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Coffee Husk as adsorbent for the heavy metals (Cr and Pb) Removal from synthetic wastewater

A thesis submitted to the School of Chemical and Bio-Engineering, Addis Ababa Institute of Technology, Addis Ababa University towards the partial fulfillment of the requirement of degree in Master of Science in chemical Engineering under Environmental Engineering stream.

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Abstract

Heavy metal contamination of water is a serious threat to the ecosystem. Many industries such as electroplating, metal plating, mining operation, and tanneries release wastewaters containing heavy metals into the environment. The objective of the study was to investigate the efficiency of coffee husk for the removal of heavy metals (chromium. and Lead) from synthetic wastewater. Adsorbent was prepared from coffee husk and treated with 2% formaldehyde solution in order to reduce biodegradation of organic compounds and avoid mould formation during continuous sorption. It's surface functional groups were analyzed using fourier transform infrared spectroscopy and the major peaks were observed at 3444 cm^{-1} , 3438 cm^{-1} and 3432 cm^{-1} which may representing bonded $-\text{OH}$ groups rather than $-\text{NH}$ group. Sorption studies were conducted in a continuous system. The sorption efficiency and adsorption capacity were studied as a function of adsorbent dose ,pH and flow rate of optimum results were found to be 99.8% at 30g, 3 and 5ml/min and 99.45% at 30g, 12 and 5ml/min which are the optimal conditions for Cr(VI) and Pb(II) respectively. The Sorption performance was improved as pH and flow rate decreased and adsorbent dose increased for Cr(VI) and pH, adsorbent dose increased and flow rate decreased for Pb(II). The highest adsorption capacity were also found to be 0.18806mg/g and 0.18mg/g at distinct pH=3 & 7.5 values for Cr(VI) and Pb(II) respectively and flow rate of 5ml/min.. Generally the study showed that coffee husk can be used as a good adsorbent for the removal of chromium and lead from synthetic waste water.

Keywords: Sorption, coffee husk, Chromium, Lead, wastewater

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Table of content

Abstract.....	i
Acknowledgements.....	ii
Table of content	iii
List of Tables	vii
List of Figures	viii
List of plates.....	viii
1. Introduction.....	1
1.1 Background	1
1.2 Heavy metal toxicity	2
1.3. Health Effects due to Heavy Metals	2
1.3.1 LEAD	3
1.3.2 Chromium.....	3
1.4. Environmental Pressures.....	4
1.5 Conventional Methods	4
1.5.1 Membrane process (Reverse osmosis technique).....	4
1.5.2 Precipitation and clarification techniques.	5
1.5.3 Activated carbon process	5
1.5.4 Ion exchange process	5
1.6 Adsorption.....	5
1.7. Biosorption.....	6
1.8. Statement of the problem	7
1.9. Objective	8
1.9.1. General Objective.....	8
1.9.2. Specific Objectives.....	8
1.10. Significance of the study.....	8
1.11. Scope of the study	9
2. Literature Review.....	10
2.1 Industrialization and Heavy metal pollution.....	10
2.2 Heavy Metals in the Environment	10

2.3 Heavy Metal Removal Options from Waste Water	11
2.4 Sources and Impacts of Heavy Metals.....	11
2.5. Heavy metal toxicity	12
2.6. Chromium	13
2.7. Conventional technologies for heavy metal removal	16
2.7.1. Chemical Precipitation	16
2.7.2. Ion exchange	16
2.7.3. Reverse osmosis	17
2.7.4. Flocculation and Coagulation.....	17
2.7.5. Flotation	17
2.7.6. Electro dialysis	18
2.8. Heavy metal removal using bio sorption	18
2.9. Adsorption.....	18
2.10. Types of Adsorbents	20
2.11. Adsorption Mechanisms	21
2.11.1 Physical adsorption	21
2.11.2. Ion exchange	21
2.11.3. Complexation	22
2.11.4 Precipitation	22
2.12. Factors affecting adsorption process.....	23
2.12.1. Contact time	23
2.12.2. Concentration	23
2.12.3. Adsorbent dose.....	23
2.12.4. pH.....	23
3. Materials and Methods.....	24
3.1 Materials.....	24
3.1.1 Apparatus and equipments used.....	24
3.1.2 Chemicals used.....	24
3.2. Methods.....	25
3.2.2. Adsorbent preparation (Bio-sorption material).....	25
3.2.3 Characterization of coffee husk.....	25

