

**INVESTIGATION OF MULTICOMPONENT
HEAVY METALS ADSORPTION CAPABILITY
USING RAW COIR DUST AND PROCESSED
COIR PITH**

A.M.P.C. Amarasinghe

159251L

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Department of Chemical & Process Engineering

University of Moratuwa

Sri Lanka

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Dr. H.H.M.P. Rathnayake
Senior Lecturer Grade II
Dept. of Chemical and Process Engineering
University of Moratuwa

ABSTRACT

Water is the most vital natural resource that sustains all living organisms on the earth and access to safe and clean water has become a crisis due to intense water pollution by anthropogenic activities, over-pumping of groundwater for irrigation purposes, limited water availability due to climate changes, regional conflicts over common water resources, etc. Wastewaters that contain various heavy metals, such as arsenic, chromium, manganese, nickel, lead, cadmium, zinc, and copper are being discharged into natural water bodies annually by many industries. Industrial processes that generate wastewater with significantly high levels of heavy metals use various techniques, such as chemical coagulation, chemical precipitation, membrane separation, extraction, electrodeposition, ion-exchange, and electrochemical techniques in order to remove the heavy metal contents. Nevertheless, most of these techniques use expensive chemicals and require considerable time, and some of them are proven to be less effective and less efficient, especially in removing trace amounts of metals. Besides above methods, adsorption technique is one of the most widely used technique to remove heavy metals from water and studies have revealed that it is much effective in removing heavy metals with high solute loading and even at minute concentrations. In the past decade, significant number of studies have been conducted worldwide on the removal of heavy metals from aqueous solutions by non-living and biologically inactive biomass. This approach of wastewater treatment is known as biosorption, and the non-living biomass used there is defined as bio sorbent. Use of bio sorbents to remove heavy metals from wastewater is a novel and developing technology in the water treatment field. Coir pith is a waste-derived material that can be utilized as a biosorbent for heavy metals removal from wastewater. In this study, directly obtained raw coir dust from coconut husks and processed coir pith were tested for their removal efficiencies of 8 heavy metals, i.e., As, Cd, Cu, Cr, Mn, Ni, Pb, and Zn. Standard heavy metal solutions were prepared for each metal and heavy metal content of standard solutions, coir pith, and coir dust were first measured using the Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) method. A multicomponent batch adsorption experimental procedure was conducted to determine the removal efficiencies of each metal by both coir dust and coir pith. In experimental procedures, respectively, 1g, 2g, 3g, 4g, and 5g of coir pith and coir dust were added to equal volumes of each metal solution and allow adsorption for 2 hours. Then filtered samples were tested for the heavy metal concentrations using

the ICP-OES method. Multicomponent heavy metal removal efficiencies of coir pith were tested by varying the adsorption temperatures and the contact time between the heavy metal solution and the coir pith sample. Analytical results show that both raw coir dust and coir pith act as suitable bio sorbents for removal of As, Cd, Cr, Ni, and Pb, and the optimum solid/liquid ratio is 0.1 g/ml at room temperature for 2 hours if contact time for all these five heavy metals. According to the results comparison between the of raw coir dust and processed coir pith, raw coir dust shows higher heavy metals removal capacities Coir pith is the most suitable biosorbent for Cu removal while coir dust is most suitable biosorbent for Mn removal. For raw coir dust metals and bio sorbents 0.08g/ml at room temperature for 2 hours contact period is the optimum solid/liquid ratio. For processed coir pith metals and bio sorbents 0.1g/ml at room temperature for 2 hours contact period is the optimum solid/liquid ratio Anyway both coir pith and coir dust are not suitable for Zn removal from aqueous solutions. For all metals except Zn, contact period of 30 minutes and temperature of 30 °C are the optimum operating conditions.

In this experimental we have used multi component heavy metal sample as a result of it both materials adsorption and desorption are happening in the same sample. When we consider heavy metal adsorption with the temperature from 30-70 °C heavy metals adsorption capacity has decreased the reason for this with the increasing of temperature kinetic energy of the metal has increased then desorption is happened inside the sample. As a result of it with increasing of temperature heavy metals adsorption capacity will decrease.

When we consider contact time of the heavy metals sample with the absorbent, For Cr, Cu and Pb show similar results. From 30 min to 2 hr material adsorption efficiency has decreased but 2 hr to 4 hr adsorption efficiency has increased the reason is for this, from 30 min to 2 hr desorption appeared in the sample but with the increasing of the contact time from 2 hr to 4 hr again heavy metals adsorption is happened in the sample. But all other heavy metals are showing decreasing trend of heavy metals adsorption capacity with the increasing of contact time.

Keywords: Coir pith, coir dust, heavy metals, adsorption, biosorption, biosorbent

DEDICATION

Dedicated with gratitude to everybody who supported me to make this a success.

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Introduction

1.1 Overview

Water is an essential natural resource that is important for every forms of life on the earth, and accessibility to clean and safe water is a prime need of all living beings in the world. According to a report published by the United Nations (UN) in 2012, nearly one billion people from developing countries do not have access to safe drinking water (GLAAS, 2012). With the increase of world population, demand for water is gradually increasing, and it is predicted that nearly half of the world population will be facing a water crisis by the year 2025 (Rijsberman, 2006). Major reasons for water crisis are intense water pollution by anthropogenic activities, over-pumping of groundwater for irrigation purposes, limited water availability due to climate changes, regional conflicts over common water resources, etc. Scarcity of safe and clean water has several negative impacts on the human population, as well as wildlife and aquatic life on earth. During the recent years, water pollution is the leading cause of safe drinking water scarcity and its related effects, such as waterborne diseases and deaths (WWDR4, 2012). New regulations are being developed and implemented worldwide to regulate the surface and groundwater pollution by industrial sources. However, access to clean and safe water remains a crisis without a proper solution. To address this issue, many technological improvements are made around the globe to recycle or to properly treat industrial wastewater or polluted water before discharging into natural water bodies.

1.2 Heavy metals pollution in water and associated health risks

Wastewater that contains various heavy metals, such as arsenic, chromium, manganese, nickel, lead, cadmium, zinc, and copper are accumulated in many industries, and it is required to undergo proper heavy metals removal prior to discharging into natural water bodies. Some of the industrial processes that generates wastewater with significantly high levels of heavy metals are paper and pulp industries, smelting, battery manufacturing, galvanizing, printing, dyeing, electronics manufacturing, metal fabrication and mining activities, electrolyzing, ceramics manufacturing, paint manufacturing, drug manufacturing, and inorganic dyestuff preparation, etc. (Liu, et al., 2008). Discharge of untreated wastewater that contains metal could be toxic to humans as well as animals, plants and all the ecosystems (Pamukoglu and Kargi, 2006). Even the low concentrations of heavy metals can be absorbed and be toxic to living

organisms (Kusvuran et al., 2012; Gavrilesco, 2004). Cu(II), Pb(II), Cd(II), As(III), Cr(III), Mn(II), Ni(II), and Zn(II) are the widely used heavy metals in industrial and some domestic activities and some of these are also important as nutrients to living organisms in trace amounts. Presence of these heavy metals at higher levels in both surface and groundwater degrades the quality of water, inhibits the growth of aquatic organisms, and thereby makes the water unsafe for use. Heavy metal ions and their supplementary complexes can accumulate in the bodies of aquatic flora and fauna and finally could reach the human body by bio-accumulation, bio-concentration, and bio-magnification through the food chains (Hong et al., 2006). Therefore, removal of heavy metal ions from water is now a subject of great concern in both the industrial sector and government agencies throughout the world. Hence, it is crucial to control the levels of heavy metals in wastewater before they are discharged into the natural water bodies.

1.3 Removal of heavy metals from wastewater

Various techniques are being used to treat the wastewater containing high levels of heavy metals, such as chemical coagulation, chemical precipitation, membrane separation, extraction, electrodeposition, ion-exchange, and electrochemical techniques. Nevertheless, most of these techniques use expensive chemicals and require considerable time. Some of them are proven to be less effective and less efficient especially in removing trace amounts of metals (Xiangliang et al., 2005). Another disadvantage of these methods is that many of them produce metal-containing sludge that requires further treatment before the disposal (Rhazi et al., 2002). Besides above methods, adsorption technique is one of the widely used techniques to remove heavy metals from aqueous solutions, and studies have revealed that it is effective in removing heavy metals with high solute loading and even at minute concentrations (usually below 100 mg/l) (Rhazi et al., 2002). Activated carbon is the commonly used and commercially available adsorbent for removing heavy metals from wastewater, which is a relatively expensive material. Therefore, many researchers have focused on developing cost-effective adsorbents, especially from biowaste-derived materials.

1.4 Biosorption of heavy metals

Research studies conducted on identifying cost-effective and readily available adsorbent has found materials with biological origin having potential as metal

adsorbents, which are known as biosorbents. In the past decade, significant number of studies have been conducted worldwide on the heavy metal removal from aqueous solutions by biowaste-derived materials. This wastewater remediation approach is known as biosorption, and the biomass materials, used in this method are defined as biosorbents. Use of biosorbents to remove heavy metals from wastewater is a novel and developing technology in the field of water treatment (Schiewer and Volesky, 2000). Economically feasible sorbents can be defined as materials that are abundantly found in nature or can be found as by-product or waste from agro-industry, that are low in cost, relatively effective and do not require any pre-processing. Several mechanisms are involved in the biosorption of heavy metals that differ qualitatively and quantitatively depending on the material (Volesky and Holan, 1995). Biomaterials have several functional groups such as amido, sulfhydryl, amino, acetamido, carboxyl, and sulfate which could attract and sequester heavy metals from solutions (Schiewer and Volesky, 2000; Volesky and Holan, 1995). Main complex mechanisms of biosorption include ionic bonds and ion exchanges, formation of complexes between metal cations and ligands contained in the structure of the cell wall biopolymers, and precipitation on the cell wall matrix of biosorbent (Schiewer and Volesky, 2000). Biosorbents are considered as an alternative to ion exchangers or other metal extraction and concentration operations in metal recovery and therefore, the biosorption process is of great importance in environmental context. There are various biomaterial types, such as plant parts, agricultural and natural residues, industrial wastes, algae, fungi, bacteria, etc. Main advantages of biosorption are that biomaterials are abundant in nature, require minimum pre-processing, cost-effective and highly efficient in the heavy removal process, which make biosorption as an attractive and feasible alternative for wastewater treatment.

Researchers have focused on several agricultural lignocellulosic adsorbents, because they are waste-derived, renewable, cost-effective, bio-degradable, and eco-friendly materials (Man et al.,2015). These materials are used to make value-added adsorbents for wastewater treatment in many parts of the world. Raw coir dust can be extracted from coconut husk as an adsorbent material that could be used for the biosorption process. Coconut husk is the mesocarp of the coconut which makes up 33%-35% of the husk (Man et al.,2015). Many studies have been conducted with the use of agricultural byproducts, such as rice straw, rice husk, palm oil fiber, and rubberwood saw dust as the adsorbent materials for wastewater treatment, but coconut husk seemed

to be a preferred one as 60% of the husk is comprised of lignin and cellulose (Sivapragasam, 2008). The hydroxyl groups of these two polymers provide sites for metal adsorption (Man et al.,2008). Coconut husks and shell by-products are largely accumulated in the environment since they are waste materials. Therefore, utilization of them as biosorbents is a sustainable option for wastewater treatment with low environmental impacts from the removal process. Further processing of extracted coir fiber from matured coconut husks can produce processed coir pith. There is a commercial process of wet-treatment and drying to produce coir pith for various commercial purposes like seeds cultivation medium, fertilizer, etc., in addition to the use as an adsorbent. Abundant amounts of raw coir dust and processed coir pith are remained after the use and they are mostly dumped without further value addition or reuse. Phenols and tannins leached from coir pith can contaminate the nearby agricultural soils and decrease agricultural productivity (Vidya et al.,2018). However, high lignin content and slow degradation rate in coir pith lead to some level of environmental pollution and therefore it is important to reuse coir pith effectively to prevent soil contamination and environmental pollution. Thus, reusing both raw coir dust and processed coir pith as adsorbents for heavy metals removal is an attractive solution for both heavy metals pollution in wastewater and the environmental effects of coir products dumped into the environment after use.

1.5 Aims and objectives

The aim of this study is to investigate the adsorption capability of raw coir dust and processed coir pith for the removal of heavy metals: Arsenic, Cadmium, Chromium, Copper, Manganese, Nickel, Lead, and Zinc from an aqueous solution.

In achieving the main objective, the following specific objectives are to be apprehended:

- To compare the feasibility of using raw coir dust and coir pith as locally available adsorbent materials.
- To determine the appropriate solid/liquid ratio for the removal of different heavy metals: Arsenic, Cadmium, Chromium, Copper, Manganese, Nickel, Lead, and Zinc from an aqueous solution.
- To determine the suitable temperature range and contact time for heavy metal adsorption using raw coir dust and coir pith.

It is expected that the findings from this research work would strengthen the information available on the use of coir pith and its use as biosorbents for the heavy metal removal from wastewater. The outcomes from this study would enhance the understanding of suitable operating conditions for the effective removal of heavy metals that will be useful for scaling up future heavy metals adsorption process using raw coir dust or processed coir pith.

1.6 Structure of the thesis

In this study, coconut husks and coir pith that are discarded as agricultural by-products were tested for their biosorption qualities to determine the efficiency of them in removing the heavy metals from aqueous solutions. Chapter 1 gives a general introduction to the research problem, state the research objectives, and describe the outline of the thesis. Chapter 2 deals with the literature review which include the important information from the previous researches related to the heavy metals pollution and its impact on environment, various heavy metals removal techniques and their constraints, biosorption technique and its advantages over other conventional methods, different types of biosorbents and their characteristics, availability of biosorbents with previous work on their use as adsorbents. This chapter also emphasizes applications of coir pith and coconut husks related biomaterials. Chapter 3 contains the methodology and it describes the materials used, sample collection & preparation techniques, methodologies followed in the laboratory and statistical analysis performed. Chapter 4 consists of results and discussion and this section present the outcome of statistical analysis of test results. Also, it interprets the results obtained and the suitability of coir pith and coir dust as biosorbents for removal of tested heavy metals. Chapter 5 gives a general conclusion of the research and recommendations for future research work with further improvements.

Literature Review

2.1 Background

From the past few decades, environmental pollution has become the major concern for industrial sector all over the globe, because it is having drastic impacts on every component on the earth. Massive increases in the human population and rapid industrial growth are the two most influential factors for the rising environmental pollution. Industries are rapidly expanded and grown to meet the demand from the growing population. Not only the industrial sector but also the agricultural sector has also dramatically developed to meet the demand from expanding world population, simultaneously increasing the risks of environmental pollution. Environmental pollutants are in all forms of gaseous, solid, and liquid, which are released into air, discharges into water, and disposed onto land, respectively, and posing threats on living organisms and associated ecosystems. Heavy metals are naturally occurring substances in nature in trace amounts, but many industries produce large quantities of heavy metal and release them into the natural environment, most importantly into natural water. Industries that generate massive loads of heavy metals are paper and pulp industries, electrolyzing, alloy manufacturing, galvanizing, metal fabrication and mining activities, ceramics manufacturing, battery manufacturing, smelting, printing, dyeing, paint preparation and inorganic dyestuff preparation (Liu et al., 2008). The presence of toxic heavy metals in the environment in different forms is of great concern, due to their non-biodegradability and persistence in the natural environment (Volesky, 1999). Especially, higher loads of heavy metal in water are extremely undesirable since they may have potentially adverse impacts on living organisms, suitability of water for usage, and aesthetic environment (Vieira and Volesky, 2010). However, some of the heavy metals are harmless for living organisms and required in minute concentrations as nutrients needed for metabolism and balanced growth, for example Copper, Zinc, Iron, Cobalt, and Selenium. Higher concentrations of heavy metals may cause toxicity that is acute, chronic, synergistic, or mutagenic (Burger and Gochfeld, 2004). Some of these heavy metals and their supplementary complexes can be accumulated in the body of aquatic organisms, such as fish and ultimately could reach the human body by the processes of bioaccumulation, bio-concentration, and bio-magnification along the food chains (Hong et al., 2006).

Cadmium is introduced into the environment from paint and pigments, and plastic stabilizers, mining and smelting operations and industrial operations, including electroplating, reprocessing cadmium scrap, and incineration of cadmium containing plastics. It is used in nickel-cadmium batteries, PVC plastics, and paint pigments. Cadmium can be found in soils because insecticides, fungicides, sludge, and commercial fertilizers that contain cadmium are used in agriculture. It may enter drinking water as a result of corrosion of galvanized pipe. Cadmium dispersed in the environment can persist in soils and sediments for decades. Both coir pith and coir dust can be used as biosorbents to remove Cd from aqueous solutions. The most salient toxicological property of cadmium is its exceptionally long half-life in the human body. Once absorbed, it irreversibly accumulates in the human body, in particular in kidneys and other vital organs such as the lungs or the liver.

Chromium is used as pigments for industries such as paper, paints, rubber, cement and other materials. Acute exposure to Cr can cause skin irritations and ulceration. Chronic exposure can cause kidney and liver damage, and circulatory and nerve tissue damages. Chromium often accumulates in the cells of aquatic organisms, which poses a danger of ingestion of heavy metals to human body through contaminated fish. Chromium (VI) is highly toxic and is the real danger to human health, mainly for people who work in the steel and textile industry.

Though copper is an essential element for human life, but excessive intake results in its accumulation in the liver and produces gastrointestinal problems, liver and kidney damage and anemia. Continued inhalation of copper-containing sprays is linked with an increase in lung cancer (Yu et.al.2000).

Nickel enters the environment through two main pathways: natural- such as weathering of minerals and rocks, and geochemical emission, and anthropogenic such as industrial and vehicular emissions. Nickel particles in the air settle to the ground or are taken out of the air in rain. Nickel salts are soluble and can occur as a leachate from nickel bearing rocks. The effect of nickel exposure varies from skin irritation to damage to lungs, the nervous system, and mucous membranes.

Manganese compounds are widely used in manufacturing of batteries, steel and unleaded petrol. Manganese dioxide is commonly used in the production of matches, fireworks, porcelain dry-cell batteries, and glass-bonding materials. It is also used as

the starting material to produce other manganese compounds. Main sources of lead are mined ores and recycled scrap metal or batteries. The main sources of lead pollution are paper and pulp industries, lead smelters, boat and ship fuels and ammunition industries and battery manufacturers. People living near hazardous waste sites may be exposed to lead by breathing air, drinking water, eating foods, or swallowing or touching dust or dirt that contains lead. Low levels of lead have been identified with anemia as it causes injury to the blood forming systems while high levels cause severe dysfunction of the kidneys, liver, the central and peripheral nervous system, and high blood press.

2.2 Sources, toxicity, and environmental fates of heavy metals

2.2.1 Sources of heavy metals

Sources of heavy metals in the natural environment include both natural phenomenon and anthropogenic activities. Weathering of rocks naturally produces heavy metals while anthropogenic activities, such as burning of petroleum, mining, and metal-working contributes to the emission of heavy metals into the atmosphere in gaseous form. Moreover, the main source of heavy metal pollution in water are metal smelters, household waste, waste from iron and steel production, metal plating or finishing operations and fertilizer applications (Nriagu et al., 2004). Soil is contaminated from heavy metals by the disposal of ash residues from coal combustion and general disposal of commercial products on land (Nriagu et al., 2004). Among all the industries that release considerably high amounts of heavy metals into the environment following four sectors are the key industries (Volesky,2007):

- acid mine drainage because of mining operations
- power generation through the combustion of enormous quantities of coal
- electroplating industry waste solutions
- Nuclear power generation activities such as uranium mining

There are three main types of heavy metals; toxic metals (e.g.: As, Hg, Cd, Cr, Cu, Ni, Co, Zn, Sn, Pb, etc.), precious metals (ex: Ag, Pd, Pt, Au, etc.) and radionuclides (e.g.: Ra, U, Th, etc.) (Wang and Chen, 2009).

2.2.2 Heavy metals in industrial effluents

Rapid industrialization has a significant impact on the release of toxic heavy metals into natural water bodies. Industrial effluents that contain heavy metals produced from different industries, such as battery manufacturing, mining, metal processing, electroplating, textile industries, tanneries, petroleum refining, pigment manufacturing, printing and photographic industries, and pesticide manufacturing (Liu et al., 2010). Heavy metals, such as arsenic, cadmium, chromium, mercury, copper, nickel, lead, and zinc have been identified as hazardous metals and these are non-biodegradable in nature and can be accumulated in the living tissues causing various adverse impacts on living organisms. Therefore, removal of heavy metals from water, soil, and air is essential.

Other sources of heavy metal include wood processing industries, pigment manufacturing industries, petroleum refineries, and photographic operations. In wood processing industries, chromated copper arsenate wood treatment produces waste containing arsenic while pigment manufacturing industries produce waste containing chromium compounds and cadmium sulfide. Petroleum refineries generate waste which contains heavy metals such as nickel, chromium and vanadium and photographic operations produce a film with high concentrations of silver. All these industries produce large quantities of wastewater, sludge, and residues that can be classified as hazardous waste which requires thorough treatment before disposal into the environment (Sörme and Lagerkvist, 2002).

2.2.3 Heavy metals in domestic wastewater

Usually, waste effluent from household largely comprise of organic and inorganic waste, but some household, as well as industrial activities may release heavy metals into domestic wastewater as well. For example, detergents used in domestic purposes contain minute levels of metals, such as chromium, copper, magnesium, iron, and strontium. Owing to the higher affinity between metals and solids heavy metals can be absorbed onto solids. Also, it is now a notable fact that urban runoff causes serious metal pollution in domestic wastewater (Raskin et al.,1997). Street dust and various solids, with various chemicals, such as pesticides, have also significantly contributed to domestic water pollution. Landfills are another domestic source of heavy metal contaminant, where solid waste disposed on the landfills contain various heavy metals both in solid and liquid forms. When anaerobic reactions occur in the landfill for a long period it leads to an acidic environment that pushes heavy metals into the environment. Heavy metal content normally high in the fertilizer made from sludge residue and when they are applied on land the metals could enter the surface water and groundwater through seepage (Chang et al., 1987). Furthermore, sewage sludge contains high levels of toxic metals that cause unwanted impacts such as phytotoxicity and microbial toxicity in food chains and surface and groundwater contamination (Chang et al., 1987). Therefore, it is important to know the physical and chemical properties of biomaterial used for agricultural purposes, particularly the total concentrations of the elements and the extractable metals at neutral pH range, which may have biologically adverse impacts.

