.33	89.67	11.21	0.993
1.0	0.883	100	8.67	91.33	9.13	1.230
2.0	0.887	100	9.33	90.67	4.53	1.451

App. Table 19. Results for Chromium adsorption (Langmuir) isotherms (UNMBP)

C_e	q_e		
1.0	0.45	2.22	2.22
3.2	0.84	1.19	3.81
14	1.8	0.56	7.84
45	2.25	0.44	19.8

App. Table 20. Results for Chromium adsorption (Langmuir) isotherms using MBP

C_e	q_e		
0.2	0.049	20.4	4.08
1.6	0.184	5.44	8.7
12.5	0.9375	1.07	13.3
37	2.5	0.4	14.8

App. Table 21. Results for Copper adsorption (Langmuir) isotherms using UNMBP

C_e	q_e		
1.3	0.435	2.30	2.99
3.0	0.85	1.18	3.54
11	1.95	0.51	5.61
31	3.45	0.30	9.3

App. Table 22. Results for Copper adsorption (Langmuir) isotherms using MBP

C_e	q_e		
0.3	0.040	25	7.5
1.38	0.1762	5.4	7.841
8.5	1.0375	0.96	8.19

23	2.65	0.26	8.65

App. Table 23. Results for Cadmium adsorption (Langmuir) isotherms using UNMBP

C_e	q_e		
1.3	0.435	2.3	2.99
3.6	0.82	1.22	4.39
10.75	1.96	0.51	5.48
29	3.55	0.28	8.12

App. Table 24. Results for Cadmium adsorption (Langmuir) isotherms using MBP

C_e	q_e		
0.6	0.2	5	3.0
2.0	0.42	2.38	4.76
9.5	1.0125	0.99	9.38
23	2.3	0.26	10

App. Table 25. Parameters of Langmuir isotherm using UNMBP

heavy Metal Ion	Slope	y-intercept($1/q_{max}$ b)	q_{max}	R^2	b
Lead(II)	0.885	0.91	1.13	0.979	0.972
Chromium(VI)	0.391	2.228	2.56	0.998	0.175
Copper(II)	0.209	2.941	4.78	0.991	0.071
Cadmium(II)	0.160	3.556	6.25	0.980	0.045

App. Table 26.Results for Lead adsorption (Freundlich) isotherms using UNMBP

q_e	C_e	$\log q_e$	$\log c_e$
1.2	0.44	0.08	-0.036
2.8	0.86	0.45	-0.06
9.5	2.025	0.98	0.31
21	3.95	1.32	0.6

App. Table 27. Results for Lead adsorption (Freundlich) isotherms using MBP

q_e	C_e	$\log q_e$	$\log c_e$
0.046	0.8	-1.34	-0.097
0.178	2.2	-0.75	0.34
1.063	7.5	0.03	0.88
4.05	19	0.61	1.3

App. Table 28. Results for Copper adsorption (Freundlich) isotherms using UNMBP

q_e	C_e	logqt	$\log C_e$
1.3	0.435	0.11	-0.36
3.0	0.85	0.48	-0.07
11	1.95	1.04	0.29
31	3.45	1.50	0.54

App. Table 29.Results for Copper adsorption (Freundlich) isotherms using MBP

q_e	C_e	logq	$\log C_e$
0.040	0.3	-1.4	-0.52
0.1862	1.38	-0.73	0.14
1.0375	8.5	0.02	0.93
3.85	23	0.59	1.36

App. Table 30. The result for Lead adsorption of pseudo 1st order kinetics using UNMBP

Time(min)	$q_e - q_t$	$\log(q_e - q_t)$	q_t(mg/g)
30	2.5	0.4	2.20
60	1.2	0.08	3.5
90	0.4	-0.4	4.70(qe)
120	0.13	-0.9	4.57

App. Table 31. The result for Lead adsorption of pseudo 1st order kinetics using MBP

Time(min)	$q_e - q_t$	$\log(q_e - q_t)$	q_t(mg/g)
30	0.75	- 0.13	4.02
60	0.04	-1.4	4.73
90			4.77(qe)