3.2.3.1. Proximate analysis	26
3.2.3.1.1. Determination of porosity	26
3.2.3.1.2. Determination of bulk density	26
3.2.3.1.3. Determination of moisture content	26
3.2.3.1.4. Determination of volatile matter	27
3.2.3.1.5. Determination of ash content	27
3.2.3.1.6. Fixed carbon determination	27
3.2.3.2. Infrared spectroscopic analysis	28
3.2.4 Adsorbate preparation	28
3.2.5 Peristaltic pump calibration.....	29
3.2.6 Experimental setup.....	29
3.2.6.1 Continuous Adsorption Experiment	29
3.2.7 Experimental factors and responses	29
3.2.7.1 Study factors	29
3.2.7.2. Factors and the Corresponding Ranges and levels	30
3.2.7.3. Experimental response	30
4. Results and discussion	31
4.1. Characterization of coffee husk	31
4.1.1. Proximate analysis of coffee husk.....	31
4.1.1.1. Bulk density of coffee husk.....	31
4.1.1.2 Dry matter and moisture content of coffee husk.....	31
4.1.1.3 Ash content of coffee husk sample.	32
4.1.1.4 Volatile content of coffee husk sample.	32
4.1.2. FTIR analysis	32
4.1.3 XRD Characterization.....	34
4.2. Analysis of variance (ANOVA) for the design model	35
4.3. Interaction effects of process variables on Cr (VI) and Pb (II) removal ..	37
4.3.1. The interaction effect of adsorbent dosage and pH (AB).....	37
4.3.2. The interaction effect of pH and Flow rate (BC)	39
4.3.3. The interaction effect of adsorbent dosage and Flowrate (AC)	40
4.4. Development of regression model analysis	40

4.5. Optimum conditions for Cr(VI) and Pb (II) removal	43
4.6. Evaluation of adsorption capacity of coffee husk using optimum Condition.....	43
4.6.1 Adsorption capacity of coffee husk at different adsorbent dosages.....	43
4.7. Adsorption capacity of coffee husk at different pH.....	44
4.8. Effect of Flow Rate	46
5. Conclusions and Recommendations	48
5.1 Conclusions	48
5.2 Recommendation.....	49
References.....	50
Appendixes	57
Appendix I: Calculation of Potassium Dichromate Requirement	57
Appendix II: Calculation of Lead nitrate Requirement	57
Appendix III: Calculation of particle density	57
Picnometer was used to determine the particle density of coffee husk as follow	
Appendix IV: Dilution of Cr(VI) Stock Solution from 1000 mg/l.....	58
Appendix V: Generated data in the laboratory	58
Appendix VI; Adsorption Efficiency determination	59
Appendix VIII : Adsorption capacity.....	61
Appendix X: Important plates of the experimental works.....	65
Appendix-XI Peristaltic pump calibration.....	67

List of Tables

Table 1 The use and health effects of some heavy metal on human being.....	13
Table 2 Factors and the corresponding ranges and Levels in continuous experiments	30
Table 3: The proximate analysis result of coffee husk samples	31
Table 4: Frequencies and respective functional groups present on the surface of coffee husk.	33
Table 5: Variables designed for the adsorption of Cr(VI) and Pb(II).....	36
Table 6 Analysis of variance(ANOVA) for percentage removal of Cr(VI) ions.	36
Table 7 Analysis of variance (ANOVA) for percentage removal of Pb(II) ions.....	37
Table 8 Model summary statistics for percentage removal of Cr(VI) ions using coffee Husk	42

List of Figures

Figure 1 FTIR spectrum of coffee husk	33
Figure 2 comparison of powder x-ray diffraction (PXR) pattern for coffee husk	35
Figure 3 3D (a) and 3D(b) plot of the interaction effect of adsorbent dosage and PH (AB) on percentage removal of Cr(VI(a)) and Pb(II)(b) ions using coffee husk respectively.	38
Figure 4.3D plot of the interaction effect of PH and flow rate (BC) on percentage.....	39
Figure 5: 3D plot of the interaction effect of Adsorbent dose and flow rate(AC) on percentage removal of Pb (II) ions using coffee husk.	40
Figure 6: The actual and predicted plot for percentage removal of Cr(VI) (a) and Pb(II)(b) ions.....	41
Figure 7:Plot of Studentized residuals versus experimental run number for Cr(VI)(a) and....	42
Figure 8: Effect of adsorbent dosage on adsorption capacity of Cr(VI)(a) and Pb(II)(b) ions	44
Figure 9: Effect of pH on adsorption capacity of Cr(VI)(a) and Pb(II)(b) ions using coffee.	45
Figure 10: Effect of flow rate on adsorption capacity of Cr (VI)(a) and Pb (II)(b) ions using	47