2.2.4 Toxicity of heavy metals

There are two major categories of heavy metals, first one is the essentials for the survival of living organisms, such as calcium, iron, etc., and the second category is the toxic heavy metals to living beings, such as lead, arsenic, etc. Most of these heavy metals are non- degradable and their accumulation in living tissues can lead to serious health issues which are sometimes even fatal. Heavy metals contained wastewater that is discharged into natural water bodies through industrial and domestic discharges can be concentrated in the environment and passed along the food chains (Castro-González and Méndez-Armenta,2008) and eventually accumulate into extreme toxic levels to human bodies. Once metals seep through surface water and soil into the groundwater it can contaminate drinking water sources as well. Human exploitation of the world's mineral resources has led to disperse of chemicals and metallic elements and have brought them into the environment in unrivalled concentrations and rates (Mansour and Gad, 2010). Heavy metals toxicity is elevated by the higher concentrations of metals and their toxicity may pose serious health threats, such as damage of mental or central nervous functions, lungs, kidneys, liver, and other vital organs, and alter the metabolic activities of the body (Lussier et al., 1985). Chronic exposure to toxic heavy metals may cause fatal diseases, such as various cancers, sclerosis, neurological degenerative diseases, muscular dystrophy, and Parkinson's disease (ul Islam et al., 2007).

Once entered the human body heavy metals express their toxicity in several different mechanisms as follows.

- i. Heavy metals are easily form precipitates with anionic substances, such as carbonate, sulfate, and phosphate. These precipitates do stay in the human body for a long time.
- ii. Heavy metals can be sequestered into organic functional groups present in the tissues of the human body, and cause changes in their biological activities (e.g., enzymes). Therefore, essential metals attached to the enzymes could be replaced by toxic chemicals (e.g., Zn could be replaced by Cu).
- iii. Some heavy metals may cause redox reactions and change the chemistry of basic elements such as carbon.

2.2.5 Heavy metal pollution scenario

Many researches have been conducted on heavy metal contamination in soil and water from various anthropogenic sources, such as agricultural practices, industrial wastes, automobile emissions, and mining activities (Li et al., 2014). Heavy metals released from anthropogenic sources are easily accumulated in the topsoil layer, causing potential problems, such as toxicity to plant and animals, accumulation in food chains and adverse health impacts on humans. Owing to the intensive industrial sector, heavy metal pollution has become a serious problem in developing countries and poorly developed roadways and automobiles are the main sources of heavy metals in those countries apart from the industrial effluents. Zinc, lead, and copper are the three most common heavy metals released from road traffic and they comprised up to 90% of the metals releasing from road runoff. Most common metals that are released from road runoff are iron, copper, lead, zinc, chromium, aluminum, nickel, and cadmium. Leaded gasoline, lubricating oil and bearing wear are the main sources of lead (Pb) that is added to urban runoff while zinc is added to the runoff by motor oil, grease, and brake emissions. Engine parts and brake emissions are the main sources of copper and cadmium is added into runoff water mainly by fuel burning and batteries (Hsu et al., 2006). These heavy metals tend to bound with road dust or particulate matter and bound metal will either be dissolved in the runoff or be swept off the roadway with dust by runoff and then enter soil and water. Then, they could be transported into the groundwater table as well.

The way in which metals are traveled in the environment is controlled by the chemical nature of metals, and the media passes through, such as water, soil, sediment particles, and the pH of the environment (Nriagu, 1996). Most of these metals are divalent cations (for example copper, zinc, cadmium, etc.) and soil particles, have a variety of charged sites (both positively and negatively charged sites) on their surfaces. These negatively charged sites attract metal cations and form bonds and prevent them from being dissolved in the water. The dissolved form of metals is easily transported and more readily available to animals and plants to take up (Goldberg et al., 1977). The behavior of heavy metals in the aquatic environment is alike to that in the physical environment. Sediment particles in aquatic environments are having binding sites similar to that of the land environment and therefore, heavy metals are bound to the sediment particles at the bottom of water bodies and some heavy metal cations are dissolved in water.

2.2.6 Context of heavy metal pollution in Sri Lanka

As a developing country, both industrial sector and agricultural sectors play important roles in Sri Lanka's economy and both sectors have contributed to environmental pollution by heavy metals. In the past decade, industrial sector of Sri Lanka has shown drastic development and environmental pollution caused by industries has become significant during the past few years. Due to the lack of proper wastewater treatment systems and proper awareness about safe disposal of wastewater in industries large quantities of heavy metals are released into the natural environment. Significant amounts of heavy metals are released from industries, such as tanneries, galvanizing industries, electroplating industries, battery manufacturing and assembling industries, mining, etc., and many of these heavy metals loads are directly ended up in inland surface water bodies, such as rivers, streams, canals, etc. Techniques available in industries to treat wastewater containing heavy metals are highly expensive and less effective at most of the times. Also, the sludge generated from wastewater treatment does contain high levels of heavy metals and unsafe disposal of the sludge into the environment may cause serious environmental issues.

In addition to this considerable amount of heavy metal is added into soil, surface water, and then groundwater by open dumping and landfilling of solid waste. Solid waste may contain some material that contains heavy metals and when they are disposed without proper management they can be leached into the soil, surface water and thereby groundwater table. Not limiting to these, agricultural activities also significantly contributing to the heavy metal pollution in the environment. In modern agricultural practices, excessive application of fertilizers and pesticides are seemed to be a common practice and some of these agrochemicals contain trace metals as active ingredients (Rosemary et al.,2014). Excessive usage of such agrochemicals could contaminate the agricultural soil, and this may cause phytotoxic effects and trace metal contamination in edible plants (Cobb et al.,2000). Soil and water ingestion and consumption of contaminated food are main pathways where human can be exposed to toxic metals. Accumulation of these heavy metals in human body can cause different health problems, such as anemia and chronic renal failures, various cancers, diseases in the digestive system and many other fatal diseases (Wanigasuriya et al.,2008). Premarathne et al. (2011) reported that elevated levels of toxic metals are found in the soils of vegetable fields in Sri Lanka. According to this research, total soil Cd concentration is 3.85 mg/kg in vegetable growing soils in the upcountry wet zone of Sri Lanka.

2.3 Technologies for removal of heavy metals from wastewater

Heavy metal removal has become a serious issue in the developing world where industrial use and discharge of heavy metals are drastically increasing. The adverse impacts of heavy metals on humans, and environment have been clearly identified. Therefore, an effective and feasible heavy metals removal method is a vital research concern among researchers (Al-Rub, 2006). The commonly used methods for removing toxic metal ions from aqueous streams include physical, chemical, and biological methods, used separately or integrated based on the requirement. The available methods are ion exchange, chemical precipitation, solvent extraction, reverse osmosis, and lime coagulation (Areco et al., 2012).

Biosorption process can be used to remove heavy metals from wastewater depending on the metal binding capacities of various biological materials (Vilar et al., 2007). Biosorption process has been lately identified as a cost-effective alternative method that could be applied for wastewaters low organic load (Pavasant et al., 2006). Biosorption is the removal of heavy metals using a passive binding process with non-living microorganisms including bacteria, fungi, and yeasts (Parvathi and Nagendran, 2007), and other biomass types that are capable of efficiently adsorbing heavy metals. Advantages of the biosorption include low cost, high efficiency for minute concentrations of heavy metals, minimal amounts of chemical requirement, no additional nutrients required, and the possibility of metal recovery (Vilar et al., 2007a).

2.3.1 Physical methods and processes

Physical and chemical methods of heavy metal removal include chemical precipitation, ion exchange, adsorption, coagulation-flocculation, oxidation, and membrane processes. Many of these physical-chemical treatment processes are not cost effective due to their demand for large quantities of chemicals and advanced technologies and machines. Following are some of the physical heavy metal removal methods.

Evaporators

In the evaporation process, a liquid solution is vaporized using an energy source. Recovery of metals is accomplished by boiling an adequate amount of water from the collected rinse stream and allowing the concentrate to be returned to the plating bath. The evaporation process is a maintenance-free, easy, and reliable process (Peters et al.,

1985). Main disadvantages of this method are high capital and operational costs for evaporative recovery systems, high-energy consumption, and undesirable constituents in the recycled bath.

Precipitation

This is a widely used method for removing heavy metals up to parts per million (ppm) levels from aqueous solutions. In the precipitation process, metals are removed from an aqueous solution by adding a reagent, which reacts to form a solid precipitate and the precipitate is removed by flocculation, filtration, or sedimentation processes (Kurniawan et al., 2006). This process is cost-effective, but its efficiency is affected by low pH and the presence of other ions. Also, the process requires the addition of other chemicals, which finally generates large quantities of sludge with higher levels of heavy metals, the disposal of which is cost-intensive (Gray and Schrefler, 2001).

Cementation

Cementation is a precipitation method that uses an electrochemical mechanism in which a metal having a higher oxidation potential passes into a solution to replace a metal having a lower oxidation potential. Copper is most frequently separated by cementation process along with noble metals, such as Pb, Ag, Au as well as As, Cd, Pb, and Sn (Case, 1974). In this method, heavy metal ions are displaced by a metal with higher oxidation potential. Due to low cost and high availability, this method is often used to recover scrap iron. Due to its long contact time, the cementation process is favorable for small wastewater flows.

Ion-exchange

In the ion-exchange process, a metal ion from an insoluble exchange material is displaced by other ionic species (Kurniawan et al., 2006). In this process, metal ions from dilute solutions are exchanged with ions held by electrostatic forces on the exchange resin. This method is specifically used in domestic water softening processes. Disadvantages of this method include high cost and partial removal of certain ions. Nevertheless, this method can achieve ppb levels of heavy metal removal while handling a relatively large volume of aqueous solution. Concentrated metal solution cannot be handled in this method because the matrix gets easily contaminated by organic substances and other solids in the wastewater. This method requires a pre-treatment

process to reduce suspended solid concentration in solution to prevent fouling or channeling.

Membrane process

Membrane processes with ultrafiltration membranes are used to remove heavy metals from wastewater containing emulsified oil and metal particles. However, main disadvantages are the requirement of cleaning these membranes and regular backflushing to ensure efficient operation (Alvarez-Vazquez et al., 2004). Membrane processes usually consist of microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. In addition, this method includes limitations with high membrane material cost, membrane fouling and compaction, limited life of membrane, applicability only to feed streams with low concentrations of metal ions, inability of membranes to resist certain types of chemicals and pH values and sometimes membranes are prone to deterioration in the presence of microorganisms (Kitagawa et al., 1977; Ramalho, 1977).

Reverse osmosis

In reverse osmosis process, heavy metals are separated by a semi-permeable membrane at a pressure higher than osmotic pressure caused by the dissolved solids in wastewater (Van Hoof et al., 1999). Both reverse osmosis and electro-dialysis processes use semi-permeable membranes for the recovery of metal ions from dilute wastewater. Major disadvantage of this method is its high cost.

Electrodialysis

In electrolysis, metal ions from the anodizing bath solution are transported through a selective membrane into a capture media using an electrical current to induce flow and thereby efficiently maintains a low metal ion concentration in the anodizing bath solution (Chao and Liang, 2008). By applying an electrical potential between the two electrodes cations and anions migrate towards respective electrodes. Major disadvantage of this method is the formation of metal hydroxides, which can clog the membrane. This process is a highly energy-dependent and labor-intensive as well as include moderately high capital cost.

Ultrafiltration

Ultrafiltration is a pressure-driven technique for separating dissolved metals in a solution based on size. This is a pressure-driven membrane operation that uses porous membrane for the heavy metal removal and molecules larger than the membrane pore size is retained at the surface of the membrane (Cañizares et al., 2002). The accumulated metal ions may form a concentrated gel layer the formation of gel layer can significantly alter the performance characteristics of the membrane (Chaufer and Deratani, 1988). The main disadvantage of this process is the generation of large quantities of sludge.

Flocculation and coagulation

This method facilitates the removal of suspended solids and colloidal particles. Coagulation is the destabilization of colloidal particles by the addition of a chemical reagent called a coagulant. Flocculation is the agglomeration of destabilized particles into micro floc and then into bulky floccules that can be settled (Golob et al., 2005).

Flotation

This method was proved to be a useful and effective separation method of metal-loaded biomass following biosorption, producing over 95% removal efficiencies (Mavrov et al., 2003). The critical parameters considered in this method are solution pH and ionic strength of metals.

2.3.2 Chemical methods and processes

Chemical precipitation

In this method, metal ions are precipitated by adding coagulants, such as alum, lime, and other organic polymers. Main disadvantage of this method is that it generates large quantity of sludge which contains heavy metal (Kurniawan et al., 2006). Aluminum chloride, calcium hydroxide (known as lime) and ferric chloride are the most widely used inorganic coagulants in chemical precipitation (Tchobanoglous and Burton, 2003). The chemical precipitation process is followed by settling of the metal precipitates in a pond and/or a clarifier. The broadly-applied precipitation technique is hydroxide treatment owing to its low cost, relative simplicity, and ease of automatic pH control. The disadvantages of this method are it increase the total dissolved solids

amount of the wastewater sample, and generation of large quantity of sludge, which may contain toxic compounds that is difficult to be treated (Matlock et al.,2002).

Hydroxide precipitation

This is one of the widely used methods and method involves the precipitation of hydroxides of heavy metals using lime or sodium hydroxide (Khraisheh et al., 2004). Due to the low cost and ease of pH controlling, lime is used for precipitation purposes. Lime remained in the solution serves as an adsorbent for the removal of heavy metal ions. The removal efficiency of metals depends on pH of the solution, oxidation state, hydrolysis capacity of the metal ion, standing time, presence of complex-forming ions, degree of agitation and settling filtering characteristics of the precipitate (Chen, 2004). The main disadvantage of this method is that optimum pH for metal hydroxide formation may lead to problems in effluent treatment of containing multi-metal ions.

Carbonate precipitation

Metal ions are precipitated in the form of carbonates using calcium or sodium carbonate. Heavy metals, such as lead, nickel, and cadmium in the form of form insoluble carbonates, which can be used in carbonate precipitation. Alternatively, inorganic carbonates such as sodium carbonate can be added to achieve the carbonate precipitation. Free carbonate ions are present only under alkali pH conditions and therefore sodium hydroxide (caustic) is often added to increase the pH of the solution. However, main disadvantage of this method is that there is a possibility of metal hydroxide precipitation along with carbonate precipitation since high pH also promotes the precipitation of metals as hydroxides.

Sulfide precipitation

Normally, most of the heavy metals form stable sulfide precipitates. Sulfide precipitation is mostly used in the refining step after metal hydroxide precipitation or when higher removal rates are required for multi-metal systems (Kaksonen et al., 2003). Since metal sulfides are highly insoluble in aqueous media, heavy metals can be precipitated by adding sulfide ions (S^{2-}). Due to the low solubility of metal sulfides, lower residual metal concentrations are normally allowed in the treated wastewater (Kaksonen et al., 2003).

Chemical reduction

Chemical reduction/oxidation (Redox) reactions convert hazardous contaminants/heavy metals into non-hazardous or less toxic compounds, which are more stable, inert, and less mobile. Key process of this method is the transfer of electrons from one compound to another compound and consequently, one reactant is oxidized and the other is reduced (Kurniawan et al., 2006). The commonly used oxidizing agents to remove heavy metals are chlorine, ozone, hydrogen peroxide, and chlorine dioxide (Fu and Wang, 2011). Incomplete oxidation and formation of intermediate contaminants usually limits the applicability and effectiveness of chemical reduction process, and this method is cost-intensive when applied for wastewaters with high contaminant concentrations and oil and grease (Monser and Adhoum, 2002).

Xanthate process

The biosorbents with sulfur-bearing groups such as sulfides, xanthates, thiols, dithiocarbamates and dithiophosphates have a high affinity towards heavy metals. Due to the low cost, ease of preparation and higher insolubility xanthates containing biosorbents are the most widely used in heavy metal removal (Bailey et al., 1999). Heavy metal removal by xanthate takes place by an ion-exchange reaction which is alike to hydroxide precipitation. However, xanthates are decomposed with time subjected to and therefore, the removal capacity of xanthate also decreased with time.

Solvent extraction

Solvent extraction is a combination of separation, purification, and recovery processes. In this method selected heavy metal species is transported from one aqueous solution to another solution using an organic solution containing a special reagent (extractant) where metals are separated, purified, and recovered (Yun et al., 1993). This method is commonly used to extract heavy metals, such as copper, uranium, cobalt, nickel and rare earth metals from aqueous solutions or ores.

Electrodeposition

Electrodeposition process involves the deposition of one metal upon another metal and this method is widely applied in electroplating industries. Electroplating is achieved by passing an electrical current through a solution containing dissolved metal ions and the metal objects which need to be plated (Sciban et al., 2007).

2.3.3 Biological methods

During the recent years, different technologies have been developed to address the challenges in heavy metal removal from water and wastewater. As a major step of the related researches biological techniques have been developed in addition to the conventional removal processes. Recently identified two main biological treatment techniques for removing heavy metals from aqueous solution were phytoremediation and bio-filtration (Murugesan et al., 2009). To remove heavy metals from sewage, biological processes are used together with physical and chemical treatment processes. Microorganisms have the ability to bind heavy metals actively through extracellular precipitation, intracellular accumulation and chemical transformations catalyzed by these microorganisms, such as oxidation, reduction, methylation and demethylation. (Tobin et al., 1990).

Phytoremediation

This technique uses plants and rhizospheric microorganisms associated with plants to remove heavy metals not only from water and wastewater but also contaminated soils, sludge, sediment (Padmavathiamma and Li, 2009). This method also remediates various other contaminants such as petroleum hydrocarbons, pesticides, solvents, polycyclic aromatic hydrocarbons, and landfill leachate. Phytoremediation uses living plants for in situ and ex situ remediation of contaminated sites and it can also be used for point and nonpoint source hazardous waste control (Padmavathiamma and Li, 2009). Main advantages of phytoremediation are its cost- effectiveness and long-term applicability (Jabeen et al., 2009).

Micro remediation

Micro-remediation is a type of biosorption and its major advantages over conventional metal removal techniques are low cost, higher efficiency, no requirement for additional nutrients, regeneration of biosorbent with the possibility of metal recovery and low sludge production (McHale and McHale, 1994). This process includes two phases as solid phase (sorbent or biosorbent; usually a biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be adsorbed (sorbate, a metal ion). In the process of attraction and binding of metal on the sorbent involve several mechanisms and the process is continued until equilibrium is attained (Romera et al., 2008).

Table 2.1: Comparison of different heavy metal removal techniques from an aqueous solution

Technique	Advantages	Disadvantages
Chemical precipitation	<ul style="list-style-type: none"> • Simple • Cost-effective at most times • Most of the metals can be removed 	<ul style="list-style-type: none"> • Large quantities of sludge are produced • High chemical requirement • Sludge disposal problem
Chemical coagulation	<ul style="list-style-type: none"> • Sludge settling 	<ul style="list-style-type: none"> • High cost
	<ul style="list-style-type: none"> • Dewatering 	<ul style="list-style-type: none"> • Higher chemical consumption
Ion exchange	<ul style="list-style-type: none"> • High regeneration of materials • Metal selective 	<ul style="list-style-type: none"> • High cost • Less amount of metal ions is removed
Membrane process and ultrafiltration	<ul style="list-style-type: none"> • Less solid waste produced • Less chemical consumption • High efficiency 	<ul style="list-style-type: none"> • High initial and running cost • Low flow rate • Removal decreases with the presence of other ions
Electrochemical methods	<ul style="list-style-type: none"> • Metal selective • No consumption of chemicals • Pure metals can be extracted 	<ul style="list-style-type: none"> • High capital cost and running cost
Coagulation and flocculation	<ul style="list-style-type: none"> • Applicable to large scale WWTP 	<ul style="list-style-type: none"> • High capital cost • Production of sludge in large quantities • Sludge disposal problems
Adsorption	<ul style="list-style-type: none"> • High effective in removing heavy metals to permissible levels 	<ul style="list-style-type: none"> • Chemical regeneration requirement • Loss of adsorption capacity by the adsorbent at each cycle • High cost

Source: (T. S. Anirudhan, 2012)

2.4 Biosorption and biosorbents

2.4.1 Introduction

Basically, sorption process involves the binding of a substance to another substance and retained in it and this encompasses both absorption and adsorption processes, while desorption is the reverse process. Adsorption is a surface phenomenon in which molecules or atoms of one phase (solid, liquid or gas) are accumulated on the other phase. The material getting adsorbed is known as the adsorbate and the material on which adsorbate is adsorbed is known as the adsorbent (Areco et al., 2012). There are two phenomena in the absorption process though they are not related. In the first phenomenon ions, atoms, or molecules enter into bulk phase-gas, liquid or solid material, and in the second phenomenon the energy of a photon is taken up by another entity, for instance, by an atom whose valence electrons make the transition between two electronic energy levels. Adsorption may also be defined as the adhesion of ions, atoms, biomolecules or molecules of gas, liquid, or dissolved solids to a adsorbent surface and a film of the adsorbate is created on the surface of the adsorbent by the adsorption process (Wang and Chen, 2006b). The adsorption process is different from absorption hence in the absorption process, a fluid permeates to a liquid or is dissolved by solid.

2.4.2 Bio sorbents

A material having the capacity to absorb other substances is identified as an adsorbent and adsorbents with biological are known as biosorbents. Major sorption processes are adsorption, ion exchange, and chromatography and in all these techniques certain adsorbates are selectively transferred from one phase to another phase. Some types of biosorbents would be a broad range, binding and collecting most heavy metals with no specific activity, while others are specific for certain metals. Biosorbent capacity of certain microorganisms towards metal ions is dependent on the chemical structure and composition of the microbial cell and these biosorbents consists of dead and metabolically inactive cells (Friis and Myers-Keith, 1986).

Recent experiments on biosorption have largely been focused on removal of contaminants from waste materials generated as by-products from large-scale industrial operations. For example, the waste mycelia available from fermentation processes, olive mill solid residues (Pagnanelli et al., 2002), activated sludge from sewage

treatment plants (Zouboulis et al., 1997), biosolids (Norton et al., 2004), aquatic macrophytes (Keskinan et al., 2004). The mechanism of biosorption mainly includes ion exchange, adsorption by physical forces, chelation, entrapment in inter and intra-fibrillar capillaries and spaces of the structural polysaccharide network as a result of the concentration gradient and diffusion through cell walls and membranes (Argun et al., 2005; Kara, 2009; Ozer et al., 2004). Chemical groups that attract and sequester the heavy metals from biomass are amino and phosphate groups in nucleic acids, acetamido groups of chitin, sulfhydryl and carboxyl groups in proteins, structural polysaccharides of fungi, amino, amido and mainly carboxyls and sulphates in polysaccharides of marine (Caramalau et al., 2009; Jeon and Park, 2005).

2.4.3 Significance of biosorbents in water treatment

Biosorption can be defined as the ability of biological materials to sequester heavy metals from aqueous solutions through metabolically mediated pathways or physio-chemical pathways of uptake (Mahvi, 2008). Microorganisms, such as bacteria, fungi, algae and yeasts have been tested for their biosorbent capability and proven to be efficient metal (Volesky and Holan, 1995c). The major advantages of biosorption technologies over conventional wastewater treatment methods include:

- High efficiency
- Low cost
- Regeneration of biosorbents
- Minimization of chemical and biological sludge
- No additional nutrient requirement
- Possibility of metal recovery (Plazinski and Rudzinski, 2010)

As discussed in the above section biosorption process involves a solid phase/ biological material and a liquid phase/ solvent containing a dissolved species to be adsorbed (sorbates, metal ions). Owing to the higher affinity of the sorbent for the sorbates species, the sorbate is attracted and bound to the sorbent, by different mechanisms and this process continues until equilibrium is established between the amount of solid-bound sorbates species and its portion remaining in the solution (Igwe et al., 2008; Volesky and Holan, 1995b).