120	0.03	-1.5	4.74

App. Table 32. The result for chromium adsorption of pseudo 1st order kinetics using UNMBP

Time(min)	q_t(mg/g)	$q_e - q_t$	$\log(q_e - q_t)$
30	2.25	2.45	0.39
60	3.5	1.2	0.08
90	4.70(qe)	0.4	-0.4
120	4.60	0.1	-1.0

App. Table 33. The result for chromium adsorption of pseudo-first order kinetics using MBP

Time(min)	q_t(mg/g)	$q_e - q_t$	$\log(q_e - q_t)$
30	4.0	0.08	-1.1
60	4.7	0.1	-1
90	4.8		
120	4.78	0.02	-1.7

App. Table 34. The result for copper adsorption of pseudo-first order kinetics using UNMBP

Time(min)	q_t(mg/g)	$q_e - q_t$	$\log(q_e - q_t)$
30	3.25	1.55	0.190
60	3.75	1.05	0.021
90	4.80(qe)	0.8	-0.1
120	4.70	0.1	-1

App. Table 35. The result for copper adsorption of pseudo-first order kinetics using MBP

Time(min)	q_t(mg/g)	$q_e - q_t$	$\log(q_e - q_t)$
30	4.4	0.55	-0.26
60	4.94	0.01	-2
90	4.95		-1.6
120	4.93	0.02	-1.7

App. Table 36. The result for cadmium adsorption of pseudo-first order kinetics using UNMBP

Time(min)	q_t	$q_e - q_t$	log(q_e - q_t)
30	1.75	2.7	0.43
60	2.25	2.2	0.34
90	4.45(qe)	0.9	0.23
120	4.43	0.02	-1.7

App.Ttable 37. The result for cadmium adsorption of pseudo-first order kinetics using MBP

Time(min)	q_t	$q_e - q_t$	log(q_e - q_t)
30	4.05	0.65	-.19
60	4.65	0.05	-1.3
90	4.7		-1.5
120	4.68	0.01-	-2

App. Table 38. Parameters of pseudo-first order kinetic model using UNMBP

Metal ion	R^2	K_1(min^{-1})	slope	y-intercept(logqe)
Lead	0.990	0.032	-0.014	0.89
Chromium	0.980	0.035	-0.015	0.93
Copper	0.984	0.021	-0.009	0.5
Cadmium	0.982	0.023	-0.010	0.89

App. Table 39. Parameters of pseudo-first order kinetic model using MBP

Metal ion	R^2	K_1(min^{-1})	slope	y-intercept(logqe)
Lead	0.994	0.0392	-0.014	0.89
Chromium	0.988	0.0461	-0.015	0.93
Copper	0.985	0.037	-0.009	0.5
Cadmium	0.983	0.044	-0.010	0.89

App. Table 40. The result for lead adsorption of pseudo-second order kinetics using UNMBP

Time(min)	q_t(mg/g)	t/qt
30	2.20	13.6
60	3.5	17.1
90	4.70(qe)	19.1
120	4.62	25.97

App. Table 41. The result for chromium adsorption of pseudo-second order kinetics using UNMBP

time(min)	q_t(mg/g)	t/qt
30	2.25	13.3
60	3.5	17.1
90	4.70(qe)	19.1
120	4.65	25.8

App. Table 42. The result for cadmium adsorption of pseudo-second order kinetics using UNMBP

Time (min)	q_t(mg/g)	t/qt
30	1.75	17.1
60	2.25	26.67
90	4.45(qe)	20.22
120	4.43	27.09

Appendix Figures

App. Figure 1. Plot of pseudo-first order kinetics of lead adsorption using UNMBP

App. Figure 2. Plot of pseudo - first order kinetics of lead adsorption using MBP

App. Figure 3. Plot of pseudo - first order kinetics of copper adsorption using UNMBP

App. Figure 4. Plot of pseudo - first order kinetics of copper adsorption using