List of plates

Plate 1 Electrical mill for size reduction.....	65
Plate 2 Sieve separation of grinded coffee husk of x size where $1\text{mm} < x < 2\text{mm}$	65
Plate 3 Washing of grinded coffee husk with plenty of distilled water (a) and Boiling (b).	66
Plate 4 Dried coffee husk (c) and treated coffee husk with formaldehyde (d)	66

1. Introduction

1.1 Background

With its multifarious uses, water is one of the most precious gifts of nature, without which no life could survive on earth. Any human activity that impairs the use of water as a resource may be called water pollution. Industries are the major contributors to water pollution. A large number of pollutants get mixed in the water; the processing wastewater contains many hazardous materials as well as heavy metals above the permissible limits.

Water pollution due to development in technology, continues to be of great concern. With increasing generation of heavy metals from technological activities, many aquatic environments face metal concentrations that exceed water quality criteria designed to protect the environment, animals and humans.

Heavy metals are chemical elements with a specific gravity that is at least 5 times the specific gravity of water and is toxic or poisonous even at low concentrations. Some well known toxic metallic elements are arsenic, (sp.gravity 5.7); iron.(7.9); chromium.(7.19); cadmium,(8.65); lead,(11.34); and mercury,(13.54). Heavy metals are highly dispersed in a wide variety of economically important minerals. They are released to the environment during mineral extraction process. Therefore, mining activities are considered as the primary anthropogenic source of heavy metals.

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

Chromium and lead are extremely toxic heavy metals of widespread use in many industries. The heavy metals pollution represents an important problem, with human health concerns and serious ecological consequences. It is therefore this study aimed to remove heavy metals particularly Chromium(VI) and Lead(II) from industrial waste waters .

1.2 Heavy metal toxicity

Heavy metals are metallic elements which are very toxic and have a high atomic weight and a relatively high density (Duruibe et al., 2007). The body needs many trace heavy metals in small concentrations, but there are another 12 poisonous heavy metals, such as lead, mercury, cadmium, chromium and nickel which are bad for the body (Ravikumar et al., 2015). These poisonous metals affect our enzyme systems and can also affect the metabolism of the body. They are highly toxic and can cause damaging effects to our body even at very low concentrations. Exposure to these elements may cause immediate as well as delayed adverse health effects like the risk of dermal damage, respiratory problems and several kinds of cancer (Anita et al., 2014).

They tend to accumulate in the food chain and in the body. Once they enter our body they get stored in soft and hard tissues which can cause chronic health effects. Environmental contamination and human exposure to heavy metals is a serious growing problem throughout the world. As the use of heavy metals has tremendously increased in the industrial process, humans are being exposed to them.

The toxicity of heavy metals occurs even in low concentrations of about 1.0-10 mg/L. Heavy metals include cadmium (Cd), copper (Cu), lead (Pb), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag), chromium (Cr), iron (Fe), and the platinum group elements (Duruibe et al., 2007). Copper and zinc are essential trace elements for living organism at low concentration less than 10 mg/L of however they become toxic at high concentration greater than 10 mg/L. Most of these metals ions (Cd, Cu, Zn, Hg, As, Ag, Cr, Fe etc) release from the industries are in simple cationic forms (Volesky, 2007).

1.3. Health Effects due to Heavy Metals

The international community is beginning to recognize the adverse health effects of heavy metals (Jiaping, 2012). Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease,

muscular dystrophy, and multiple sclerosis. Allergies are not uncommon, and repeated long-term contact with some metals (or their compounds) may cause cancer. For some heavy metals, toxic levels can be just above the background concentrations naturally found in nature. Therefore, it is important to learn about heavy metals and take protective measures against excessive exposure (Prakasham et al., 1999).