2.4.4 Advantages and disadvantages of biosorption

Practical applications of biosorption technology are of paramount importance in industry and environmental protection. To use biosorbents for metal removal from water and wastewater has some profound advantages over conventional methods of metal removal. Both physical and chemical metal removal techniques are cost-intensive and yet not much feasible in reducing their concentrations to the levels that are not harmful to the environment. Therefore, biosorption technique has been identified as a promising alternative method to wastewater, due to its low cost and high metal binding capacity (Igwe et al., 2008). Until now, researches in biosorption suggests it an ideal alternative for decontamination of metal-containing effluents and solutions. Advantages and disadvantages of biosorption by non-living biomass are as follows (Mosavi et al., 2010; Mouni et al., 2010; Munagapati et al., 2010; Nadeem et al., 2010):

Advantages

- Expensive nutrients that are required for cell growth in feed solution are not required in this method. Therefore, disposal of surplus nutrients or metabolic products does not have adverse impacts on environment.
- Biomass can be procured from the existing fermentation industries, which is available as a waste after fermentation.
- Non-living biomass is growth-independent and therefore not subjected to toxicity limitation of cells.
- Since the cells are non-living, processing conditions are not restricted to those conducive for the cell growth.
- Non-living biomass usually behaves as an ion exchanger and the process is very rapid. Metal loading on biomass is often very high, leading to very efficient metal uptake.
- The biosorption process is not regulated by the physiological constraint of living microbial cells.
- No aseptic conditions are required in biosorption process.

Disadvantages

- Since biomass cells are not metabolizing, potential for biological process improvement is limited. Production of the adsorptive agent occurs during pre-

growth and therefore, characteristics of the biosorbents cannot be biologically controlled.

- Early saturation causes problems specially when metal interactive sites are occupied, metal desorption is necessary before further use, irrespective of the metal value.
- No potential for altering the metal valency state biologically.

2.4.5 Characteristics of biosorbents

There are several key characteristics that control the adsorption ability of adsorbents. These are the physicochemical characteristics of adsorbents materials such as specific surface area, pore- volume, ash content, particle sizes, pH, charge/polarity, and surface functional groups.

Specific surface area

The solid adsorbents are often characterized by their specific surface area (a_s) and pore size distribution (A_s). The value of A_s refers to unit mass (m) of adsorbent (Tóth 1971):

$$a_s = \frac{A_s}{m}$$

The pore size distribution relates to the size and number of pores present in the solid adsorbent and there are three main types of pores as macropores, mesopores and micropores. Macropores are having widths exceeding 50 nm while mesopores are having widths between 2 nm and 50 nm and micropores are having widths not exceeding about 2 nm (Tóth, 2000). A large specific surface area provides large adsorption capacity but having large internal surface area in a relatively small volume inevitably leads to large numbers of small sized pores between adsorption surfaces. The accessibility of adsorbate molecules to the internal adsorption surface depends on the size of the micropores and pore size of the micropores can be considered as an important property for that determines the absorptivity of adsorbents.

Pore volume

The pore volume and its distribution in the adsorbents are the important properties of an adsorbent. Pore volume distributions can be determined by either gas adsorption porosimetry (typically N₂, Ar or CO₂) or mercury intrusion porosimetry. Gas porosimetry measures pores from 3.5⁰A to about 4000⁰A in diameter while mercury porosimetry measures pores from 30⁰A up to 900 μ m in diameter. The pore size range is from 200 to 800⁰A in diameter is defined as micropores and from 20 to 90⁰A in diameter is defined as mesopores.

Ash content

Ash content is also an important property of an adsorbent which has significant impact on adsorption, and it is different for different minerals and their derivatives (Jianqiu et al., 2010; Zhong et al., 2012).

Particle size

Surface area of a particle depends on its particle size and increase in particle size usually decreases metal adsorption capacity of the adsorbent while the increase in pore size increases the metal adsorption capacity (Kumar et al., 2010). For a given mass of an adsorbent the removal efficiency and sorption capacity increases with the decrease of the particle size because when more surface area is available the number of sites also increases (Ho et al., 2002b).

pH

Adsorption capacities of adsorbents are strongly dependent on initial solution pH and it also affects the magnitude of negative charge on adsorbents surface (Abate and Masini, 2005; Ho et al., 1994). The adsorption capacity of an adsorbent increases with increasing pH in solution. In acidic medium low adsorption capacities are observed for metal ions because of the strongly competing hydrogen ions with adsorbate for negatively charged sites on the adsorbent. When solution pH increases, the hydrogen ion concentration of the solution is decreased thereby reducing the competition for binding sites in adsorbent.

Surface Charge/polarity

Surface polarity corresponds to affinity with polar substances such as water or alcohols. Polar adsorbents such as porous alumina, zeolites, silica gel and aluminosilicates are called “hydrophilic” adsorbents and nonpolar adsorbents such as polymer adsorbents, carbonaceous adsorbents and silicates are generally called “hydrophobic” adsorbents. These non-polar adsorbents have more affinity with oil or hydrocarbons than water (Ho et al., 2002d; Marczewski, 2007).

Surface functional groups

There are several functional groups in the adsorbents which are categorized as surface oxygenated groups or nonoxygenated groups. Major surface oxygen functional groups for biosorbents are carbonyl groups, lactone, and phenolic groups (Arpa et al., 2000; Boota et al., 2009). Since adsorption is a surface phenomenon, the rate of adsorption and extent of adsorption are highly dependent on the specific surface area of the adsorbent used. For example, the amount of adsorption per unit weight of fly ash depends on its composition, porosity, and texture (Kara et al., 2007).

2.4.6 Mechanism of metal biosorption

There are two main phases in the biosorption processes as the solid phase (sorbent or biosorbents: biological material) and the liquid phase (solvent: normally water) which contains a dissolved species to be adsorbed (sorbate: metal ions). The sorbate and sorbent are attracted and bound to each other by different mechanisms and the process continues until equilibrium is reached between the amount of solid bound sorbate species and sorbate amount remaining in the solution. The distribution of sorbate between the solid and liquid phases is determined by the degree of sorbent affinity for the sorbates. Main mechanisms that are involved in the adsorption process are physisorption, chemisorption and biosorption.

Physisorption

Physisorption which is also known as physical sorption is a type of adsorption, in which the adsorption adheres to the surface only through weak intermolecular interactions known as Van der Waal forces (Ren et al., 2008). In physisorption, adsorption takes place in multilayer and process requires low activation energy and the energy state of

adsorbate is not altered. Therefore, this process has low enthalpy and low ambient temperature and also it is a reversible process (Chakravarty et al., 2010). In physisorption process even a small change is visible in the electronic states of adsorbent and adsorbate and the chemical nature of the liquid may not be changed by adsorption and subsequent desorption as the adsorbed species are chemically identical with those in the liquid phase.

Chemisorption

Chemisorption or chemical adsorption is a type of adsorption where a molecule adheres to a surface through the formation of a chemical bond, as opposed to the Van der Waals forces which cause physisorption and therefore strength of the interaction is stronger than pure physical adsorption. In contrast to the physisorption, chemisorption is characterized by high temperatures and high enthalpy (Volesky, 1999b). In chemisorption, adsorption takes place only in a monolayer and the process is characterized by high activation energy.

Biosorption

Biosorption is defined as the removal of metals or metalloid species, metallic compounds and particulates from an aqueous solution by the materials with biological origin (Volesky, 1999b). Biosorption process has a significant application in the area of wastewater treatment, especially since conventional physical and chemical techniques of removing soluble metals are generally expensive when the contaminant concentrations are higher (Vieira and Volesky, 2010).

Biosorption mechanism

Depending on living and nonliving status of the biomass there are two types of bindings that can occur in biologically derived materials as passive binding and active binding (Drake and Rayson, 1996). Passive binding occurs in both living and nonliving cells and it involves rapid and reversible ion exchange with cell surface (Lin and Rayson, 1998). Active binding is characterized by a much slower, irreversible, metal uptake in living cells, because of metabolic activity and this process is often termed as bioaccumulation (Martinez-Garcia et al., 2006). The metal-binding mechanisms postulated are as follows:

i. Ion exchange

Recent researches have revealed some indications that ion exchange plays an important role in metal sorption by algal biomass. For marine algae, the active functional groups such as carboxyl groups of alginic acid and the carboxyl and sulfate groups of fucoidan are responsible for ions exchange (Davis et al., 2003).

ii. Physical adsorption

This is the adsorption technique mediated by the help of van der Waals' forces. It is reported that copper, zinc, cadmium, cobalt, and uranium sorption by biomasses of algae, fungi and yeasts take place through electrostatic interactions between the metal ions in solutions and cell walls of microbial cells (Rowell and Yaghi, 2006).

iii. Transport across cell membrane

The heavy metal's ions can cross the microbial cell membranes along with the metabolically important ions such as potassium, magnesium, and sodium. The toxic metals' ions which are having the same charge and ionic radius associated with essential ions may confuse the bacterial metabolism system and it is not associated with the metabolic activity (Stein, 1986).

iv. Complexation

In the heavy metal removal process, complexes are formed between the active groups of cell surface and metal ions and this is called complexation (Treen-Sears et al., 1984). It is reported that biosorption of Cu occurs through both adsorption and formation of coordination bonds between metals and amino and carboxyl groups of cell wall polysaccharides by *C. vulgaris* and *Z. ramigera* (Kapoor and Viraraghavan, 1995). Also researches findings state that cadmium, calcium, zinc, magnesium, mercury, and copper accumulation by *Pseudomonas syringae* occurs by the mechanism of complexation. Metallo-organic molecules are formed by the chelating of the toxic metal with the organic molecules.

v. Precipitation

Precipitation is either occurred by the action of cellular metabolism or independently. When precipitation occurred through cellular metabolism, the

active defense system of the microorganisms produces compounds to resist the toxic metals and these compounds help the precipitation process and subsequently, metal is removed (Chen et al., 2000; Schneider et al., 2001). When precipitation occur independently, the metal is removed as a result of chemical interaction between the metal and the cell surface (Öztürk et al., 2004). The favorable temperature for biosorption process is 20-35°C (Kaewsarn, 2002). pH of the solution affects the solubility of the metals, the activity of the functional groups in the biomass. Moreover, precipitation process is affected by the presence of multi ions in the aqueous medium and biomass load in the system. Scarcity of metal concentration in an aqueous system may lead to a decrease in metal uptake (Fourest and Roux 1992).

2.4.7 Factors affecting biosorption

The adsorption process is a complex phenomenon and the sorption performance is depending on the number of binding sites, which is related to the chemical composition of the chosen biosorbent (Vieira and Volesky, 2010). The efficiency or metal adsorption capacity depends on the following factors: (i) Nature of adsorbate (ii) Nature of adsorbent (iii) Specific area of the adsorbent (iv) pH (v) Pressure (vi) Temperature (vii) Activation of the adsorbent (viii) Enthalpy of adsorption (ix) contact time.

i. Nature of adsorbate

The physiochemical natures of adsorbates have significant impact on both adsorption capacity and rate of the adsorption. Since physical adsorption is non-specific in nature, every metal is adsorbed on the surface of any solid in varying extents (Çetinkaya Dönmez et al., 1999). Easily ionized materials are adsorbed to a greater extent whereas low ionized materials are adsorbed to a lesser extent and pH is the regulating factor for ionization (Davis et al., 2003).

ii. Nature of biosorbent

Physisorption does not depend on the nature of adsorbent but chemisorption depends on the nature of both adsorbent and adsorbate (Naiya et al., 2009). For example, iron, nickel, and platinum readily adsorb the hydrogen while silica gel adsorbs moisture and tungsten adsorbs oxygen. Most used biosorbents are activated carbon, silica gel, metal oxides, alumina and clay and each of this biosorbent has its own

characteristics and functional groups.

iii. Specific area of the adsorbent

Specific area is the surface area available for adsorption per 1 gram of adsorbent and the amount of adsorption largely depends on the surface area of the solid. The higher the surface area the higher the biosorption capacity (Vilar et al., 2007b). Hence, porous or powder form of the adsorbent have higher adsorption capacity than the block of a same material (Pierotti and Rouquerol, 1985).

iv. pH of water

The solubility of adsorbates and the activation of binding sites greatly depend on pH of the solution. In general, adsorption of a typical organic pollutant from water is increased with decreasing pH. Metal adsorption is highly depending on the nature of the species solution. For example, at lower pH, H⁺ competes with metal ions for exchange sites and thereby partially releasing the metal ions. At lower pH, more protons are available which decrease the electrostatic attraction between cationic adsorbate and positively charged sites of the adsorbent and therefore heavy metals are completely released under extreme acidic conditions (Annadurai et al., 2003).

v. Pressure

With the increase of pressure *s* in the adsorption system, the temperature is also increased, and the activity of adsorption may increase (Kratochvil et al., 1995). At a given temperature amount of metals adsorbed are initially increased with the increasing pressure and in both physisorption and chemisorption processes (Zu et al., 2006). At high pressure, the amount of metal adsorbed reach to a constant level (Volesky, 1999a).

vi. Temperature

Temperature excites the metals and binding sites of adsorbents (Özer and Özer, 2003) and researches have shown that physisorption process is rapid at low temperatures, whereas chemisorption is quite fast at high temperatures. In general, both chemical and physical adsorption decrease with increasing temperature since both processes are exothermic (Gereli et al., 2006).

vii. Activation of the adsorbent

The adsorption process solely depends on the activation of the outer surface of

adsorbents and adsorbates and this is done by some activation agents. Normally some acidic or alkaline solution or salt are used as activation agents. Once activation agent is added to the solution, the ionizing strength and pH of the system changes and either adsorbent or adsorbate or both become activated and then the rate of adsorption capacity increases leading to ultimate increase of adsorption capacity (Aksu, 2001).

viii. Enthalpy of adsorption.

Temperature directly affects the adsorption process and usually in high temperatures pore sizes are changed and rate of intra-particle diffusion is enhanced. Therefore, metal adsorption capacity is increased with the increasing temperature (Benhammou et al., 2005). The positive enthalpy values for metal adsorption indicate endothermic nature of the process while negative enthalpy exothermic reactions. With the increasing temperature, free energy change of the process is decreased, indicating that the process is spontaneous, and spontaneity also increases with an increasing temperature.

ix. Co-ions

The presence of other ions which are known as co-ions can affect the sorption of metal ions through the mechanism called competitive adsorption (Mishra et al., 1998). In general, wastewater contain different heavy metals and competition among the co-ions is a common phenomenon. This interaction among co-ions can be synergistic, antagonistic, or non-interactive, but the behavior cannot be predicted based on single metal studies (Ting and Teo, 1994; Tsezos et al., 1996).

x. Initial metal concentration

When the binding sites of adsorbent material are not saturated, the initial concentration of the metal ion concentration tend to be higher and therefore the metal uptake is also higher (Reddad et al., 2002). However, increase in the amount of the available metal ions results in decrease of fraction of metal-bound (Blanco et al., 1999). The relationship between variable initial metal concentrations and adsorption capacity, at a fixed temperature and fixed biomass concentration, is represented by sorption isotherms (Çolak et al., 2011; Feng et al., 2011).

xi. Biomass concentration

With the increasing biomass concentration, the amount of metal-bound per biomass is decreased (L Vidhya, 2018). At an optimum pH level, the increase of biomass concentration causes a diminution of the maximum specific metal adsorption due to cell aggregation phenomena. However, at acidic pH values increasing biomass concentration may lead to decrease of the amount of metal-bound per biomass due to the partial hydrolysis of the bacterial cell wall constituents.

xii. Contact time

Binding of metal ions to aquatic particulates is a fast-chemical reaction, and its equilibrium time only depends on the mass transfer resistance (Waite et al., 1994). To establish an appropriate contact time between the biosorbents and metallic ions solution, adsorption capacities of metal ion need to be measured as a function of time. In metal adsorption process removal rate higher at the beginning and gradually decreases with time. Main reason for this would be the larger surface area of the biosorbents that are being available at the beginning of the adsorption process.

Table 2.2: Some commonly used biosorbents and their adsorption capabilities

Type of biosorbent	Adsorbate	Biosorption capacity/efficiency (mg/g or %)	Isotherm model	Mechanism
Tea industry waste	Cr (VI)	54.65 mg/g	Langmuir	-
Sugar industry waste (bagasse)	Cd (II), Fe (II)	96.4%, 93.8%	-	-
Peach and apricot stones	Pb (II)	97.64%, 93%	Langmuir	-
Antibiotic waste	Cationic dye (Basic blue 41)	111 mg/g	Freundlich	Ion exchange or complexation
Sludge	Ni (II), Cu (II), Pb (II), Cd (II)	13.7, 13.9, 14.1, 14.8 mg/g	Freundlich	Ion exchange and physio-chemical adsorption
Waste green sands	Zn (II)	10.0 mg/g	-	-
Fly ash	Pb	22 mg/g	-	Precipitation

Source: (Sri Lakshmi Ramya Krishna Kanamarlapudi, 2017)

2.4.8 Use of and pith fiber as biosorbents

As reported in the literature coir waste has a high lignin (30-31%) and cellulose (26.8%) content and its carbon-nitrogen ratio is 112:1. Lignin is a complex amorphous polymer which surrounds the cellulose in cell. Lignin is relatively inert to hydrolysis and owing to the high lignin content, and coir waste takes long time to decompose because of its lignocellulose bonds. Coir pith has a calorific value of 3,975 kcal per kg close to 4,200 kcal per kg of coal and hence it can be used as fuel briquette and also in tobacco flue curing, pig iron manufacture, gas absorbent cotton, etc. Coir pith has a high water-holding capacity as of 8 times of its weight and it also contain low Sulphur content, fixed carbon level, fats, and ash. Nutrient content of coir pith varies depending on the location available, rate of decomposition, and storage method. Coir pith has excellent moisture retention even after drying, high porosity and has the ability to stores and releases nutrients over extended periods of time. In addition, coir pith has greater physical resiliency that withstands compression and excellent aeration/oxygenation providing enhanced root penetration.

Table 2.3: Characteristics of coir pith

Parameter	Unit	Value
Lignin	%	29.6
Holocellulose	%	42.3
Bulk Density	g/cc	0.097
Particle Density	g/cc	0.985
Pore space volume	%	88.5
Particle size	µm	344

Adsorption theory and mechanism of heavy metal adsorption into coir pith

The irregular and porous structures on surface of adsorbent play a significant role in adsorption process. The functional group is one of the key factors influencing the mechanism of metal binding process on natural adsorbents. The shifts in the wavelength showed that there was a metal-binding process taking place at the surface of the CCP. Coir pith is having a high percentage composition of lignin (29.6%) and holocellulose (42.3%) which are responsible for its physical stability causing poor biodegradability. Lignin and cellulose are biopolymers bearing multiple phenolic,

carboxyl, hydroxyl and amino groups which are responsible for the removal of pollutants from wastewater. The low bulk densities and high pore space volumes of coir pith are favorable for the process of adsorption.

Coir pith is used as an alternative to commonly available physical, chemical and bio-adsorbents for heavy metal ion removal from aqueous solutions. Researches have revealed that coir pith is an effective adsorbent for Pb, and Cd removal and removal efficiency is mainly affected by dose of the adsorbent, metal ion concentration, and pH of the solution (Amarasinghe, 2011). Also activated carbon (AC) derived from waste coconut buttons (CB) was proven to be a suitable adsorbent for the removal of heavy metal ions such as Pb (II), Hg(II) and Cu (II) from industrial effluents through the batch adsorption process (Anirudhan and Sreekumari, 2011).

The adsorbent has good adsorption potential for Pb (II) and Cu (II) at pH 6.0 and for Hg (II) at pH 7.0. Besides, biochar obtained from the pyrolysis process has found to be a highly effective biosorbent for the removal of Chromium (VI) from an aqueous solution (Vidhya et al., 2018).

Methodology

3.1 Coir pith sample preparation

Raw coir dust and processed coir pith were directly obtained from a production plant, where coir pith is manufactured for commercial purposes. Coir dust is generated as a waste in the coir fiber manufacturing process and can be easily obtained. Processed coir pith is a product coming out from this manufacturing process. Prior to the sample preparation both coir dust and coir pith were ground to obtain homogenized mixture and sieved to remove large and alien particles. No further treatment was conducted for all the raw coir dust and processed coir pith samples as the objective was to test the possibility of direct application of these materials for heavy metal adsorption. Aqueous solutions with heavy metals were prepared by taking 200 mL of standard stock samples.

3.2 Aqueous heavy metal solutions preparation for ICP-OES experiments

Multicomponent heavy metal adsorption using the prepared raw coir dust and processed coir pith samples were tested using the Inductively Coupled Plasma- Optical Emission Spectrometry (ICP-OES) technique. Aqueous solutions with known concentrations of multicomponent heavy metals obtained by using the standard stock samples. Standard stock solutions were prepared to obtain the aqueous solutions containing specific metal ions, which are to be treated with the raw coir dust and processed coir pith samples. Initially, standard solutions with 1,000 $\mu\text{g/mL}$ concentration of each metal ions were prepared and then diluted aqueous samples are prepared with required concentrations. Specifications of the used reagents and standard samples are as follows.

- Reagent-grade solutions
 - Reagent water - must be interference free
 - Hydrochloric acid (concentrated), HCl
 - Hydrochloric acid (50% [v/v]), HCl
 - Hydrochloric acid (5% [v/v]), HCl
 - Nitric acid (concentrated), HNO_3
 - Nitric acid (50% [v/v]), HNO_3
 - Hydrofluoric acid (concentrated), HF

- Standard stock solutions
 - Arsenic standard stock solution (1000 µg/mL As)
 - Cadmium standard stock solution (1000 µg/mL Cd)
 - Chromium standard stock solution (1000 µg/mL Cr)
 - Copper standard stock solution (1000 µg/mL Cu)
 - Lead standard stock solution (1000 µg/mL Pb)
 - Manganese standard stock solution (1000 µg/mL Mn)
 - Nickel standard stock solution (1000 µg/mL Ni)
 - Zinc standard stock solution (1000 µg/mL Zn)
 - Working-level standard solutions and blanks

The following reagents and standards were used for microwave acid digestion of raw coir dust and processed coir pith samples before ICP-OES experiments.