Heavy metals are associated with myriad adverse health effects, including allergic reactions (e.g., beryllium, chromium), neurotoxicity (e.g., lead), nephrotoxicity (e.g., mercuric chloride, cadmium chloride), and cancer (e.g., arsenic, hexavalent chromium). Humans are often exposed to heavy metals in various ways—mainly through the inhalation of metals in the workplace or polluted neighborhoods, or through the ingestion of food (particularly seafood) that contains high levels of heavy metals or paint chips that contain lead (Jarup,2003).

1.3.1 LEAD

Lead (Pb) is considered as one of the priority metals from the point of view of potential health hazards to human, and it is listed by the Environmental Protection Agency (EPA) as one of 129 priority pollutants (A.O. Dada et al.,2013). Lead as a pollutant is a major concern as it has been used as one of the raw materials for battery manufacturing, printing, pigments, fuels, photographic materials and explosive manufacturing. The presence of lead in drinking water even at low concentration may cause diseases such as anemia, encephalopathy, hepatitis and nephritic syndrome (S. Mohan et al., 2008). Severe lead poisoning can cause encephalopathy with permanent damage, while moderate lead poisoning result in neurobehavioral and intelligent deficit. Lead poisoning in humans causes severe damage to kidney, nervous system, reproductive system, liver and brain. According to the United States Environmental Protection Agency (USEPA) the maximum permissible limits in wastewater and potable water are 0.1 mg/L and 0.015 mg/L for lead (II) (Suleman Qaiser et al.,2009).

1.3.2 Chromium

Chromium has been used widely in a variety of industries e.g. textile manufacturing(chrom complex dyeing), wood preserving, chrome tanning and metal finishing plants etc. In wastewater and some natural water chromium exists in two oxidation states, hexavalent chromium Cr(VI)

and trivalent chromium Cr(III). The toxicity of Cr(VI) is believed to be much higher than Cr(III), it is necessary to treat the Cr(VI) containing wastewater before discharged into the environment(Y. Chen et al.,2005). Among the different heavy metals, chromium is a common and very toxic pollutant introduced into natural waters from a variety of industries. (Aksu Z. et al., 2002).

1.4. Environmental Pressures

Stricter regulations with regard to the metal discharges are being enforced particularly in industrialized countries. Toxicology of heavy metals confirms their dangerous impacts. Due to their high toxicity, industrial wastewaters containing heavy metals are strictly regulated and must be treated before being discharged in to the environment. The currently practiced technologies for removal of heavy metals from industrial effluents appear to be inadequate and expensive. They often cause secondary problems with metal bearing sludges. It is therefore essential to develop alternative technologies to treat metal bearing effluents.

1.5 Conventional Methods

Several technologies have been used to treat metal containing aqueous solution, for the last few decades (Wang et al., 2004). Conventional methods for removing heavy metals from industrial wastewater include reduction, reduction followed by chemical precipitation, adsorption on the activated carbon, solvent extraction, cementation, freeze separation, reverse osmosis, ion-exchange and electrolytic methods which are often inadequate for the effective treatment. Major draw backs of some conventional processes can be summarized as follows:-

1.5.1 Membrane process (Reverse osmosis technique)

The concentration of metal ions in the feed stream has to be reasonably low for successful operation of membrane processes. As metal concentration increases, the rejection of the membrane is lowered; membrane scaling is often noted and also high energy will be required to treat them. Cost of membrane is high and productivity decreases with time.

1.5.2 Precipitation and clarification techniques.

It requires excessive amount of chemicals. Consequently, the cost of precipitation can be prohibitively high. Metal complexes with other reagents cannot be treated. The complex has to be broken prior to the precipitation. Not effective in case of wastewater containing very low concentration of metal.

1.5.3 Activated carbon process

Activated carbons are costly inefficient. Its process must be repeated after every regeneration process following the elution of the saturated carbon. After every regeneration step, the activated carbon loses some of its weight and its uptake capacity reduces by approximately 10-20%. A carbon loss also adds some extra cost to the process, adding to the costs of the regeneration and activation steps.

1.5.4 Ion exchange process

Precipitates such as calcium sulphate or ferric oxide can foul ion exchange resins. Ion exchange resins are often very expensive than adsorbents. Resin ions in every cycle have to be replaced. The metal removal capacity of resins is usually affected by the presence of calcium and magnesium ions in the solution.

1.6 Adsorption

Earlier research evidences showed that boosting up the industrial production also gave rise to saturation levels of toxic heavy metals in the environment close to industrial estates. Specific studies on evaluating the toxicity caused by industrial effluents rich in the toxic metals have also been carried out. The environmental contamination situation demands a treatment programs for the effluents coming out from different industries such as lather, electroplating, textile industries etc. and safe disposal of the effluents (Majid M. et al., 2005).

The use of natural adsorbents for removal of heavy metals is related to the treatment of industrial effluents. Plant materials are mainly comprised of cellulose materials that can absorb heavy metal cations in aqueous solution. Numerous waste biomass sources are available in nature in which adsorption properties have been reported e.g rice husk, saw dust, tea and coffee waste,

orange peel peanut shells, activated carbon, dry tree leaves and barks (Asma et al., 2005; Ferda and Selen, 2012; Kishore et al., 2008; Nuria et al., 2010). Adsorption of heavy metal ions occur as a result of physicochemical interaction, mainly ion exchange or complex formation between metal ions and the functional groups present on the adsorbent surface. In the present study coffee husk was used for the removal of lead and chromium from the synthetic waste water prepared in the Laboratory.

1.7. Biosorption

Bio sorption is relatively suitable technique, which can be used to reduce the load of heavy metals in the wastewater since various biological materials have metal binding capacities. The major advantages of bio sorption over conventional treatments include low cost, high efficiency, minimization of chemical and biological sludge, no additional nutrient requirement, and regeneration of bio sorbent and possibility of metal recovery (D. Kratochvil et al., 2006). The focuses on the potential of a wide variety of low cost sorbents for the removal of heavy metals, requires less prior processing, abundantly available in nature, a by-product or waste material of another industry. Coffee husk that was used as an adsorbent in this study is the agricultural by-products or waste obtained from coffee processing units. Coffee husk is an abundant and low-cost adsorbent material on a large scale in many African countries especially in Ethiopia.

Ethiopia is home land of coffee & the prominent producer of coffee in Africa, and has many Coffee processing units. The huge amount of coffee production and the increasing number of coffee husk from processing units in the country indicates the likely increase in quantities of coffee husk residue from processing units. In this study, coffee husk, which is an agricultural waste was used as an adsorbent to remove lead(II)/(Pb²⁺) and chromium(VI)/(Cr⁺⁶) from synthetic waste water prepared in the laboratory under different experiment operational conditions such as flow rate, amount of adsorbent and P^H in Continuous adsorption Experiment.

1.8. Statement of the problem

Environmental pollution derived from domestic and industrial activities was the main threat to the surface and ground water qualities in Ethiopia. Many industries were operated in small and medium scales; these small units can generate a considerable pollution in the environment. It was reported that the majority (90%) of these industries in the country discharge their wastewaters into nearby water bodies and open lands without proper treatment (EPA, 2005). Therefore, the absence of controlled waste management strategies and waste treatment plants, untreated wastes are dumped into water bodies and the surrounding environments. Electroplating, Textile and Tannery industries are among those industries which discharge wastewater without proper treatment. Most of them discharge this wastewater to the receiving water bodies. These wastewaters mainly contain heavy metals and other contaminants at levels that are hazardous to the environment and human health. Studies showed that the vegetable cultivated along the AKaki River contain heavy metals which may attribute partly due to the discharge of untreated wastewater from electroplating industries in Addis Ababa (Fissha Itanna, 1998).

An array of suitable methods exists for the removal of metal pollutants from wastewater that include precipitation, evaporation, electroplating, ion exchange, membrane separation etc. However, these methods also have several disadvantages, such as incomplete metal removal, excessive use of reagents, energy requirements and generation of toxic sludge or other intermediate waste products that require additional disposal procedures and further treatments. Most of these methods become ineffective as well as uneconomical (Z.R.Holan et al., 1994). Studies indicated that treatment techniques like adsorption using agricultural residue are the cheap available option for developing countries like Ethiopia. However, the efficiency of different agricultural residues including coffee husk are not yet investigated in Ethiopia in continuous treatment way. In this study, the adsorbent prepared from locally available materials was tested to see its adsorption efficiency under different operational conditions in continuous experiment which had not been conducted in Ethiopia using coffee husk as adsorbent for the removal efficiency of heavy metals particularly Cr (VI) and Pb (II) from synthetic waste water and seen its industrial applications.