- Concentrated nitric acid (HNO₃)
- Concentrated hydrochloric acid (HCl)
- Reagent water

3.3 Experimental procedure

Multicomponent batch adsorption tests were conducted to determine the removal efficiencies of all eight metals, i.e., Arsenic, Cadmium, Chromium, Copper, Manganese, Nickel, Lead and Zinc using both raw coir dust and processed coir pith samples. Both coir pith and coir dust samples were initially prepared using the Microwave-Assisted Acid Digestion Method and then their initial heavy metal concentrations were measured using Inductively Coupled Plasma- Optical Emission Spectrometry (ICP OES) method.

Eight aqueous solutions were prepared for each heavy metal to be tested and initial heavy metal concentrations were measured using the ICP-OES method. Five portions were obtained from each heavy metal solution, and volumes of all five samples were kept equal to test the adsorption efficiencies of different quantities of coir samples. To these five aqueous solutions, 1g, 2g, 3g, 4g and 5g of coir pith were added, respectively, and kept for 2 hours. Same procedure was repeated for coir dust samples as well. After 2 hours, samples were filtered using qualitative filter papers and each liquid filtrate was tested for all 08 heavy metal concentrations using the ICP-OES method. All these

analyses were conducted at room temperature (30 °C). In order to test the adsorption efficiency coir pith at different contact times, two portions with same volumes were obtained from each heavy metal solution and to each sample 2g of coir pith was added. One sample was let stand for 30 minutes while the other sample was let stand for 4 hours. Same procedure was repeated for coir dust sample as well. After respective contact times, each sample was filtered using qualitative filters paper and heavy metal concentration of all eight metals were measure from each liquid filtrate using the ICP-OES method. All these analyses were conducted at room temperature (30 °C).

In order to test the adsorption efficiency coir pith at different temperatures, two portions with same volumes were obtained from each heavy metal solution and to each sample 2g of coir pith was added. One sample was kept in 50 °C for 2 hours while the other sample was kept at 70 °C for the same contact time. Same procedure was repeated for coir dust samples as well. After 2 hours, each sample was filtered using qualitative filters paper and concentrations of all heavy metals were measured in each filtrate using the ICP-OES method.

Inductively Coupled Plasma- Optical Emission Spectrometry-Method 6010D

Instrument was calibrated using typical mixed-calibration standard solutions and calibration curves for each heavy metal was prepared. Samples of raw coir pith, raw coir dust and aqueous solutions were analyzed for their heavy metal concentration.

For all the concentration values obtained removal efficiencies were calculated as follows.

$$\text{Removal efficiency} = \frac{A - B}{A} \%$$

Where,

A: Heavy metal concentration in standard aqueous solution

B: Heavy metal concentration in the filtered sample

Then graphs were drawn between removal efficiencies and dosage of adsorbent to find the liquid/ solid ration at optimum removal efficiency.

For all the coir pith and coir dust samples solid(metal-mg)/ solid (adsorbent-g) ratios were calculated according to the following calculation steps.

Concentration of the standard metal solution = x ppm = X mg/L

Amount of heavy metal in the 50 ml of standard metal solution = $(X \text{ mg} / 1000 \text{ ml}) * 50 \text{ ml}$

$$= 0.05X \text{ mg}$$

Heavy metal concentration in the filtrate = Y

Amount of heavy metal in the 50 ml of the filtrate = $(Y \text{ mg} / 1000 \text{ ml}) * 50 \text{ ml}$

$$= 0.05Y \text{ mg}$$

Amount of the heavy metal adsorbed = $0.05(X - Y)$

Solid(metal-mg)/ solid (adsorbent-g) ratios = $0.05(X - Y) / \text{weight of the adsorbent}$

Results and Discussion

Heavy metal concentrations (in ppm) for coir pith samples at different dosages and their respective removal efficiency percentages are presented in Table 4.1. According to the analytical results, removal efficiencies for Arsenic, Cadmium, Chromium, Copper, Nickel and Lead gradually increase with the dosage of the adsorbent. But removal efficiencies for Manganese and Zinc are zero and results show that concentrations of Mn and Zn have increased after adsorbent has been added.

Heavy metal concentrations (in ppm) for raw coir dust samples at different dosages and their respective removal efficiency percentages are presented in Table 4.2. According to the analytical results, removal efficiencies for Cadmium, Chromium, Nickel and Lead are gradually increasing with the dosage of the adsorbent. Removal efficiencies for Arsenic, Manganese, and Copper also show some increasing trend with the increase of adsorbent dosage but the pattern is not gradual.

Heavy metal concentrations (in ppm) for raw coir pith samples at two different temperatures and their respective removal efficiency percentages are presented in Table 4.3. According to the analytical results except for Manganese and Zinc, all other heavy metals show considerably high removal efficiencies in both temperatures.

Heavy metal concentrations (in ppm) for raw coir pith samples at two different contact times and their respective removal efficiency percentages are presented in Table 4.4. According to the analytical results except for Manganese and Zinc, all other heavy metals show considerably high removal efficiencies at both contact times.

Table 4.1: Heavy metal concentrations (in ppm) for coir pith samples at different dosages and their respective removal efficiency percentages for 2 hours

Sample ID	As (188.980 nm)		Cd (214.439 nm)		Cr (267.716 nm)		Cu (327.395 nm)		Mn (257.610 nm)		Ni (231.604 nm)		Pb (220.353 nm)		Zn (213.857 nm)	
	Conc (ppm)	Removal %	Conc (ppm)	Removal %	Conc (ppm)	Removal %	Conc (ppm)	Removal %	Conc (ppm)	Removal %	Conc (ppm)	Removal %	Conc (ppm)	Removal %	Conc (ppm)	Removal %
Standard aqueous solution	1.0355	-	1.0150	-	1.0506	-	1.0372	-	1.0361	-	1.0422	-	0.9878	-	1.0404	-
C1	0.9720	6.13%	0.9447	6.93%	0.9631	8.33%	0.9837	5.16%	1.0400	0	0.9445	9.37%	0.8968	9.21%	1.2903	0
C2	0.9426	8.97%	0.9224	9.12%	0.9424	10.30%	0.9754	5.96%	1.1006	0	0.9180	11.92%	0.8694	11.99%	1.3365	0
C3	0.9176	11.39%	0.8865	12.66%	0.9095	13.43%	0.9712	6.36%	1.1551	0	0.8924	14.37%	0.8317	15.80%	1.4440	0
C4	0.8997	13.11%	0.8723	14.06%	0.8954	14.77%	0.9389	9.48%	1.1717	0	0.8660	16.91%	0.8211	16.88%	1.5486	0
C5	0.8683	16.15%	0.8428	16.97%	0.8644	17.72%	0.9125	12.02%	1.2268	0	0.8365	19.74%	0.7860	20.43%	1.5460	0

C1- Filtrate obtained from the sample with 1 g of coir pith
 C2- Filtrate obtained from the sample with 2 g of coir pith
 C3- Filtrate obtained from the sample with 3 g of coir pith

C4- Filtrate obtained from the sample with 4 g of coir pith
 C5- Filtrate obtained from the sample with 5 g of coir pith

Table 4.2: Heavy metal concentrations (in ppm) for coir dust samples at different dosages and their respective removal efficiency percentages for 2 hours

Sample ID	As (188.980 nm)		Cd (214.439 nm)		Cr (267.716 nm)		Cu (327.395 nm)		Mn (257.610 nm)		Ni (231.604 nm)		Pb (220.353 nm)		Zn (213.857 nm)	
	Conc (ppm)	Removal %	Conc (ppm)	Removal %	Conc (ppm)	Removal %	Conc (ppm)	Removal %	Conc (ppm)	Removal %	Conc (ppm)	Removal %	Conc (ppm)	Removal %	Conc (ppm)	Removal %
Standard aqueous solution	1.0355	-	1.0150	-	1.0506	-	1.0372	-	1.0361	-	1.0422	-	0.9878	-	1.0404	-
R1	0.9047	12.63%	0.8432	16.93%	0.8961	14.71%	0.9914	4.42%	0.9425	9.03%	0.8513	18.32%	0.7875	20.28%	1.1467	0
R2	0.8897	14.08%	0.8391	17.33%	0.8895	15.33%	0.9837	5.16%	0.9716	6.23%	0.8443	18.99%	0.7852	20.51%	1.2071	0
R3	0.9001	13.08%	0.8342	17.81%	0.8914	15.15%	0.9797	5.54%	0.9523	8.09%	0.8407	19.33%	0.7761	21.43%	1.1998	0
R4	0.8526	17.66%	0.7991	21.27%	0.8520	18.90%	0.9681	6.66%	0.9028	12.87%	0.8168	21.63%	0.7479	24.29%	2.1123	0
R5	0.9332	9.88%	0.8829	13.01%	0.9235	12.10%	0.9832	5.21%	1.0946	0	0.8857	15.02%	0.8341	15.56%	1.2907	0

R1- Filtrate obtained from the sample with 1 g of coir dust
R2- Filtrate obtained from the sample with 2 g of coir dust
R3- Filtrate obtained from the sample with 3 g of coir dust

R4- Filtrate obtained from the sample with 4 g of coir dust
R5- Filtrate obtained from the sample with 5 g of coir dust

Table 4.3: Heavy metal concentrations (in ppm) for raw coir pith samples at two different temperatures and their respective removal efficiency percentages

Sample ID	As (188.980 nm)		Cd (214.439 nm)		Cr (267.716 nm)		Cu (327.395 nm)		Mn (257.610 nm)		Ni (231.604 nm)		Pb (220.353 nm)		Zn (213.857 nm)	
	Conc (ppm)	Removal %	Conc (ppm)	Removal %	Conc (ppm)	Removal %	Conc (ppm)	Removal %	Conc (ppm)	Removal %	Conc (ppm)	Removal %	Conc (ppm)	Removal %	Conc (ppm)	Removal %
Standard aqueous solution	1.0355	-	1.0150	-	1.0506	-	1.0372	-	1.0361	-	1.0422	-	0.9878	-	1.0404	-
T1	0.9557	7.71%	0.9571	5.70%	0.9010	14.24%	0.8811	15.05%	1.0488	0	0.9152	12.19%	0.9225	6.61%	1.4070	0
T2	0.9724	6.09%	0.9756	3.88%	0.9013	14.21%	0.8772	15.43%	1.0649	0	0.9444	9.38%	0.9504	3.79%	1.3399	0

T1- Filtrate obtained from the sample with 2 g of coir pith kept at 50°C

T2- Filtrate obtained from the sample with 2 g of coir pith kept at 70°C

Table 4.4: Heavy metal concentrations (in ppm) for raw coir pith samples at two different contact times and their respective removal efficiency percentages

Sample ID	As (188.980 nm)		Cd (214.439 nm)		Cr (267.716 nm)		Cu (327.395 nm)		Mn (257.610 nm)		Ni (231.604 nm)		Pb (220.353 nm)		Zn (213.857 nm)	
	Conc (ppm)	Removal %	Conc (ppm)	Removal %	Conc (ppm)	Removal %	Conc (ppm)	Removal %	Conc (ppm)	Removal %	Conc (ppm)	Removal %	Conc (ppm)	Removal %	Conc (ppm)	Removal %
Standard aqueous solution	1.0355	-	1.0150	-	1.0506	-	1.0372	-	1.0361	-	1.0422	-	0.9878	-	1.0404	-
D1	0.8866	14.38%	0.9070	10.64%	0.8542	18.69%	0.8159	21.34%	0.9696	6.42%	0.8528	18.17%	0.7280	26.30%	4.1011	0
D2	0.9544	7.83%	0.9629	5.13%	0.9082	13.55%	0.8699	16.13%	1.0653	0	0.9596	7.93%	0.8182	17.17%	1.4074	0

D1- Filtrate obtained from the sample with 2 g of coir pith kept for 30 minutes

D2- Filtrate obtained from the sample with 2 g of coir pith kept for 4 hours

Table 4.5: Ratio between amount of adsorbed heavy metal (mg) and amount of the adsorbent (g) for each heavy metal for coir pith at room temperature for 2 hours contact time

Weight of the adsorbent	As mg per 1 mg of adsorbent	Cd mg per 1 mg of adsorbent	Cr mg per 1 mg of adsorbent	Cu mg per 1 mg of adsorbent	Mn mg per 1 mg of adsorbent	Ni mg per 1 mg of adsorbent	Pb mg per 1 mg of adsorbent	Zn mg per 1 mg of adsorbent
Coir pith								
1g	0.0486	0.0472	0.0482	0.0492	0.0520	0.0472	0.0448	0.0645
2g	0.0236	0.0231	0.0236	0.0244	0.0275	0.0230	0.0217	0.0334
3g	0.0153	0.0148	0.0152	0.0162	0.0193	0.0149	0.0139	0.0241
4g	0.0112	0.0109	0.0112	0.0117	0.0146	0.0108	0.0103	0.0194
5g	0.0087	0.0084	0.0086	0.0091	0.0123	0.0084	0.0079	0.0155
Average	0.02148	0.02088	0.02136	0.02212	0.02514	0.02086	0.01972	0.03138
Total	0.1074	0.1044	0.1068	0.1106	0.1257	0.1043	0.0986	0.1569
Coir dust								
1g	0.0467	0.0441	0.0462	0.0492	0.0547	0.0443	0.0417	0.0645
2g	0.0226	0.0211	0.0224	0.0248	0.0236	0.0213	0.0197	0.0287
3g	0.0148	0.0140	0.0148	0.0164	0.0162	0.0141	0.0131	0.0201
4g	0.0113	0.0104	0.0111	0.0122	0.0119	0.0105	0.0097	0.0150
5g	0.0085	0.0080	0.0085	0.0097	0.0090	0.0082	0.0075	0.0211
Average	0.02078	0.01952	0.0206	0.02246	0.02308	0.01968	0.01834	0.02988
Total	0.1039	0.0976	0.103	0.1123	0.1154	0.0984	0.0917	0.1494

Figure 4.1 to Figure 4.7 show the graphs drawn between dose of the adsorbent (g) and removal efficiencies of metals (%).

Removal efficiency of Arsenic by coir pith and coir dust

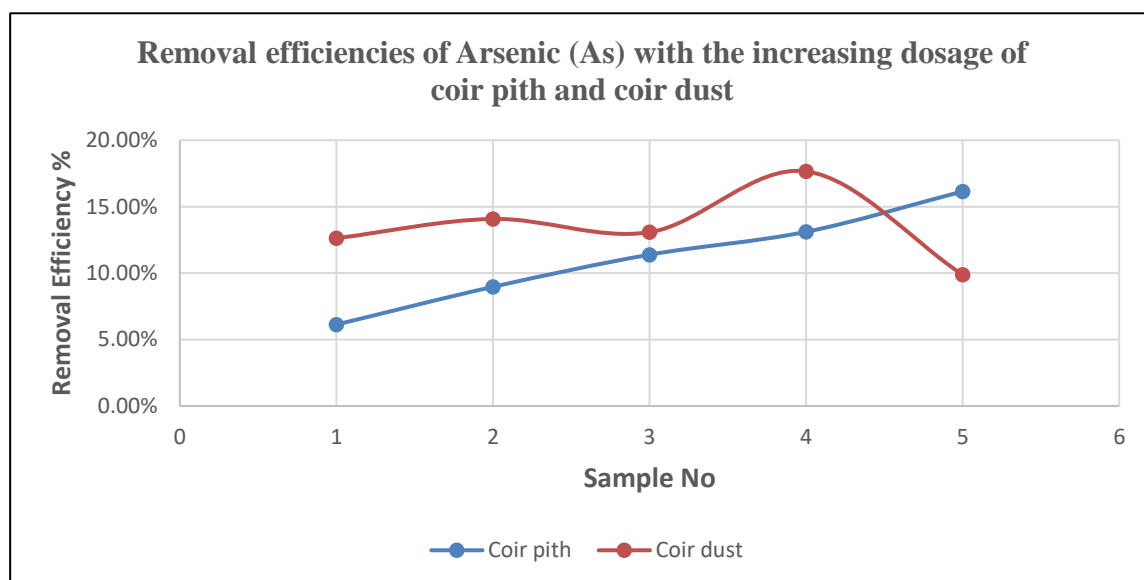


Figure 4.1: Graph between removal efficiencies of As with the increasing dosage of raw coir dust and processed coir pith

When considering the graph of removal efficiency vs coir pith dosage for Arsenic, removal efficiency is increased gradually with the increasing dose of bio sorbent and maximum efficiency was obtained at the maximum dose of coir pith, which is 5 g. But when coir dust was tested for its adsorbing capacity for Arsenic results shows that there is a clear fluctuation of As removal capacity with increasing coir dust dose. Coir dust is having the highest metal removal efficiency with the highest dose used, 4g. Therefore, optimum solid/liquid ratio of Arsenic adsorption for coir pith is 0.1g/ml (5 g/50 ml) and 0.08 g/ml for coir dust at room temperature for 2 hours of contact period. As content in the raw coir pith sample and raw coir dust sample was also tested in this study and test values were 1.8476 ppm and 1.6119 ppm respectively. Main reason for these values could be the presence of As in the adsorbent as well. Since the adsorbent already contains As, efficiency of adsorbing more As into both coir pith and coir dust could be low and could result in low removal percentages.

Removal efficiency of Cadmium by coir pith and coir dust

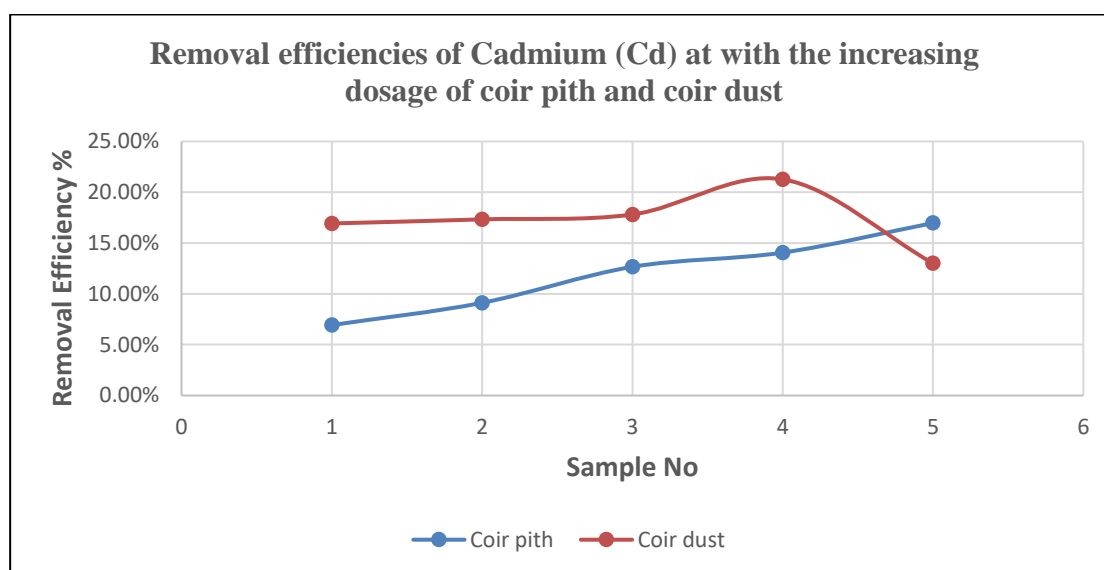


Figure 4.2: Graph between removal efficiencies of Cd with the increasing dosage of raw coir dust and processed coir pith

For Cd removal, coir pith has shown increasing removal efficiencies with increasing adsorbent dosage and relatively clear trend was observed. Maximum removal efficiency for Cd from coir pith was recorded at 5 g of the adsorbent and therefore more suitable solid/liquid ratio for Cd removal is 0.1 g/ml at room temperature for 2 hours of contact period. But removal efficiencies for coir dust show clear fluctuation in values and maximum removal was recorded at 4g where optimum solid/liquid ratio for Cd for coir dust is 0.08 g/ml at room temperature for 2 hours contact period. Cd concentration in raw coir pith sample is 0.0992 ppm and that of coir dust sample is 0.0789 ppm which are quite low values.

Removal efficiency of Chromium by coir pith and coir dust

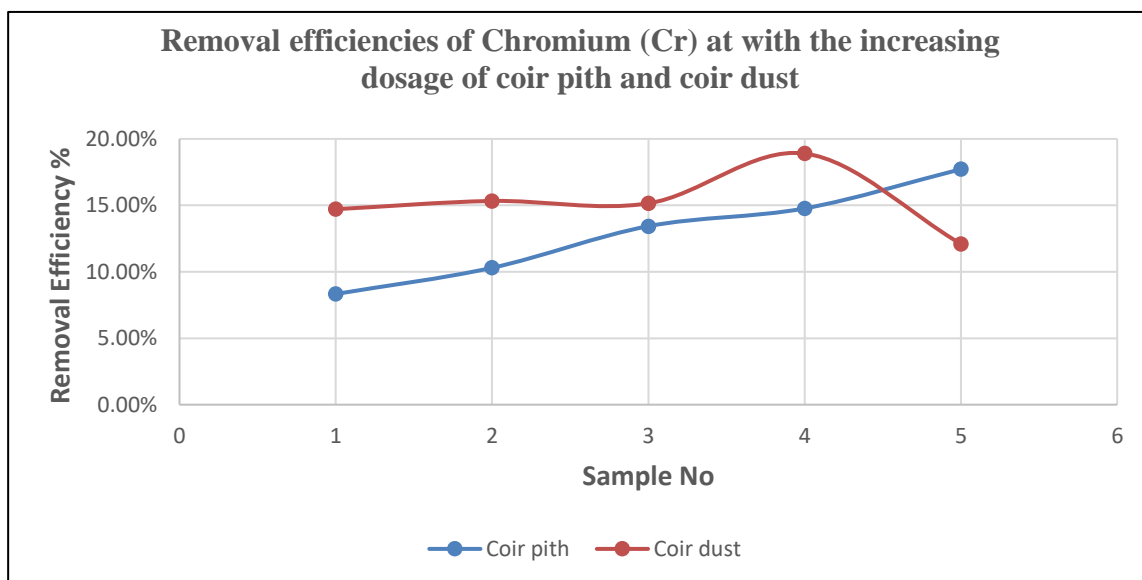


Figure 4.3: Graph between removal efficiencies of Cr with the increasing dosage of raw coir dust and processed coir pith

According to the analytical results, coir pith shows increasing removal efficiencies with increasing adsorbent dosage for Chromium adsorption while removal efficiency for coir dust increases up to 4g and then start to decrease. Maximum removal efficiencies for coir pith was recorded at 5g while the value for coir dust is 4g. Therefore, optimum solid/liquid ratio for coir dust is 0.1 g/ml and 0.08 g/ml for coir dust respectively at room temperature for 2 hours contact period. Cr concentration in raw coir pith sample is 0.9541ppm and that of coir dust sample is 0.8428 ppm which are relatively low values.