Coffee is one of the most popular beverages in the world in terms of consumption in which its production was 6.7 million metric tons annually in 1998-2000 and rose to 7 million metric tons annually in 2010 (Bhatnagar and Sillanp, 2010). Ethiopia, is the primary center of origin and genetic diversity of Arabica coffee (*Coffea arabica*), which was produced up to 301, 000 tons in 2006 but this was increased to 419,000 tons by the end of 2010 (Henok Kassa et al., 2011). Clearly, this indicates that coffee husk is the main by-products generated by the coffee processing industries and disposed into land and fired. Due to the presence of polyphenols which are considered as anti nutritional and phototoxic substances such as caffeine, tannin, organic acids restricts its larger extent uses in agriculture and imposing problems on the environment.

1.9. Objective

1.9.1. General Objective

To evaluate the heavy metals (Pb and Cr) removal efficiency of coffee husk from synthetic waste water.

1.9.2. Specific Objectives

The specific objectives are:

-) To characterize coffee husk
-) To evaluate of performance of continuous flow packed bed column systems containing adsorbent.
-) To examine operational parameters such as sorbent amount, pH, , flow rate on sorption efficiency from aqueous solution
-) To determine the optimum adsorption behavior of adsorbents using response surface methodology

1.10. Significance of the study

Generally, the expected outcome of this research is development of adsorption technology that can solve in the environmental pollution related with heavy metal ions contamination, especially

water pollution. This intern reduces the problem of cancer caused by contamination of water with heavy metal ions specifically, chromium and Lead which are well known human carcinogen.

In addition to this, using coffee husk as an adsorbent is one way of waste management and recycling. It is also very important for industrial sectors to use this eco-friendly removal mechanism for eco-management and audit scheme accreditation. As a result, this research expected to donate with a better understanding for Environmental Protection Authority in decision making to take care of environmental degradation due to discharge of high level of chromium and Lead concentration. Hence, the information generated in this study may serve as baseline information for researchers to further develop the treatment process at pilot scale and full scale. It will provide dual benefits for coffee processors though creating the opportunities of recycling and selling their wastes in the form of adsorbent. Moreover, the study will give cheap and cost effective treatment option for the industries.

This study was conducted to suggest cost effective and high efficient technique, which can be used to reduce the load of heavy metals particularly chromium(VI) and Lead(II) ions discharged to environment from different industries to meet effluent discharges concentration of the government regulation.

1.11. Scope of the study

Synthetic waste water was prepared from potassium dichromate and Lead nitrate. Adsorption method has proven to be an excellent way to treat west water from chrome complex dyeing in textile industries, electroplating industries, petrochemicals industries, etc. Different adsorbent materials had been used to remove heavy metals from waste water. In this study coffee husk was used directly for adsorption experiment. Adsorbent from agricultural(coffee husk)wastes was evaluated for adsorption of chromium(VI) and Lead(II) from synthetic waste water, and adsorbent dosage , flow rate, and pH effects on adsorption process was analyzed in Continuous adsorption Experiment.

2. Literature Review

2.1 Industrialization and Heavy metal pollution

Industrialization to achieve economic development has resulted in global environmental degradation. Wastewaters obtained from industries are generally much more polluted than the domestic or even commercial wastewaters. Still, however, several industrialists try to discharge their effluents into natural river streams, through unauthorized direct discharges. Such a tendency, on the part of industries may pollute the entire river water to a grave extent, thereby making its purification almost an impossible task. Sometimes, the industries discharge their polluted wastewaters into municipal sewers, thereby making the task of treating that municipal sewage, a very difficult and costly exercise.

The industries are, therefore, generally prevented by laws, from discharging their untreated effluents. Therefore, it becomes, necessary for the industry to treat their wastewaters in their individual treatment plants, before discharging their effluents either on land or lakes or rivers, or in municipal sewers. The characteristics of the produced wastewater are usually vary from industry to industry, and also vary from process to process even in the same industry (Frank R., 2003).

Environmental pollution due to development in modern industrial practice is one of the most significant problems of this century. Of this the contamination of water resources by hazardous pollutants has attracted much serious attention in the last few decades. This is particularly due to their toxic, acute and chronic health effects.

2.2 Heavy Metals in the Environment

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

industrialized countries. Hence, there is a need for controlling the heavy metal emission into the environment.

2.3 Heavy Metal Removal Options from Waste Water

There are several different options currently available for the removal of heavy metals from industrial wastewaters. The most common treatment is chemical precipitation with lime or caustic soda where recovery of metals or water is not a consideration. This technique has certain major disadvantages such as residual solubility of the metals, large requirement of chemicals and generation of a large volume of sludge which requires careful disposal in further steps (Spearot and Peck,1984;Peters et al.,1985; Brierley et al.,1986). Other available treatments such as ion-exchange, reverse osmosis and electro dialysis require high capital investment and running cost (Aderhold et al.,1996). Adsorption is by far the most versatile and widely used technique for the removal of metal ions. Activated carbon has been the standard for industrial wastewater treatment for almost three decades (Fornwalt and Hutchins, 1966). Despite its widespread use, activated carbon still remains an expensive material. In recent years, the research interest in to the low-cost alternatives to activated carbon has grown.

2.4 Sources and Impacts of Heavy Metals

Heavy metals have been used by humans for thousands of years. Heavy metal cations can be introduced into agricultural soils by application of fertilizers, limiting materials, sewage sludge, composts, and other industrial and urban waste materials. Therefore, heavy-metal adsorption reactions, in a competitive system, are important to determine heavy-metal availability to plants and their mobility throughout the soil. The study was conducted to¹³ evaluate the selectivity sequence and estimate the competitive adsorption of several heavy metals in seven different soils with different chemical and mineralogical characteristics. The most common sequences were Cr > Pb > Cu > Cd > Zn > Ni and Pb > Cr > Cu > Cd > Ni > Zn. Chromium, lead and copper were the heavy-metal cations most strongly adsorbed by all soils, whereas cadmium, nickel, and zinc were the least adsorbed, in the competitive situation (Paulo et al., 2001).

Chromium is used in metal alloys and pigments for paints, cement, paper, rubber and other materials. The main human activities that increase chromium concentration in the environment are chemical, leather and textile manufacturing, steel and electro plating industries. Lead occurs in mines and smelters as well as welding of lead painted metal, and in battery plants. Low or moderate exposure may take place in the glass industry.

Chromium ingestion beyond permissible quantities causes various chronic disorders in human beings (Prakasham et al., 1999). Strong exposure to chromium causes cancer in digestive tract and lungs (Donald et al., 1970) and may cause nausea, vomiting, severe diarrhea and hemorrhage (Browning, 1969).

Lead poisoning is headache, irritability, abdominal pain and various symptoms related to the nervous system. Lead encephalopathy is characterized by sleeplessness and restlessness. Children may be affected by behavioral disturbances, learning and concentration difficulties. Recent research has shown that long-term low level lead exposure in children may also lead to diminished intellectual capacity. Prolonged exposure to heavy metals such as cadmium, copper, lead, nickel, and zinc can cause deleterious health effects in humans (Lars Jarup, 2003).

2.5. Heavy metal toxicity

Heavy metals are metallic elements which are very toxic and have a high atomic weight and a relatively high density (Duruibe et al., 2007). The body needs many trace heavy metals in small concentrations, but there are another 12 poisonous heavy metals, such as lead, mercury, cadmium, chromium and nickel which are bad for the body (Ravikumar et al., 2015). These poisonous metals affect our enzyme systems and can also affect the metabolism of the body. They are highly toxic and can cause damaging effects to our body even at very low concentrations. Exposure to these elements may cause immediate as well as delayed adverse health effects like the risk of dermal damage, respiratory problems and several kinds of cancer (Anita et al., 2014).

They tend to accumulate in the food chain and in the body. Once they enter our body they get stored in soft and hard tissues which can cause chronic health effects. Environmental contamination and human exposure to heavy metals is a serious growing problem throughout the world. As the use of heavy metals has tremendously increased in the industrial process, humans are being exposed to them (Table 1).