Removal efficiency of Copper by coir pith and coir dust

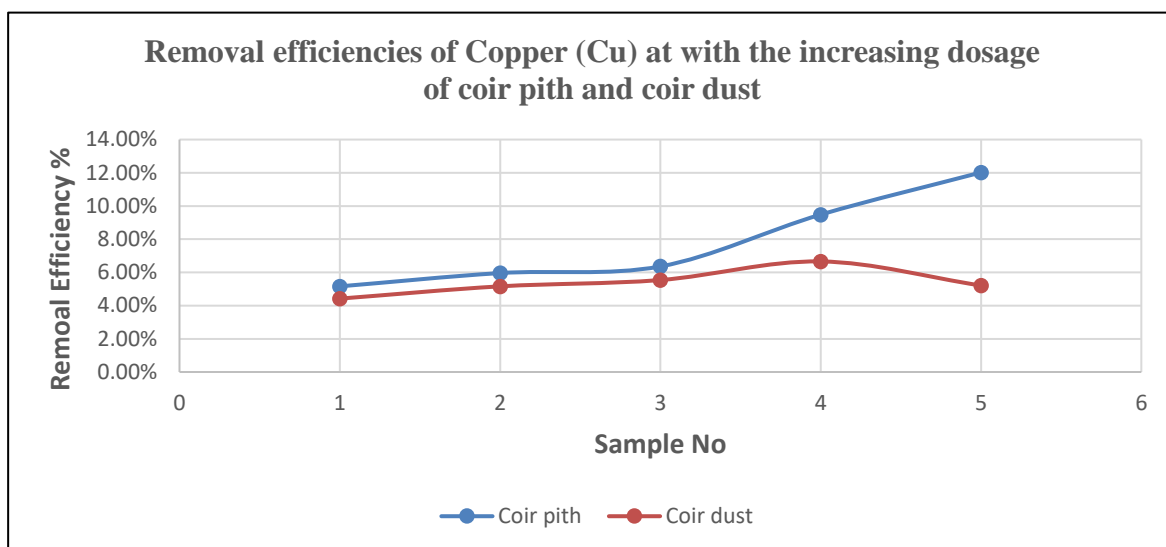


Figure 4.4: Graph between removal efficiencies of Cu with the increasing dosage of raw coir dust and processed coir pith

When considering removal efficiencies of coir pith for Copper, it has increased gradually with the increasing dose of biosorbent and maximum efficiency was obtained at the maximum dose of coir pith, which is 5 g. But when coir dust was tested for its adsorbing capacity for Cu results shows that there is a clear fluctuation of Cu removal capacity with increasing coir dust dose. Coir dust is having the highest metal removal efficiency with 4g of dose. Therefore, optimum solid/liquid ratio for coir pith and coir dust are 0.1g/ml (5 g/50 ml) and 0.08 g/ml (4g/50ml) respectively at room temperature for 2 hours of contact period. Cu content in the raw coir pith sample and raw coir dust sample was also tested in this study and test values were 1.5338 ppm and 2.3244 ppm respectively and which are significantly high values and this may be the reason for their low Cu adsorption capacities.

Removal efficiency of Nickel by coir pith and coir dust

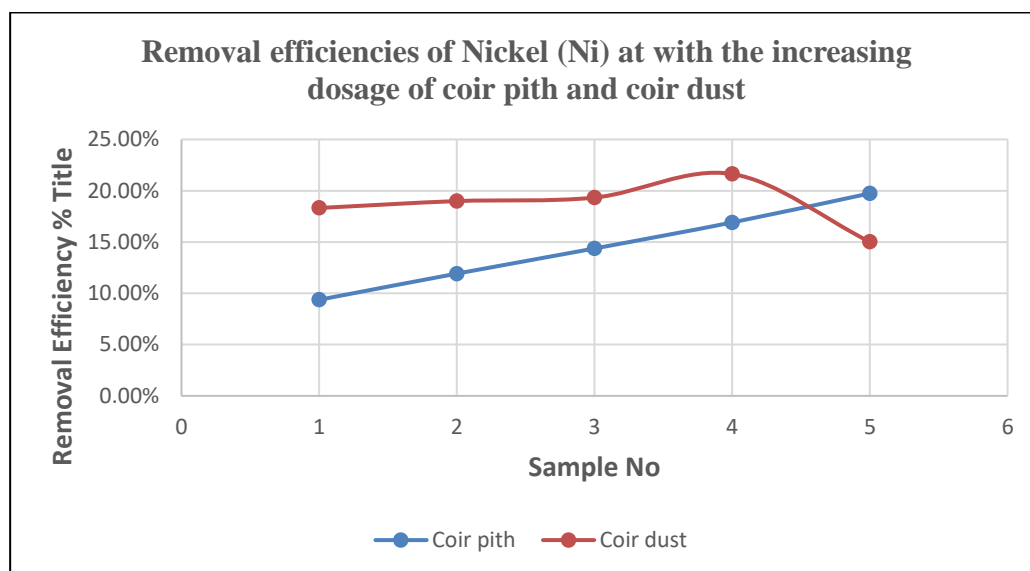


Figure 4.5: Graph between removal efficiencies of Ni with the increasing dosage of raw coir dust and processed coir pith

When considering removal efficiencies of coir pith for Nickel, it has increased gradually with the increasing dose of biosorbent and maximum efficiency was obtained at the maximum dose of coir pith, which is 5 g. But when coir dust was tested for its adsorbing capacity for Ni results shows that there is a clear fluctuation of Ni removal capacity with increasing coir dust dose. Coir dust is having the highest metal removal efficiency with 4g of dose. Therefore, optimum solid/liquid ratio for coir pith and coir dust are 0.1g/ml (5 g/50 ml) and 0.08 g/ml (4g/50ml) respectively at room temperature for 2 hours of contact period. Ni concentration in raw coir pith sample is 1.5965 ppm and that of coir dust sample is 1.1283 ppm which are quite higher values.

Removal efficiency of Lead by coir pith and coir dust

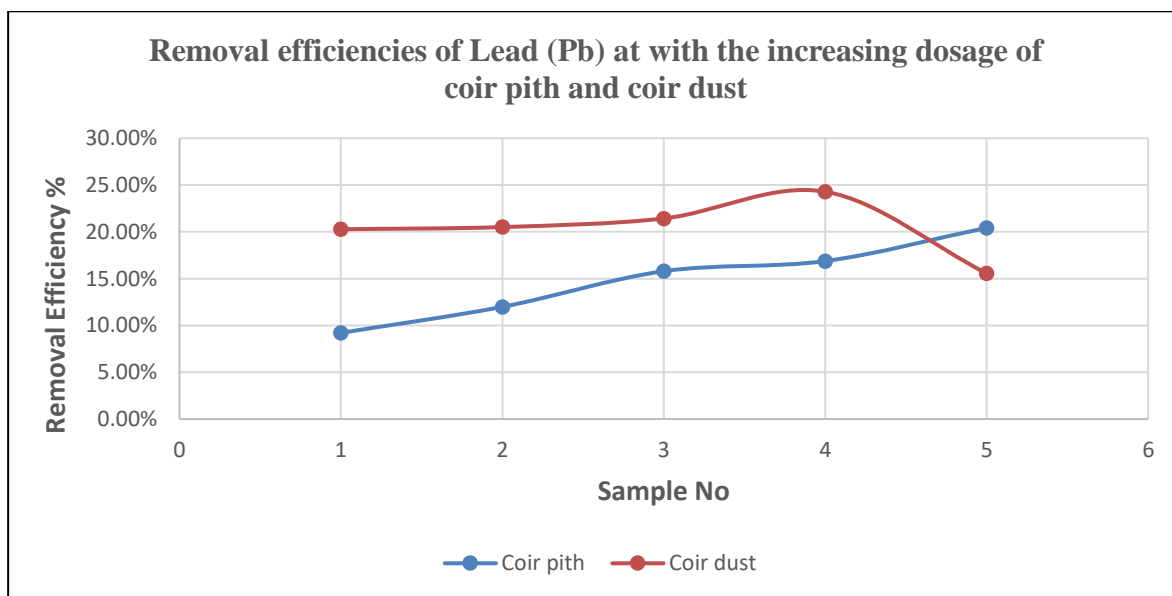


Figure 4.6: Graph between removal efficiencies of Pb with the increasing dosage of raw coir dust and processed coir pith

For Pb removal, coir pith has shown increasing removal efficiencies with increasing adsorbent dosage relatively clear trend was observed and maximum removal efficiency was recorded at 5 g of the adsorbent and therefore optimum solid/liquid ratio for Pd removal is 0.1 g/ml at room temperature for 2 hours of contact period. But for coir dust Pb adsorption efficiency is increasing gradually up to 4g of dose and then start to decrease. Therefore, optimum solid/liquid ratio is 0.08 g/ml at room temperature for 2 hours of contact period. Pb concentration in raw coir pith sample is 1.6302 ppm and that of coir dust sample is 1.2747 ppm which are quite low values.

Removal efficiency of Manganese by coir pith and coir dust

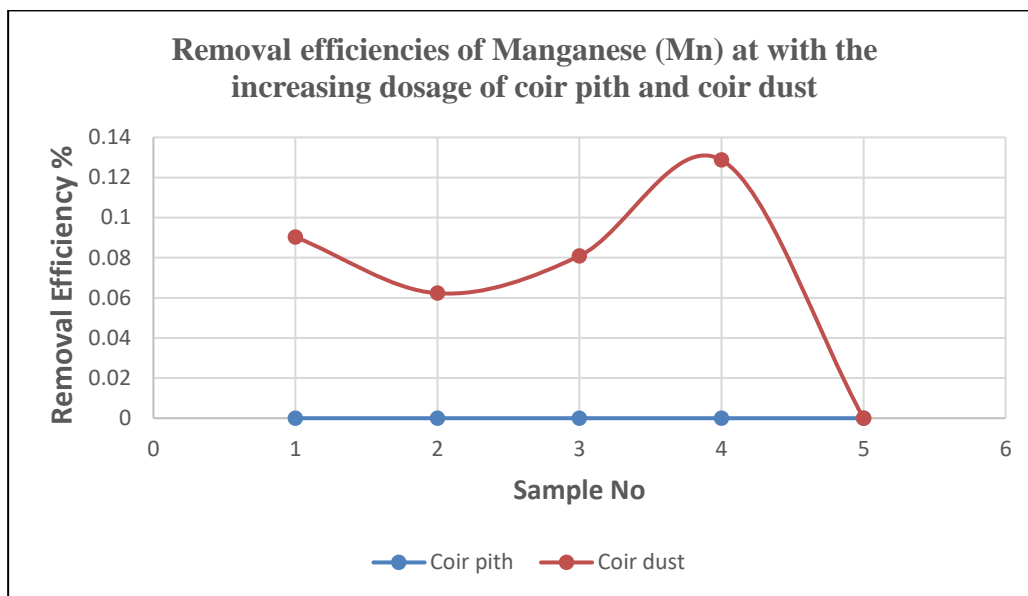


Figure 4.7: Graph between removal efficiencies of Mn with the increasing dosage of raw coir dust and processed coir pith

All the filtered samples for Mn that used coir pith as biosorbent have shown elevated levels of Mn concentration than the initial standard metal solution and therefore coir pith cannot be used as biosorbent to remove Mn from aqueous solutions. However, with coir dust as the biosorbent removal efficiencies have been increased with increasing coir dust dosage up to 4g and then at 5g of coir dust dosage removal efficiency is 0. Therefore, optimum Mn removal efficiency by coir dust is achieved at 0.08g/ml solid/liquid ratio at room temperature for 2 hours contact period. Initial Mn concentrations of coir pith and coir dust samples are 6.5859 ppm and 4.8421 ppm and higher Mn content in coir pith could be the reason for elevated Mn levels in filtered samples.

Both coir pith and coir dust were showed elevated levels of Zn after adding to the initial standard samples and therefore both biosorbents showed 0 removal efficiencies at all dosages. So, coir pith and coir dust cannot be used as biosorbents to remove Zn from Aqueous solutions.

Figure 4.8 to Figure 4.13 show the graphs of heavy removal efficiencies by 2 g of coir pith with temperature variation.

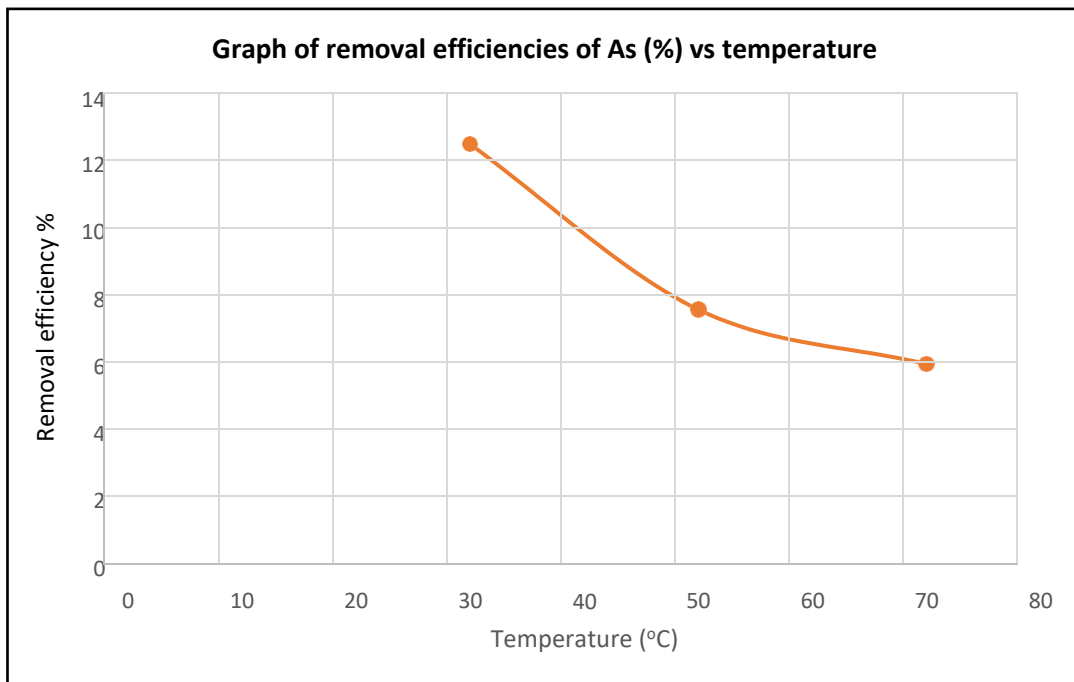


Figure 4.8: Graph between removal efficiencies of coir pith for As and temperature

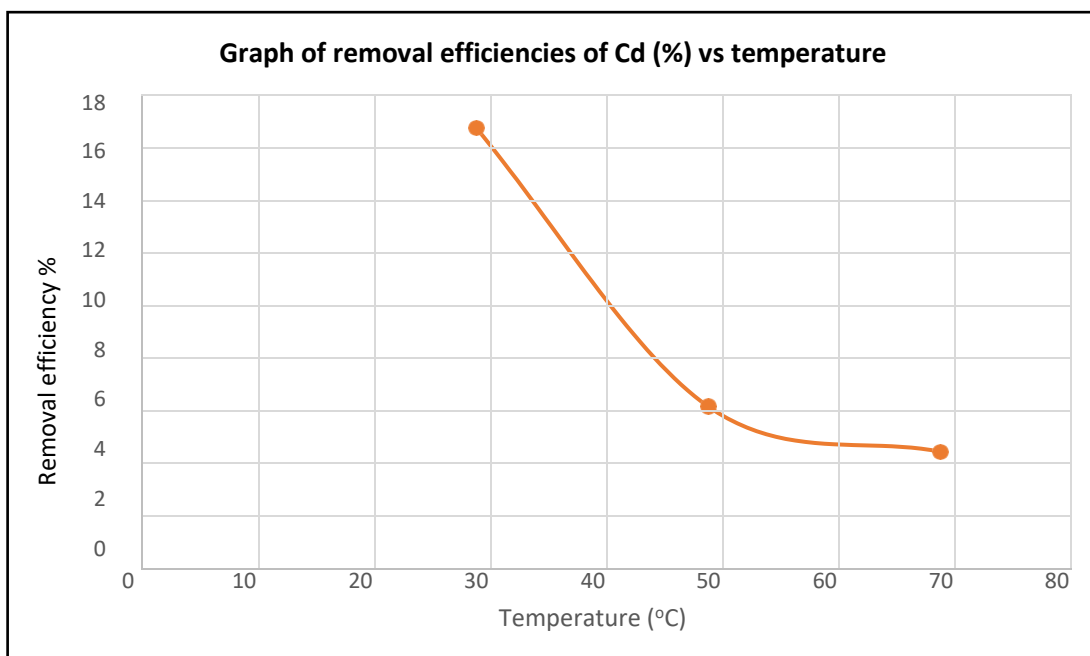


Figure 4.9: Graph between removal efficiencies of coir pith for Cd and temperature

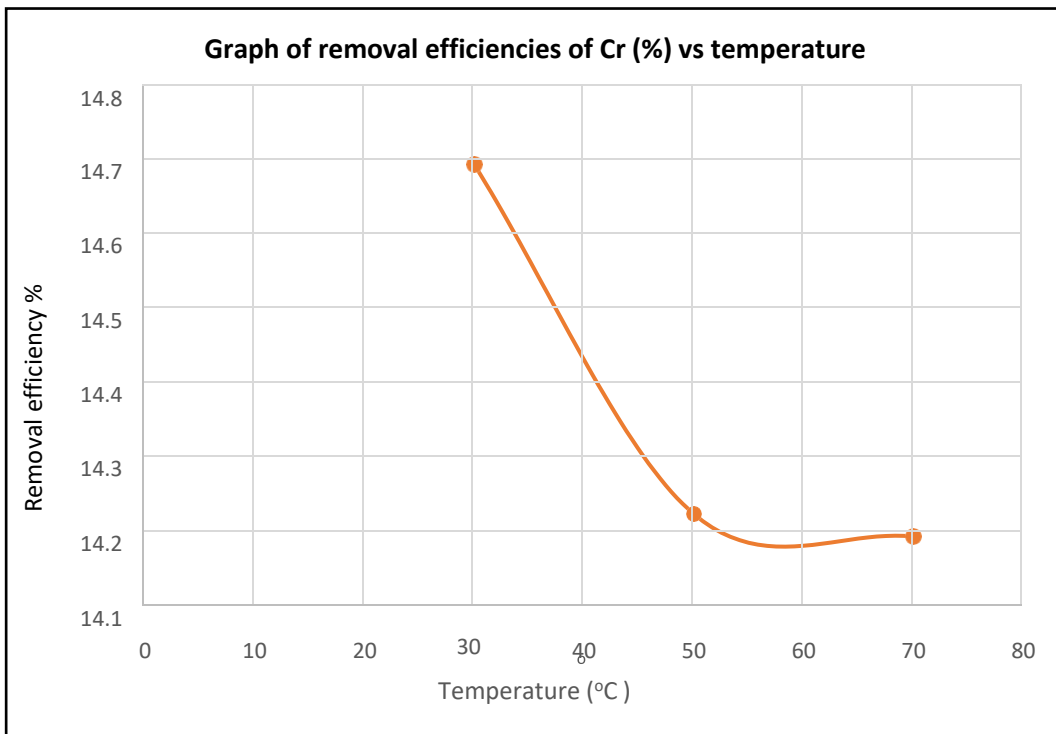


Figure 4.10: Graph between removal efficiencies of coir pith for Cr and temperature

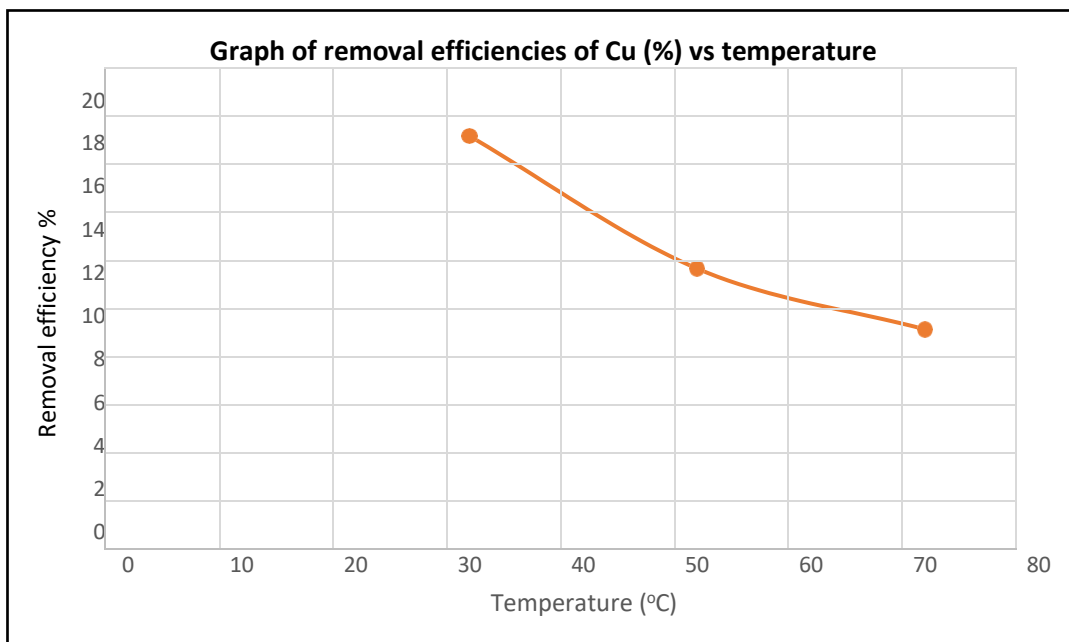


Figure 4.11: Graph between removal efficiencies of coir pith for Cu and temperature

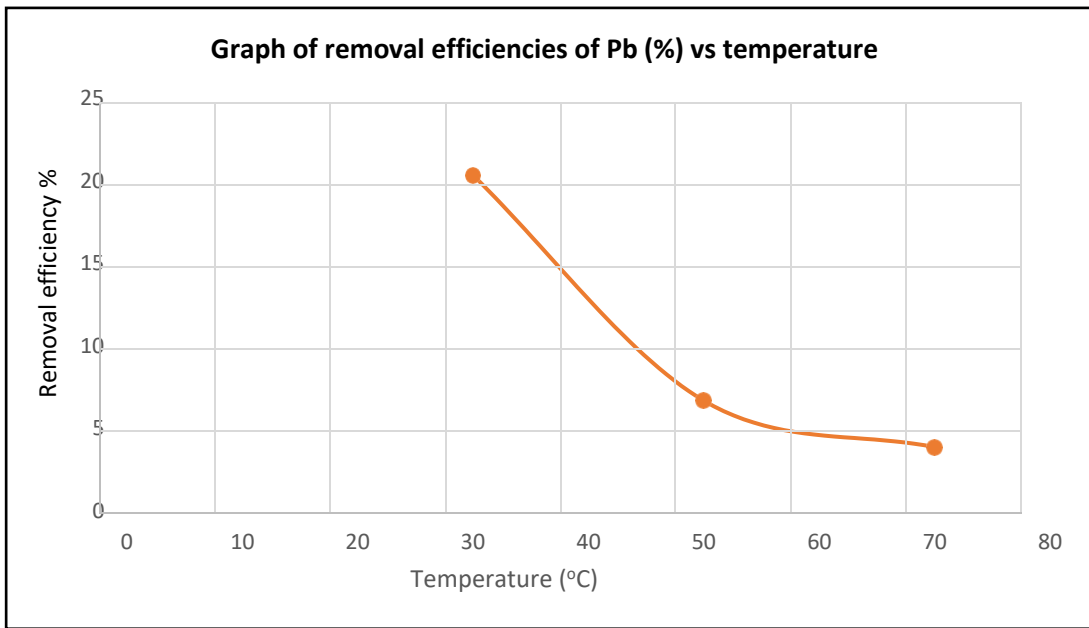


Figure 4.12: Graph between removal efficiencies of coir pith for Ni and temperature

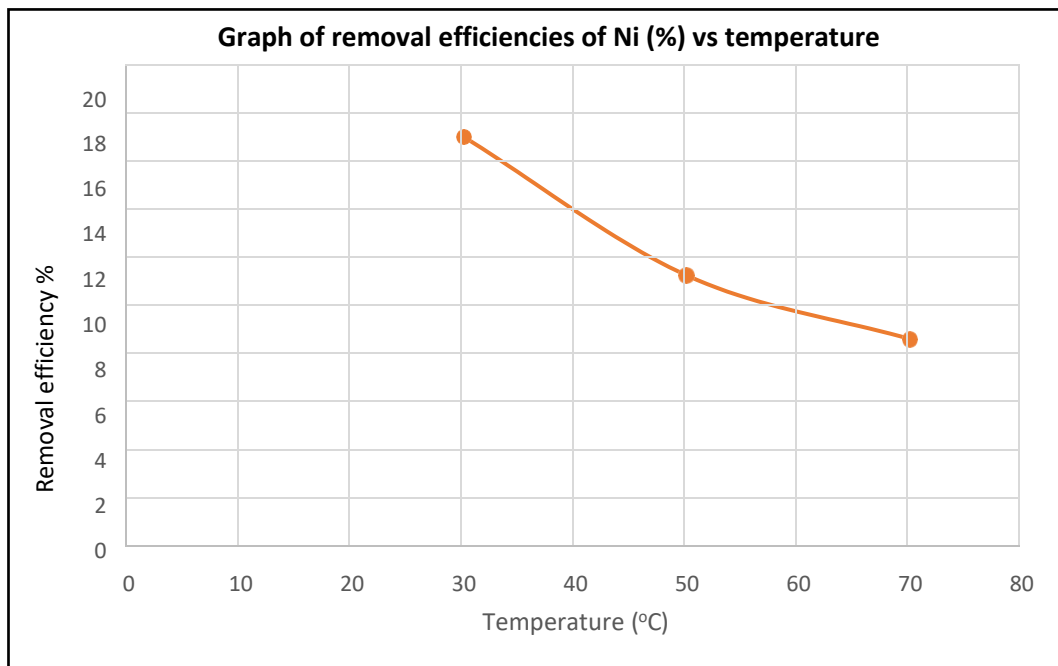


Figure 4.13: Graph between removal efficiencies of coir pith for Ni and temperature

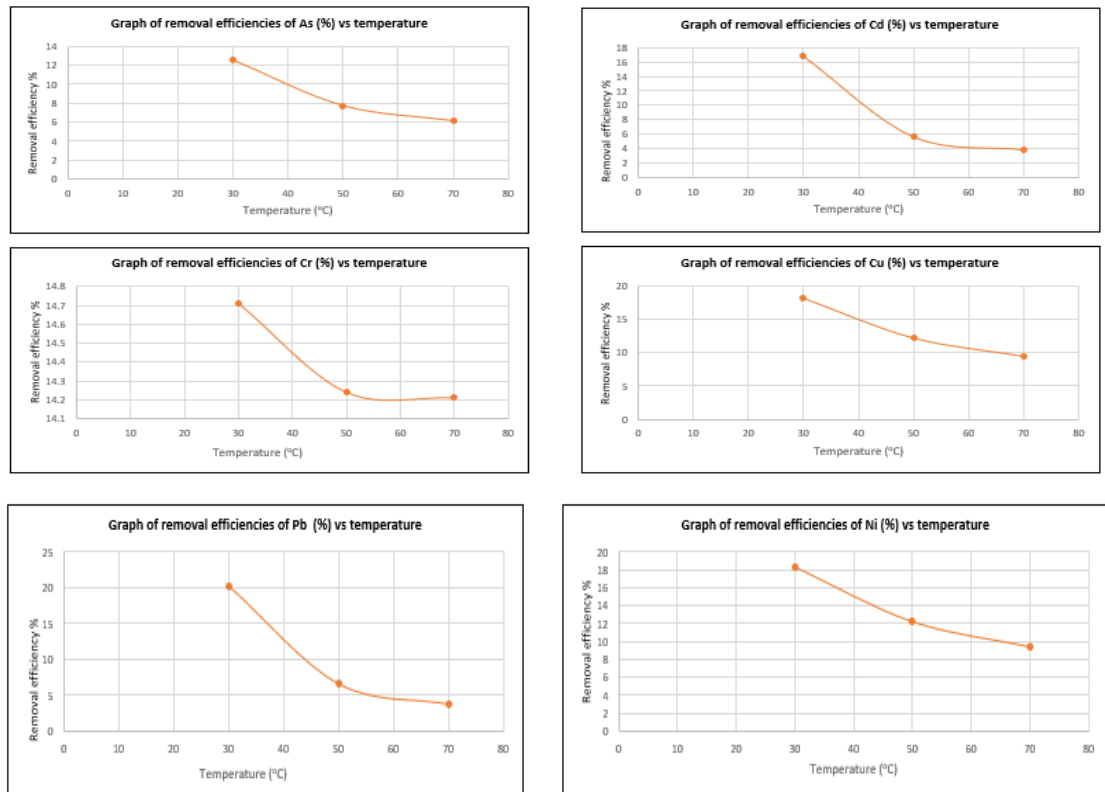


Figure 4.14: Summary of heavy metal removal efficiencies of coir pith and temperature

Optimum temperature condition for metal removal efficiency was tested with three temperatures 30°C, 50°C and 70°C by coir pith and Mn and Zn showed 0 removal efficiencies for all temperatures. According to the graphs between removal efficiencies and temperature, except Cu all the other heavy metal removal efficiencies were higher at 50°C indicating that lower temperatures accelerates the adsorption process and with the increasing temperature removal efficiencies are decreased.

According to above graphs with increasing of temperature adsorption efficiency has decreased the reasons are with the increasing of temperature kinetic energy of the heavy metals has increased then desorption is happened in the sample.

Figure 4.15 to Figure 4.20 shows the graphs of heavy removal efficiencies by 2 g of coir pith with the variation of contact time.

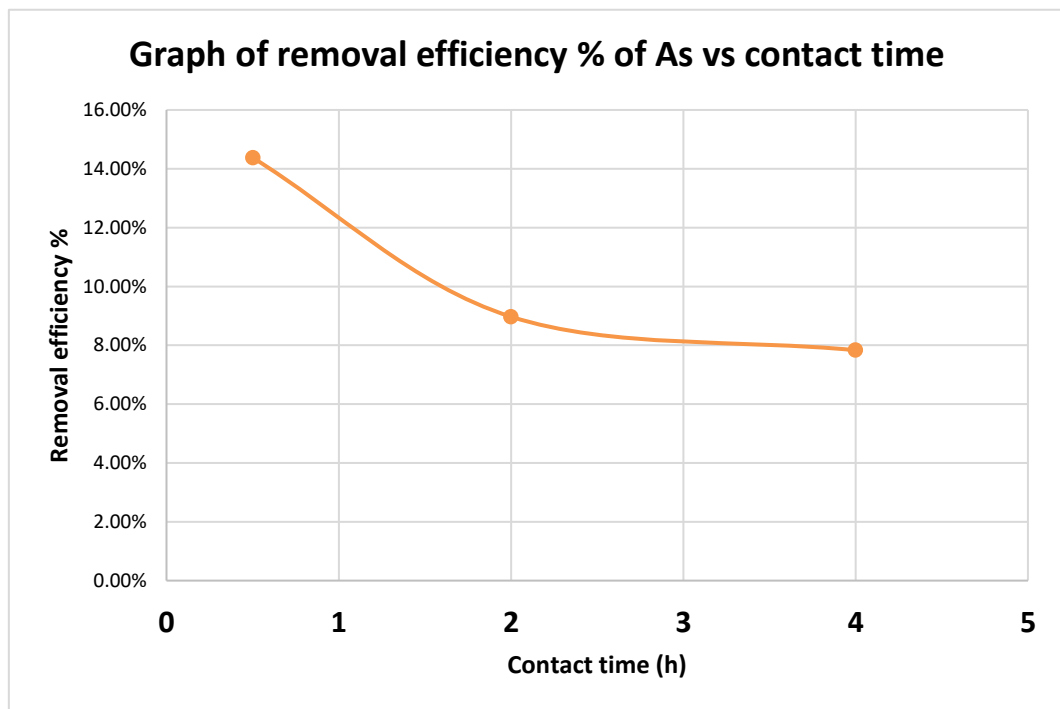


Figure 4.15: Graph between removal efficiencies of coir pith for As and contact time

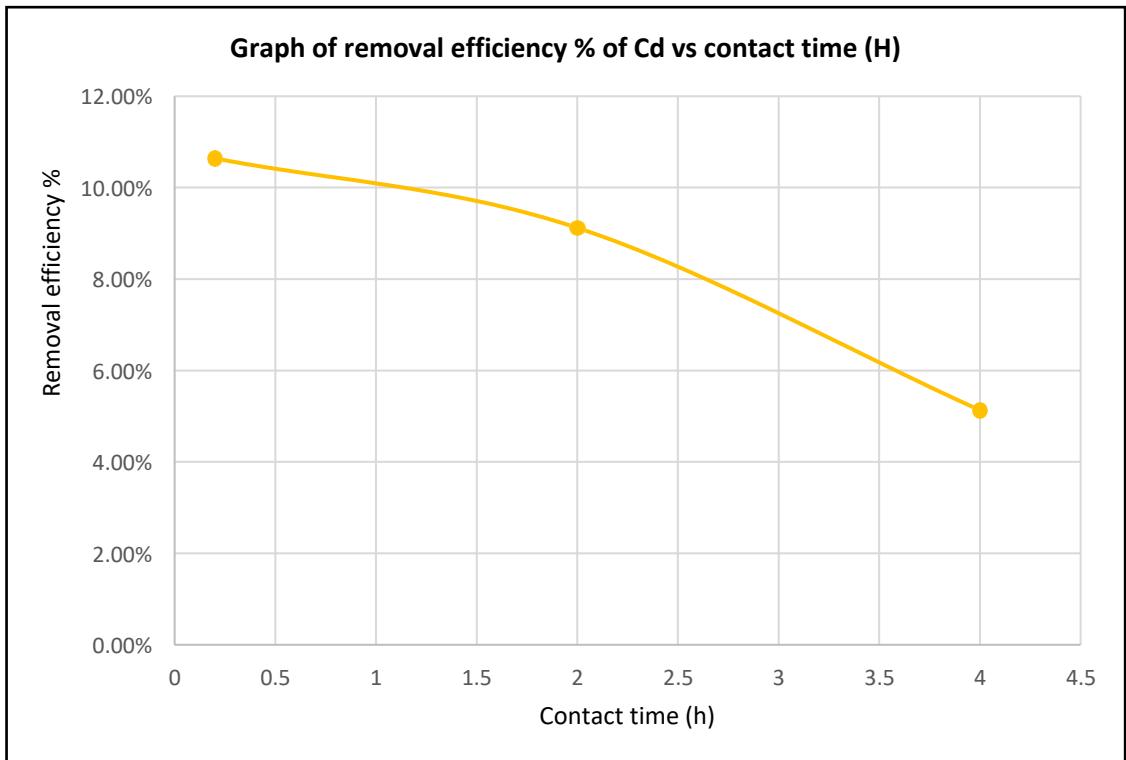


Figure 4.16: Graph between removal efficiencies of coir pith for Cd and contact time

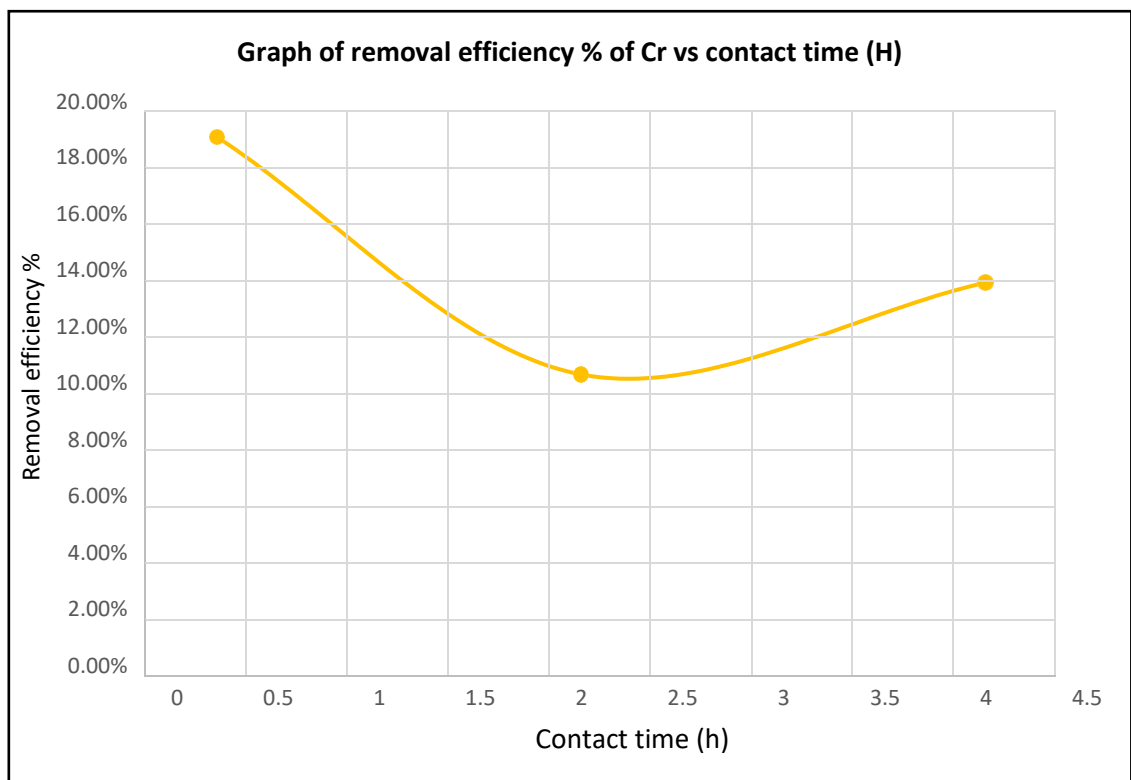


Figure 4.17: Graph between removal efficiencies of coir pith for Cr and contact time

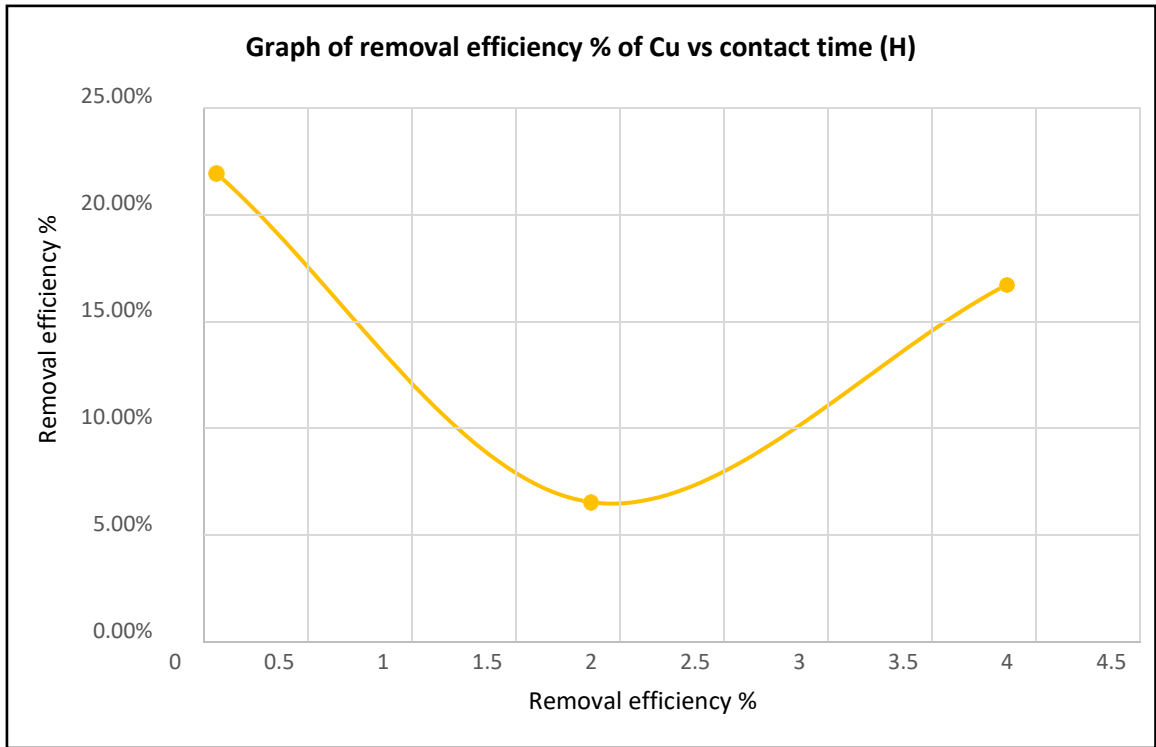


Figure 4.18: Graph between removal efficiencies of coir pith for Cu and contact time

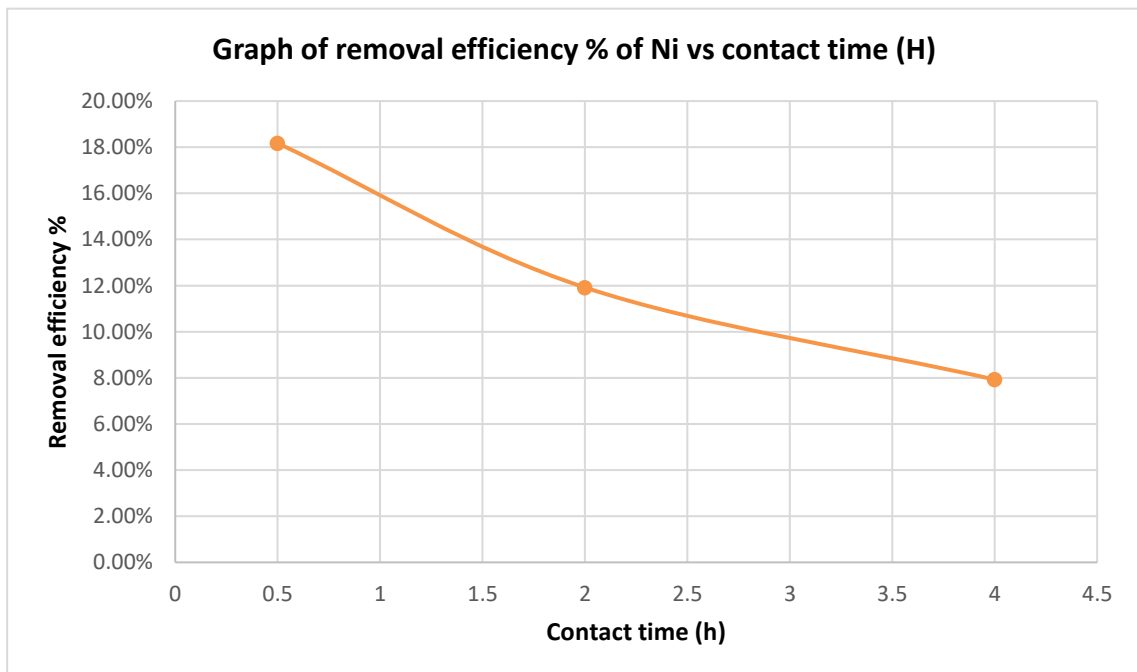


Figure 4.19: Graph between removal efficiencies of coir pith for Ni and contact time

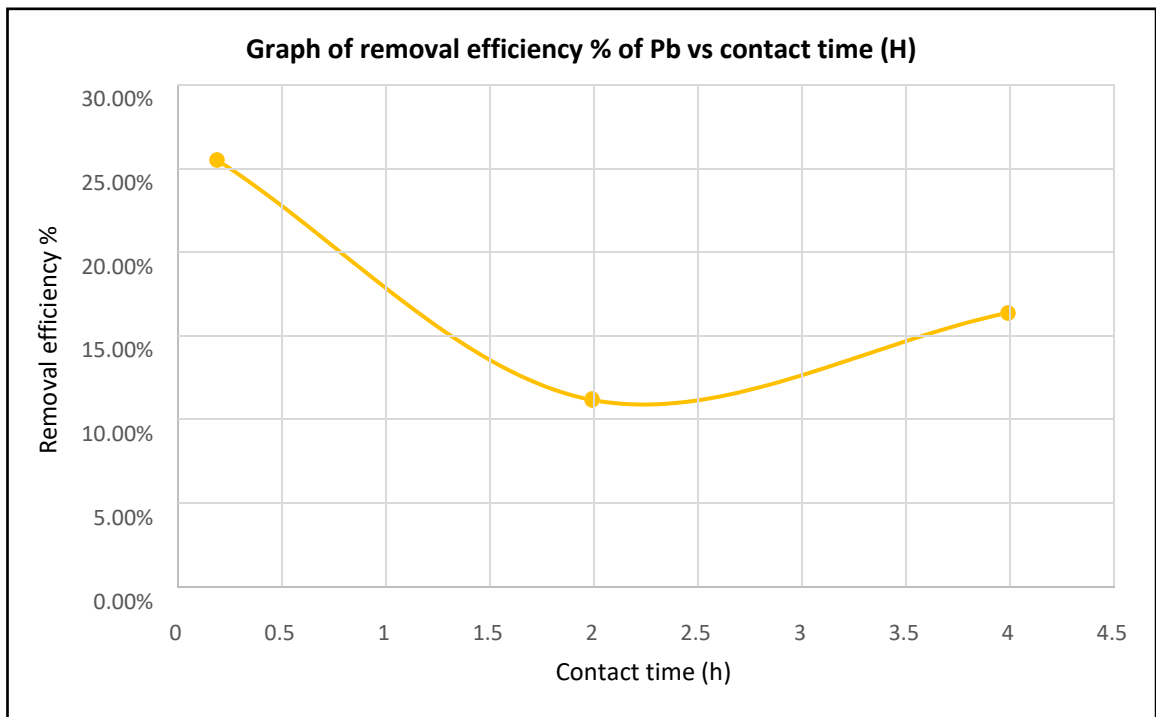


Figure 4.20: Graph between removal efficiencies of coir pith for Pb and contact time

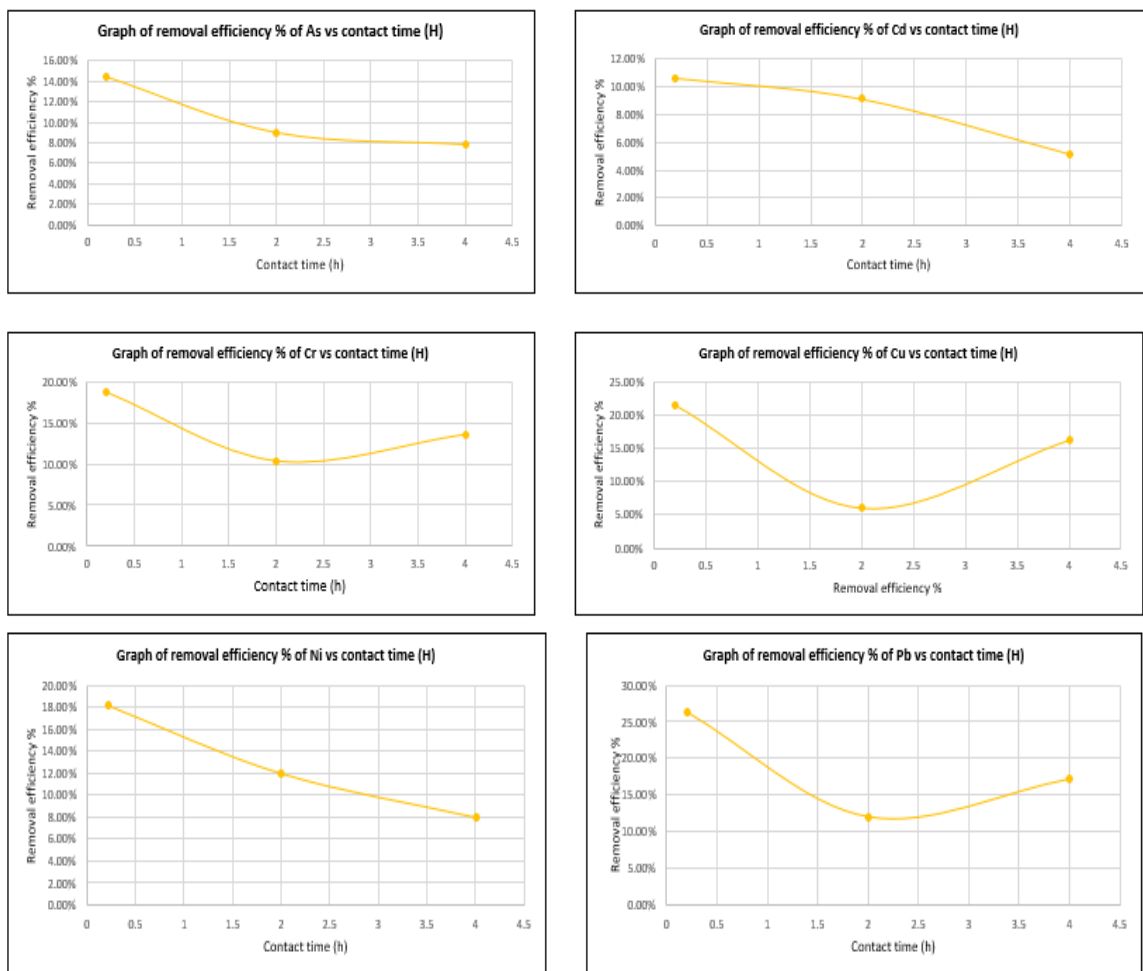


Figure 4.21: Summary of heavy metal removal efficiencies of coir pith and contact time

30 minutes, 2 hours, and 4 hours contact periods were tested in this study for removal each metal by coir pith and graphs between removal efficiency % and contact time in hours showed that removal of As, Cr, Cd, Cu, Ni, and Pb are optimum in 30 minutes contact period over 4 hours contact time. But Mn removal efficiency at 4 hours contact period was 0 while coir pith only has significant removal efficiency at lower contact time and therefore graph cannot be drafted for Mn removal efficiencies by coir pith. For Cr, Cu, and Pb from 30 min to 2 hr adsorption efficiency has decreased that means desorption is happened in that time period. From 2 hr to 4 hr time period adsorption efficiency has increased the reason is for that in that time period adsorption has happened in the sample. This kind of adsorption and desorption are happened in same sample due to this is multicomponent heavy metal sample For other heavy metals with the increasing of contact time adsorption efficiency has decreased due to contact time is high desorption has happened in the sample.

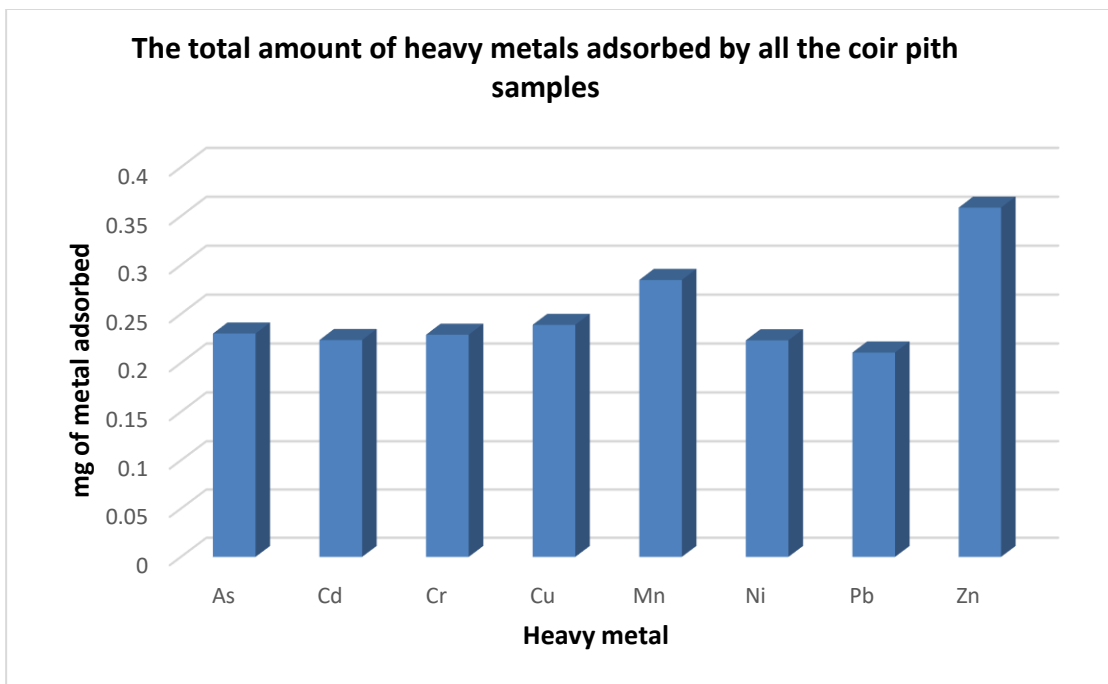


Figure 4.22: Graph of heavy metal amount adsorbed by all the coir pith samples

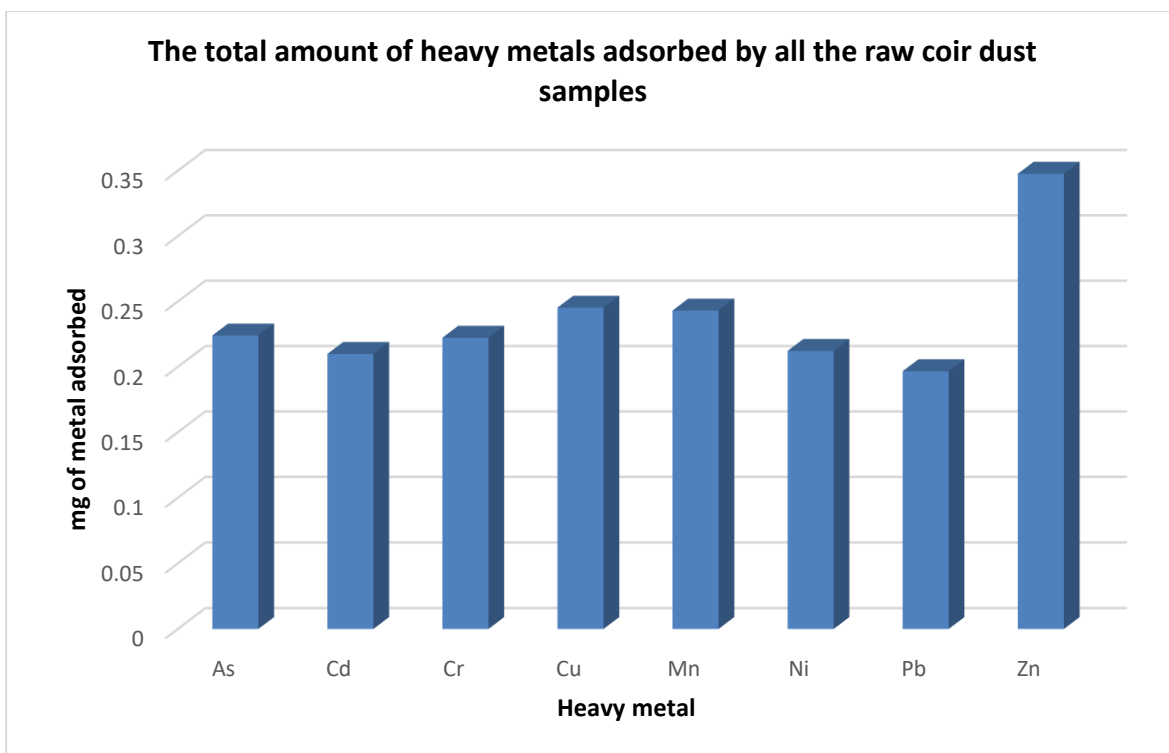


Figure 4.23: Graph of heavy metal amount adsorbed by all the coir dust samples

Main objective of this study was to evaluate the efficiency of coir pith and coir dust for the removal of heavy metals; Arsenic, Cadmium, Chromium, Copper, Manganese, Nickel, Lead and Zinc from an aqueous solution. Additionally, research methodology was developed to determine the optimum conditions (temperature and contact time) for effective heavy metal removal from an aqueous solution. According to the laboratory test results and statistical data, graphs were prepared to determine the relationship between the quantity bio sorbent and the metal removal efficiency which could be more precisely expressed as solid/liquid ratio for optimum heavy metal adsorption. When considering the heavy metal adsorption by all coir dust sample, a fluctuation can be observed and highest adsorption rate was recorded at 4 g. when coir dust weight is increased further the adsorption rate is decreased and the reason for this is that coir dust already containing some level of heavy metals and after it starts to adsorb heavy metals it reaches up to maximum adsorption capacity. Once the maximum capacity is reached the desorption process begins and through this heavy metal is again released into the solution. According to the results coir pith is the most suitable biosorbent for all heavy metal except Zn since it has higher saturation capacity and therefore coir pith can retain higher amount of heavy metals. Also the initial heavy metal solution concentrations

which were selected to these studies were varied within comparatively low ranges and those low concentrations were selected because literature review revealed that most of the coir pith and coir dust samples could adsorb the concentrations within this range.

In this experimental we have used multi component heavy metal sample as a result of it both materials adsorption and desorption are happening in the same sample .When we consider heavy metal adsorption with the temperature from 30-70 °C heavy metals adsorption capacity has decreased the reason for this with the increasing of temperature kinetic energy of the metal has increased then desorption is happened in side the sample. As a result of it with increasing of temperature heavy metals adsorption capacity will decrease.

When we consider contact time of the heavy metals sample with the absorbent, For Cr, Cu and Pb show similar results. From 30 min to 2 hr material adsorption efficiency has decreased but 2hr to 4hr adsorption efficiency has increased the reason is for this, from 30 min to 2 hr desorption appeared in the sample but with the increasing of the contact time from 2 hr to 4 hr again heavy metals adsorption is happened in the sample . But all other heavy metals are showing decreasing trend of heavy metals adsorption capacity with the increasing of contact time.

Conclusion

The main aim of the study was to evaluate the capability and effect of temperature, solid/liquid ratio and contact period of coir pith for the removal of heavy metals; Arsenic, Cadmium, Chromium, Copper, Manganese, Nickel, Lead and Zinc from an aqueous solution. According to the analytical results, for removal of As, Cd, Cr, Ni and Pb both coir pith and coir dust act as suitable biosorbents and for all these 5 metals, the best efficient solid/liquid ratio is 0.1 g/ml for coir pith and 0.08 g/mL for coir dust at room temperature for 2 hours contact period. For Cu removal coir dust is the suitable biosorbent while coir dust is most suitable biosorbent for Mn removal. For Cu and Mn, solid/liquid ratio for coir pith is 0.1g/ml and 0.08 g/ml for coir dust at room temperature for 2 hours contact period is the optimum solid/liquid ratio. However, both coir pith and coir dust are not suitable for Zn removal from aqueous solutions. For all metals except Zn contact period of 30 minutes and temperature of 50⁰C are the optimum operating conditions. In this review, significance of coir pith and coir dust as biosorbents for the adsorption of toxic heavy metal ions from aqueous solutions have been investigated based on their respective removal capacities at varying reaction conditions. Findings of this research have revealed that many heavy metals could be extracted in substantial amounts by both coir pith and coir dust and these materials have identified as cost- effective, non-toxic, and biocompatible adsorbents. Although the amount of the available literature data for the application of coir pith and coir dust for adsorption of heavy metals from aqueous solution is increasing at a remarkable pace, there are still several gaps which need more attention, such as enhancement of biosorption capacity through modification of biosorbent, assessment of biosorbents under multi-component pollutants, mechanistic modelling to correctly understand the sorption mechanisms, investigation of these materials with real industrial effluents, regeneration studies and continuous flow studies. There is a need for future studies to verify the performance of the coir pith and coir dust as low-cost adsorbents at the pilot plant scale. There is a great need for additional research concerning how to further process or disposed of coir pith and coir dust after it has been used to extract heavy metals which could be toxic, slow to biodegrade, or subjected to leaching. Despite various challenges has been identified and clarified, a widespread and greatly the progress of in this area can be expected in the future.

References

- Abate, G., Masini, J.C. 2005. Influence of pH, ionic strength and humic acid on adsorption of Cd (II) and Pb (II) onto vermiculite. *Colloids and Surfaces a-Physicochemical and Engineering Aspects*, 262(1-3), 33-39.
- Aksu, Z. 2001. Equilibrium and kinetic modelling of cadmium (II) biosorption by *C. vulgaris* in a batch system: effect of temperature. *Separation and Purification Technology*, 21(3), 285- 294.
- Al-Rub, F.A.A. 2006. Biosorption of zinc on palm tree leaves: Equilibrium, kinetics, and thermodynamics studies. *Separation Science and Technology*, 41(15), 3499-3515.
- Alvarez-Vazquez, H., Jefferson, B., Judd, S.J. 2004. Membrane bioreactors vs conventional biological treatment of landfill leachate: a brief review. *Journal of Chemical Technology and Biotechnology*, 79(10), 1043-1049.
- Amarasinghe, B., 2011. Lead and Cadmium Removal from Aqueous Medium Using Coir. *Journal of Tropical Forestry and Environment*, 01(01), pp. 36-47.
- Annadurai, G., Juang, R.S., Lee, D.J. 2003. Adsorption of heavy metals from water using banana and orange peels. *Water Science and Technology*, 47(1), 185-19
- Areco, M.M., Hanela, S., Duran, J., dos Santos Afonso, M. 2012. Biosorption of Cu (II), Zn (II), Cd (II) and Pb (II) by dead biomasses of green alga *Ulva lactuca* and the development of a sustainable matrix for adsorption implementation. *Journal of Hazardous Materials*, 213– 214(0), 123-132.
- Areco, M.M., Hanela, S., Duran, J., dos Santos Afonso, M. 2012. Biosorption of Cu (II), Zn (II), Cd (II) and Pb (II) by dead biomasses of green alga *Ulva lactuca* and the development of a sustainable matrix for adsorption implementation. *Journal of Hazardous Materials*, 213– 214(0), 123-132.

Argun, M.E., Dursun, S., Gur, K., Ozdemir, C., Karatas, M., Dogan, S. 2005. Adsorption of copper on modified wood (pine) materials. *Cellulose Chemistry and Technology*, 39(5-6), 581- 591.

Arpa, C., Basyilmaz, E., Bektas, S., Genc, O., Yurum, Y. 2000. Cation exchange properties of low rank Turkish coals: removal of Hg (II), Cd (II) and Pb (II) from wastewater. *Fuel Processing Technology*, 68(2), 111-120.

Baek, N., Shin, U., Yoon, J. 2005. A study on the design and analysis of a heat pump heating system using wastewater as a heat source. *Solar Energy*, 78(3), 427-440.

Bailey, S.E., Olin, T.J., Bricka, R.M., Adrian, D.D. 1999. A review of potentially low-cost sorbents for heavy metals. *Water Research*, 33(11), 2469-2479.

Bayramoglu, G., Bektas, S., Arica, M.Y. 2003. Biosorption of heavy metal ions on immobilized white-rot fungus *Trametes versicolor*. *Journal of Hazardous Materials*, 101(3), 285-300.

Belfort, G. 1984. *Synthetic Membrane Process: Fundamentals and Water Applications*. Access Online via Elsevier

Benhammou, A., Yaacoubi, A., Nibou, L., Tanouti, B. 2005. Adsorption of metal ions onto Moroccan stevensite: kinetic and isotherm studies. *Journal of Colloid and Interface Science*, 282(2), 320-326.

Blanco, A., Sanz, B., Llama, M.J., Serra, J.L. 1999. Biosorption of heavy metals to immobilized *Phormium laminosum* biomass. *Journal of Biotechnology*, 69(2-3), 227-240.

Boota, R., Bhatti, H.N., Hanif, M.A. 2009. Removal of Cu (II) and Zn (II) Using Lignocellulosic Fiber Derived from *Citrus reticulata* (Kinnow) Waste Biomass. *Separation Science and Technology*, 44(16), 4000-4022.

Bricka, R.M., Hill, D.O. 1989. Metal immobilization by solidification of hydroxide and xanthate sludges. In *Environmental Aspects of Stabilization and Solidification of*

Hazardous and Radioactive Wastes. American Society for Testing and Materials (ASTM) STP 1033, eds., Philadelphia, 257-272.

Burger, J., Gochfeld, M. 2004. Marine Birds as Sentinels of Environmental Pollution. *Eco Health*, 1(3), 263-274.

Caramalau, C., Bulgariu, L., Macoveanu, M. 2009. Adsorption characteristics of Co (II) ions from aqueous solutions on Romanian peat moss. *Environmental Engineering and Management Journal*, 8(5), 1089-1095.

Case, O.P. 1974. Metallic recovery from wastewaters utilising cementation. EPA-270/2-74-008, U.S. Washington DC

Castro-González, M.I., Méndez-Armenta, M. 2008. Heavy metals: Implications associated to fish consumption. *Environmental Toxicology and Pharmacology*, 26(3), 263-271.

Cañizares, P., Pérez, Á., Camarillo, R. 2002. Recovery of heavy metals by means of ultrafiltration with water-soluble polymers: calculation of design parameters. *Desalination*, 144(1), 279-285.

Chang, A., Page, A., Warneke, J. 1987. Long-term sludge applications on cadmium and zinc accumulation in Swiss chard and radish. *Journal of Environmental Quality*, 16(3), 217-221.

Chao, Y.-M., Liang, T. 2008. A feasibility study of industrial wastewater recovery using electrodialysis reversal. *Desalination*, 221(1), 433-439.

Charerntanyarak, L. 1999. Heavy metals removal by chemical coagulation and precipitation. *Water Science and Technology*, 39(10), 135-138.

Chaufer, B., Deratani, A. 1988. Removal of metal ions by complexation-ultra filtration using water-soluble macromolecules: Perspective of application to wastewater treatment. *Nuclear and chemical waste management*, 8(3), 175-187.

- Chen, B.-Y., Utgikar, V.P., Harmon, S.M., Tabak, H.H., Bishop, D.F., Govind, R. 2000. Studies on biosorption of zinc (II) and copper (II) on *Desulfovibrio desulfuricans*. *International Biodeterioration and Biodegradation*, 46(1), 11-18.
- Chen, G. 2004. Electrochemical technologies in wastewater treatment. *Separation and Purification Technology*, 38(1), 11-41.
- Choi, S.B., Yun, Y.S. 2006. Biosorption of cadmium by various types of dried sludge: An equilibrium study and investigation of mechanisms. *Journal of Hazardous Materials*, 138(2), 378-383.
- Cobb, G.B., Sands, K., Waters, M., Wixson, B.G. and Dorrward-King, E. (2000). Accumulation of heavy metals by vegetables grown in mine waste. *Environmental Toxicology Chemistry*. 19, 600 - 607.
- Dabrowski, A., Hubicki, Z., Podkościelny, P., Robens, E. 2004. Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method. *Chemosphere*, 56(2), 91-106.
- Davis, T.A., Volesky, B., Mucci, A. 2003. A review of the biochemistry of heavy metal biosorption by brown algae. *Water Research*, 37(18), 4311-4330.
- Drake, L.R., Rayson, G.D. 1996. Peer Reviewed: Plant-Derived Materials for Metal Ion- Selective Binding and Preconcentration. *Analytical Chemistry*, 68(1), 22A- 27A.
- Feng, N., Guo, X., Liang, S., Zhu, Y., Liu, J. 2011. Biosorption of heavy metals from aqueous solutions by chemically modified orange peel. *Journal of Hazardous Materials*, 185(1), 49-54.
- Fourest, E., Roux, J.C. 1992. Heavy metal biosorption by fungal mycelial by-product: mechanisms and influence of pH. *Applied Microbiology and Biotechnology*, 37(3), 399-403.

Friis, N., Myers-Keith, P. 1986. Biosorption of uranium and lead by *Streptomyces longwoodensis*. *Biotechnology and Bioengineering*, 28(1), 21-28.

Fritzmann, C., Löwenberg, J., Wintgens, T., Melin, T. 2007. State-of-the-art of reverse osmosis desalination. *Desalination*, 216(1), 1-76.

Fu, F., Wang, Q. 2011. Removal of heavy metal ions from wastewaters: A review. *Journal of Environmental Management*, 92(3), 407-418.

Gadd, G.M. 1988. Accumulation of metals by microorganisms and algae. *Biotechnology*, 6, 401-433.

Gavrilescu, M. 2004. Removal of heavy metals from the environment by biosorption. *Engineering in Life Sciences*, 4(3), 219-232.

Gereli, G., Seki, Y., Murat Kusoglu, I., Yurdakoç, K. 2006. Equilibrium and kinetics for the sorption of promethazine hydrochloride onto K10 montmorillonite. *Journal of Colloid and Interface Science*, 299(1), 155-162.

GLAAS, 2012. Global analysis and assessment of sanitation and drinking-water (GLAAS). A report by the challenge of extending and sustaining services, WHO, 1-112.

Golob, V., Vinder, A., Simoni, M. 2005. Efficiency of the coagulation/flocculation method for the treatment of dyebath effluents. *Dyes and Pigments*, 67(2), 93-97.

Gray, W.G., Schrefler, B.A. 2001. Thermodynamic approach to effective stress in partially saturated porous media. *European Journal of Mechanics-A/Solids*, 20(4), 521-538.

Gregory, M.W. 1993. Wastewater evaporator system, Google Patents.

Han, R., Li, H., Li, Y., Zhang, J., Xiao, H., Shi, J. 2006. Biosorption of copper and lead ions by waste beer yeast. *Journal of Hazardous Materials*, 137(3), 1569-1576.

Ho, Y., Porter, J., McKay, G. 2002. Equilibrium Isotherm Studies for the Sorption of Divalent Metal Ions onto Peat: Copper, Nickel and Lead Single Component Systems. *Water, Air, & Soil Pollution*, 141(1), 1-33.

Ho, Y.S., Wase, D.A.J., Forster, C.F. 1994. Adsorption of divalent copper ions from aqueous solution by sphagnum moss peat. *Process Safety and Environmental Protection: Transactions of the Institution of Chemical Engineers, Part B*, 72(3), 185-194.

Hong, S., Nuerdongbai, W., Bing, D., Mao-wu, F. 2006. Removal of Heavy Metals form Wastewater by Using Activated Carbon Adsorption. *Jiangsu Environmental Science and Technology*, S2.

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Hsu, M.J., Selvaraj, K., Agoramoorthy, G. 2006. Taiwan's industrial heavy metal pollution threatens terrestrial biota. *Environmental Pollution*, 143(2), 327-334.

Igwe, J.C., Abia, A.A., Ibeh, C.A. 2008. Adsorption kinetics and intra particulate diffusivities of Hg (II), As (III) and Pb (II) ions on unmodified and thiolate coconut fiber. *International Journal of Environmental Science and Technology: (IJEST)*, 5(1), 83-92.

Iqbal, M., Schiewer, S., Cameron, R. 2009b. Mechanistic elucidation and evaluation of biosorption of metal ions by grapefruit peel using FTIR spectroscopy, kinetics

Jabeen, R., Ahmad, A., Iqbal, M. 2009. Phytoremediation of Heavy Metals: Physiological and Molecular Mechanisms. *Botanical Review*, 75(4), 339-364.

Jeon, C., Park, K.H. 2005. Adsorption and desorption characteristics of mercury (II) ions using aminated chitosan bead. *Water Research*, 39(16), 3938-3944.

Jianqiu, C., Zhijun, H., Zhiliang, W., Rong, J. 2010. Adsorption characteristic of bioadsorbent for antibiotics. *Technology of Water Treatment*, 12, 018.

Kaewsarn, P. 2002. Biosorption of copper (II) from aqueous solutions by pre-treated biomass of marine algae *Padina* sp. *Chemosphere*, 47(10), 1081-1085.

- Kaksonen, A., Riekkola-Vanhanen, M.-L., Puhakka, J. 2003. Optimization of metal sulphide precipitation in fluidized-bed treatment of acidic wastewater. *Water Research*, 37(2), 255-266.
- Kapoor, A., Viraraghavan, T. 1995. Fungal biosorption-an alternative treatment option for heavy metal bearing wastewaters: a review. *Bioresource Technology*, 53(3), 195-206.
- Kara, A. 2009. Adsorption of Cr (VI) ions onto Poly (ethylene glycol dimethacrylate-1- vinyl- 1,2,4-triazole). *Journal of Applied Polymer Science*, 114(2), 948-955.
- Kara, S., Aydinler, C., Demirbas, E., Kobya, M., Dizge, N. 2007. Modeling the effects of adsorbent dose and particle size on the adsorption of reactive textile dyes by fly ash. *Desalination*, 212(1-3), 282-293.
- Keskinkan, O., Goksu, M.Z.L., Basibuyuk, M., Forster, C.F. 2004. Heavy metal adsorption properties of a submerged aquatic plant (*Ceratophyllum demersum*). *Bioresource Technology*, 92(2), 197-200.
- Khraisheh, M.A., Al-degs, Y.S., Mcminn, W.A. 2004. Remediation of wastewater containing heavy metals using raw and modified diatomite. *Chemical Engineering Journal*, 99(2), 177- 184.
- Kitagawa, T., Nishikawa, Y., Frankenfeld, J., Li, N. 1977. Wastewater treatment by liquid membrane process. *Environmental Science and Technology*, 11(6), 602- 605.
- Kratochvil, D., Fourest, E., Volesky, B. 1995. Biosorption of copper by *Sargassum fluitans* biomass in fixed-bed column. *Biotechnology Letters*, 17(7), 777-782.
- Kumar, D., Pandey, L.K., Gaur, J.P. 2010. Evaluation of various isotherm models, and metal sorption potential of cyanobacterial mats in single and multi-metal systems. *Colloids and Surfaces B: Biointerfaces*, 81(2), 476-485.
- Kurniawan, T.A., Chan, G., Lo, W. H., Babel, S. 2006. Physico-chemical treatment

techniques for wastewater laden with heavy metals. *Chemical Engineering Journal*, 118(1), 83-98.

Kusvuran, E., Yildirim, D., Samil, A., Gulnaz, O. 2012. A study: Removal of Cu (II), Cd (II), and Pb (II) Ions from Real Industrial Water and Contaminated Water Using Activated Sludge Biomass. *CLEAN–Soil, Air, Water*.

Li, Z., Ma, Z., van der Kuijp, T.J., Yuan, Z., Huang, L. 2014. A review of soil heavy metal pollution from mines in China: Pollution and health risk assessment. *Science of the Total Environment*, 468–469(0), 843-853.

Lin, S., Rayson, G.D. 1998. Impact of surface modification on binding affinity distributions of *Datura innoxia* biomass to metal ions. *Environmental Science and Technology*, 32(10), 1488- 1493.

Liu, Z.R., Zhou, L. M., Wei, P., Zeng, K., Wen, C.X., Lan, H.-h. 2008. Competitive adsorption of heavy metal ions on peat. *Journal of China University of Mining and Technology*, 18(2), 255-260.

Liu, Z.S., Lin, C.L., Chou, J.D. 2010. Studies of Cd (II), Pb (II) and Cr (III) distribution characteristics in bottom ash following agglomeration/defluidization in a fluidized bed boiler incinerating artificial waste. *Fuel Processing Technology*, 91(6), 591-599.

Lussier, S., Gentile, J., Walker, J. 1985. Acute and chronic effects of heavy metals and cyanide on *Mysidopsis bahia* (crustacea: mysidacea). *Aquatic Toxicology*, 7(1), 25-35.

L Vidhya, M. D. K. S. a. S.-K. K., 2018. Removal of Cr (VI) from aqueous solution using coir pith biochar- An eco-friendly approach. *Indian Journal of Chemical Technology*, Volume 25, pp. 266-273.

Mahvi, A.H. 2008. Application of agricultural fibers in pollution removal from aqueous solution. *International Journal of Environmental Science and Technology*, 5(2), 275-285.

- Mansour, S.A., Gad, M.F. 2010. Risk assessment of pesticides and heavy metals contaminants in vegetables: A novel bioassay method using *Daphnia magna* Straus. *Food and Chemical Toxicology*, 48(1), 377-389.
- Marder, L., Bernardes, A.M., Zoppas Ferreira, J. 2004. Cadmium electroplating wastewater treatment using a laboratory-scale electro dialysis system. *Separation and Purification Technology*, 37(3), 247-255.
- Martinez-Garcia, G., Bachmann, R.T., Williams, C.J., Burgoyne, A., Edyvean, R.G. 2006. Olive oil waste as a biosorbent for heavy metals. *International Biodeterioration and Biodegradation*, 58(3), 231-238.
- Mavrov, V., Erwe, T., Blöcher, C., Chmiel, H. 2003. Study of new integrated processes combining adsorption, membrane separation and flotation for heavy metal removal from wastewater. *Desalination*, 157(1), 97-104.
- McHale, A., McHale, S. 1994. Microbial biosorption of metals: potential in the treatment of metal pollution. *Biotechnology Advances*, 12(4), 647-652.
- Mishra, S.P., Tiwari, D., Dubey, R., Mishra, M. 1998. Biosorptive behaviour of casein for Zn^{2+} , Hg^{2+} and Cr^{3+} : effects of physico-chemical treatments. *Bioresource Technology*, 63(1), 1-5.
- Monser, L., Adhoum, N. 2002. Modified activated carbon for the removal of copper, zinc, chromium and cyanide from wastewater. *Separation and Purification Technology*, 26(2-3), 137-146.
- Mosavi, S.B., Karimi, S., Feiziasl, V. 2010. Biosorption of Lead and Nickel by *Medicago sativa* (alfalfa) and *Datura* from Contaminated Solution. *Asian Journal of Chemistry*, 22(3), 1700- 1704.
- Mouni, L., Merabet, D., Bouzaza, A., Belkhiri, L. 2010. Removal of Pb^{2+} and Zn^{2+} from the aqueous solutions by activated carbon prepared from Dates stone. *Desalination and Water Treatment*, 16(1-3), 66-73.

- Munagapati, V.S., Yarramuthi, V., Nadavala, S.K., Alla, S.R., Abburi, K. 2010. Biosorption of Cu (II), Cd (II) and Pb (II) by *Acacia leucocephala* bark powder: Kinetics, equilibrium and thermodynamics. *Chemical Engineering Journal*, 157(2-3), 357-365.
- Murugesan, K., Kim, Y.M., Jeon, J.R., Chang, Y.S. 2009. Effect of metal ions on reactive dye decolorization by laccase from *Ganoderma lucidum*. *Journal of Hazardous Materials*, 168(1), 523-529.
- Nadeem, U., Kant, R., Tripathi, V.S., Chattopadhyaya, M.C. 2010. Biosorption of chromium (VI) by some algae. *Journal of the Indian Chemical Society*, 87(4), 517-519.
- Naiya, T.K., Chowdhury, P., Bhattacharya, A.K., Das, S.K. 2009. Saw dust and neem bark as low-cost natural biosorbent for adsorptive removal of Zn (II) and Cd (II) ions from aqueous solutions. *Chemical Engineering Journal*, 148(1), 68-79.
- Norton, L., Baskaran, K., McKenzie, T. 2004. Biosorption of zinc from aqueous solutions using biosolids. *Advances in Environmental Research*, 8(3-4), 629-635.
- Nriagu, J.O., Kang, S.J., Murin, J.R., Wang, X.Q. 2004. Behavior of oxyanions of As, Se, and Mo in full-scale wastewater treatment plants. *Geochemical Investigations in Earth and Space Science: A Tribute to Issac R. Kaplan*(9), 211-231.
- Nriagu, J.O. 1990. Global metal pollution: Poisoning the biosphere. *Environment: Science and Policy for Sustainable Development*, 32(7), 7-33.
- Nriagu, J.O. 1996. History of global metal pollution. *SCIENCE-NEW YORK THEN WASHINGTON-*, 223-223.
- Ozer, A., Ozer, D., Ozer, A. 2004. The adsorption of copper (II) ions on to dehydrated wheat bran (DWB): determination of the equilibrium and thermodynamic parameters. *Process Biochemistry*, 39(12), 2183-2191.

Padmavathiamma, P.K., Li, L.Y. 2009. Phytoremediation of Metal-Contaminated Soil in Temperate Humid Regions of British Columbia, Canada. *International Journal of Phytoremediation*, 11(6), 575-590.

Pagnanelli, F., Petrangeli Papini, M., Toro, L., Trifoni, M., Veglio, F. 2000. Biosorption of metal ions on *Arthrobacter* sp.: biomass characterization and biosorption modeling. *Environmental Science and Technology*, 34(13), 2773-2778.

Pagnanelli, F., Toro, L., Veglio, F. 2002. Olive mill solid residues as heavy metal sorbent material: a preliminary study. *Waste Management*, 22(8), 901-907.

Pamukoglu, A.Y., Kargi, F. 2006. Batch kinetics and isotherms for biosorption of copper (II) ions onto pre-treated powdered waste sludge (PWS). *Journal of Hazardous Materials*, 138(3), 479-484.

Parvathi, K., Nagendran, R. 2007. Biosorption of Chromium from Effluent Generated in Chrome-Electroplating Unit using *Saccharomyces cerevisiae*. *Separation Science and Technology*, 42(3), 625 - 638.

Pavasant, P., Apiratikul, R., Sungkhum, V., Suthiparinyanont, P., Wattanachira, S., Marhaba,

T.F. 2006. Biosorption of Cu^{2+} , Cd^{2+} , Pb^{2+} , and Zn^{2+} using dried marine green macroalga *Caulerpa lentillifera*. *Bioresource Technology*, 97(18), 2321-2329.

Peters, R.W., Ku, Y., Bhattacharyya, D. 1985. Evaluation of recent treatment techniques for removal of heavy metals from industrial wastewaters. *AICHE symposium series*. pp. 165-203.

Pierotti, R., Rouquerol, J. 1985. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure and Applied Chemistry*, 57(4), 603-619

Pitawala, A. A. H., 2017. An overview of heavy metal contamination in coastal sediments of Sri Lanka. *Journal of Tropical Forestry and Environment*, 07(02), pp. 1-

9.

Premarathne, H.M.P.L., Hettiarachchi, G.M. and Indraratne, S.P. (2005). Accumulation of Cadmium in intensive vegetable growing soils in the Upcountry. *Tropical Agricultural Research*, 17, 93 - 103.

Premarathne, H.M.P.L., Hettiarachchi, G.M. and Indraratne, S.P. (2011). Trace metal concentration in crops and soils collected from intensively cultivated areas of Sri Lanka. *Pedologist*.230 - 240.

Ramalho, R.S. 1977. *Introduction to wastewater treatment processes*. Academic Press, New York.

Raskin, I., Smith, R.D., Salt, D.E. 1997. Phytoremediation of metals: using plants to remove pollutants from the environment. *Current opinion in biotechnology*, 8(2), 221-226.

Reddad, Z., Gerente, C., Andres, Y., Le Cloirec, P. 2002. Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies. *Environmental Science and Technology*, 36(9), 2067-2073.

Ren, Y.M., Wei, X.Z., Zhang, M.L. 2008. Adsorption character for removal Cu (II) by magnetic Cu (II) ion imprinted composite adsorbent. *Journal of Hazardous Materials*, 158(1), 14-22.

Rhazi, M., Desbrieres, J., Tolaimate, A., Rinaudo, M., Vottero, P., Alagui, A. 2002. Contribution to the study of the complexation of copper by chitosan and oligomers. *Polymer*, 43(4), 1267-1276.

Rijsberman, F.R. 2006. Water scarcity: Fact or fiction. *Agricultural water management*, 80(1), 5-22.

Romera, E., Gonzalez, F., Ballester, A., Blazquez, M.L., Munoz, J.A. 2008. Biosorption of Cd, Ni, and Zn with mixtures of different types of algae. *Environmental Engineering Science*, 25(7), 999-1008.

Rosemary, F., Vitharana, U.W.A., Indraratne, S.P. and Weerasooriya, S.V.R., 2015. Concentrations of trace metals in selected land uses of a dry zone soil catena of Sri Lanka. *Tropical Agricultural Research*, 25(4), pp.512–522

Rowell, J.L., Yaghi, O.M. 2006. Effects of functionalization, catenation, and variation of the metal oxide and organic linking units on the low-pressure hydrogen adsorption properties of metal-organic frameworks. *Journal of the American Chemical Society*, 128(4), 1304-1315.

Schiewer, S., Volesky, B. 2000. Biosorption processes for heavy metal removal. *environmental microbe-metal interactions*, 14, 329-362.

Schneider, I.A., Rubio, J., Smith, R.W. 2001. Biosorption of metals onto plant biomass: exchange adsorption or surface precipitation? *International Journal of Mineral Processing*, 62(1), 111-120.

Sheel Ratan, I. S. J. S. a. N. R., 2016. The Removal of Nickel from Wastewater by Modified Coconut Coir Pith. *Chemical Sciences Journal*, 07(03).

Simmons, P., Tobin, J.M., Singleton, I. 1995. Considerations on the use of commercially available yeast biomass for the treatment of metal-containing effluents. *Journal of Industrial Microbiology and Biotechnology*, 14(3), 240-246.

Sörme, L., Lagerkvist, R. 2002. Sources of heavy metals in urban wastewater in Stockholm. *Science of the Total Environment*, 298(1-3), 131-145.

T. S. Anirudhan*, S. S. S., 2012. Adsorptive removal of heavy metal ions from industrial effluents using. *Journal of Environmental Sciences*, 23(12), pp. 1989-1998

Tchobanoglous, G., Burton, F.L. 2003. *Wastewater engineering. MANAGEMENT*, 7, 1- 4.

Ting, Y., Teo, W. 1994. Uptake of cadmium and zinc by yeast: effects of co-metal ion and physical/chemical treatments. *Bioresource Technology*, 50(2), 113-117.

Tobin, J.M., Cooper, D.G., Neufeld, R.J. 1990. Investigation of the mechanism of metal uptake by denatured *Rhizopus arrhizus* biomass. *Enzyme Microb. Technol.*, 12, 591-595.

Toth, J. 1971. State equations of the solid-gas interface layers. *Acta Chim Acad Sci Hungar*, 69(3), 311-328.

Treen-Sears, M.E., Volesky, B., Neufeld, R.J. 1984. Ion exchange/complexation of the uranyl ion by *Rhizopus* biosorbent. *Biotechnology and Bioengineering*, 26(11),1323-1329.

Tsezos, M., Remoudaki, E., Angelatou, V. 1996. A study of the effects of competing ions on the biosorption of metals. *International Biodeterioration and Biodegradation*, 38(1), 19-29.

Tóth, J. 2000. Calculation of the BET-Compatible Surface Area from Any Type I Isotherms Measured above the Critical Temperature. *Journal of Colloid and Interface Science*, 225(2), 378-383.

ul Islam, E., Yang, X.-e., He, Z.-l., Mahmood, Q. 2007. Assessing potential dietary toxicity of heavy metals in selected vegetables and food crops. *Journal of Zhejiang University Science B*, 8(1), 1-13.

Van Hoof, S., Hashim, A., Kordes, A. 1999. The effect of ultrafiltration as pretreatment to reverse osmosis in wastewater reuse and seawater desalination applications. *Desalination*, 124(1), 231-242

Vieira, R.H., Volesky, B. 2010. Biosorption: a solution to pollution. *International Microbiology*, 3(1), 17-24.

Vilar, V., Botelho, C., Boaventura, R. 2007a. Modeling equilibrium and kinetics of metal uptake by algal biomass in continuous stirred and packed bed adsorbers. *Adsorption-Journal of the International Adsorption Society*, 13(5), 587-601.

Vilar, V.J., Botelho, C., Boaventura, R.A. 2007b. Methylene blue adsorption by algal biomass-based materials: Biosorbents characterization and process behaviour. *Journal of Hazardous Materials*, 147(1), 120-132.

Volesky, B., Holan, Z. 1995. Biosorption of heavy metals. *Biotechnology Progress*, 11(3), 235- 250.

Volesky, B. 1999. Biosorption for the Next Century. in: *Process Metallurgy*, (Eds.) R. Amils, A. Ballester, Vol. Volume 9, Elsevier, pp. 161-170.

Volesky, B. 2007. Biosorption and me. *Water Research*, 41(18), 4017-4029.

Waite, T., Davis, J., Payne, T., Waychunas, G., Xu, N. 1994. Uranium (VI) adsorption to ferrihydrite: Application of a surface complexation model. *Geochimica Et Cosmochimica Acta*, 58(24), 5465-5478.

Wang, J., Chen, C. 2006. Biosorption of heavy metals by *Saccharomyces cerevisiae*: A review. *Biotechnology Advances*, 24(5), 427-451.

Wang, J.L., Chen, C. 2009. Biosorbents for heavy metals removal and their future. *Biotechnology Advances*, 27(2), 195-226.

Wanigasuriya, K.P., Peries, H. and Illeperuma, N. (2008). Could ochratoxinA in food commodities be the cause of chronic kidney disease in Sri Lanka. *Transactions of the Royal Society of Tropical Medicine and Hygiene*.102, 726 - 728.

WWDR4. 2012. The 4th edition of the UN World Water Development Report (WWDR4). The United Nations Educational, Scientific and Cultural Organization (UNESCO), 4, 1-250.

Xiangliang, P., Jianlong, W., Daoyong, Z. 2005. Biosorption of Pb (II) by *Pleurotus ostreatus* immobilized in calcium alginate gel. *Process Biochemistry*, 40(8), 2799-2803.

Yun, C.H., Prasad, R., Guha, A.K., Sirkar, K.K. 1993. Hollow fiber solvent extraction removal of toxic heavy metals from aqueous waste streams. *Industrial and Engineering Chemistry Research*, 32(6), 1186-1195.

Zhong, L. X., Peng, X. W., Yang, D., Sun, R. C. 2012. Adsorption of heavy metals by a porous bioadsorbent from lignocellulosic biomass reconstructed in an ionic liquid. *Journal of Agricultural and Food Chemistry*, 60(22), 5621-5628.

Zouboulis, A.I., Matis, K.A., Hancock, I.C. 1997. Biosorption of metals from dilute aqueous solutions. *Separation and Purification Methods*, 26(2), 255-295.

ZU, Y. G., ZHAO, X. H., HU, M. S., REN, Y., XIAO, P., ZHU, L., CAO, Y. J., ZHANG, Y.

2006. Biosorption effects of copper ions on *Candida utilis* under negative pressure cavitation. *Journal of Environmental Sciences*, 18(6), 1254- 1259.

Çetinkaya Dönmez, G., Aksu, Z., Öztürk, A., Kutsal, T. 1999. A comparative study on heavy metal biosorption characteristics of some algae. *Process Biochemistry*, 34(9), 885-892.

Çolak, F., Atar, N., Yazcolu, D., Olgun, A. 2011. Biosorption of lead from aqueous solutions by *Bacillus* strains possessing heavy-metal resistance. *Chemical Engineering Journal*, 173(2), 422-428.

Özer, A., Özer, D. 2003. Comparative study of the biosorption of Pb (II), Ni (II) and Cr (VI) ions onto *S. cerevisiae*: determination of biosorption heats. *Journal of Hazardous Materials*, 100(1), 219-229.

Öztürk, A., Artan, T., Ayar, A. 2004. Biosorption of nickel (II) and copper (II) ions from aqueous solution by *Streptomyces coelicolor* A3 (2). *Colloids and Surfaces B: Biointerfaces*, 34(2), 105-111.

Šiban, M., Radeti, B., Kevrešan, Ž., Klašnja, M. 2007. Adsorption of heavy metals from electroplating wastewater by wood sawdust. *Bioresource Technology*, 98(2), 402-

409.