Table 1 The use and health effects of some heavy metal on human being

Heavy metals	Uses	Health effects	References
Cadmium	Electroplating, fertilizers, mineral processing and Battery manufacturing	Cancer, lung insufficiency, Disturbances in cardiovascular system, liver and kidney damage	Sharma, 1995
Copper	Copper and brass plating, mining, metal industries and copper-ammonium rayon industries	Normocytic, hypochromic anemia, leucopenia and osteoporosis	Aksu and Kutsal, 1997
Chromium	Metal plating, electroplating, leather, mining, galvanometry, dye production	Ulcer, skin irritation, liver and kidney damage	Landis and Yo, 2003; Kumar et al., 2007
Lead	Metal plating, textile, battery manufacturer, automotive and petroleum industries	Spontaneous abortion, damage nervous system, kidney and brain damage	Tunali et al., 2006
Mercury	Metallurgy industries, chemical manufacturing and metal finishing	Memory problems, increased heart rate, tremors, kidney and brain damage	Abia., 2005, Abia., 2006

Source: (WHO, 2008)

2.6. Chromium

Chromium is an essential nutrient for plant and animal metabolism. However, the increasing accumulation of chromium in the environment from industrial outputs has caused great concern. Chromium-contaminated wastewaters can originate from dyes and pigment manufacturing, wood

preserving, electroplating and leather tanning. Chromium exists in III (3+) and VI (6+) oxidation states, as all other oxidation states are not stable in aqueous solutions. Both valences of chromium are potentially harmful (Dakiky et al., 2002). Hexavalent chromium which is primarily present in the form of chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) poses significantly higher levels of toxicity than III(+) valence states (Sharma and Forster, 1995). Conventional methods for removing Cr (VI) ions from industrial wastewater include reduction (reduction followed by chemical precipitation adsorption on activated carbon, solvent extraction, freeze separation, reverse osmosis, ion exchange, photo reduction and electrolytic methods. These methods have found limited application because they often involve high capital and operational costs. (Ozer and Ozerorfina, 2003). Adsorption is an effective and versatile method for removing chromium. Natural materials that are available in large quantities or certain waste products from industrial or agricultural operations have been reported as potential adsorbent for removal of hexavalent chromium Fly ash from thermal power plant (Panday et al., 1985), waste slurry from a fertilizer plant (Srivastava et al., 1989) and Fe (III)/Cr (III) hydroxide obtained from the petrochemical industry (Namasivayam, 1993), blast furnace flue dust and photo film waste sludge (Selvaraj et al., 1997) have been examined for the removal of hexavalent chromium. The adsorption of Cr (VI) on bituminous coal, sphagnum peat moss (Sharma and Forster, 1993), coconut husks and palm pressed fibers, sawdust, sugarcane bagasses, sugar beet pulp and maize hask (Sharma and Forster, 1994) has been reported. Chromium contamination of soil and groundwater is one of the significant environmental problems today. Chromium is believed to be the second common inorganic contaminant after lead. The toxicity of chromium does not reside solely with the elemental form but varies greatly among a wide variety of chromium compounds.

Oxidation state and solubility are crucial factors in this regard (Salimi et al., 2006). Under common environmental conditions Cr (III) compounds are sparingly soluble in water, whereas Cr (VI) compounds are quite soluble. Chromium (III) is considered to be essential to mammals for glucose, lipid, and protein metabolism and hence is an essential dietary element (Salimin et al., 2006).

On the other hand, Cr (VI) is much more toxic and mobile in groundwater than the relatively immobile Cr(III) and possesses mutagenic and carcinogenic activity (Shadreck and Mugadza, 2013). In humans, Cr (VI) exposure caused marked irritation of the respiratory track and ulceration and perforation of the nasal septum in workers in the chromate producing and using industries. Ingestion of 1.0 g to 5.0 g of Cr (VI) as chromate results in severe acute gastrointestinal disorders, hemorrhagic diathesis, and convulsions. Death may occur following cardiovascular shock (Mansor and Hasieb, 2012). The maximum levels permitted in drinking water are 5 mg/L for trivalent and 0.05 mg/L for hexavalent chromium (Acar and Malkoc, 2004). But, there is still uncertainty regarding what daily dose of Cr (VI) is considered toxic and what ingestion concentration of Cr (VI) is acceptable.

Humans are exposed to chromium through breathing, eating or drinking and through skin contact with chromium or chromium compounds. The level of chromium in air and water is generally low. In drinking water the level of chromium is usually low as well, but contaminated well water may contain the dangerous chromium (VI). For most people eating food that contains chromium (III), it is the main route of chromium uptake, as chromium (III) occurs naturally in many vegetables, fruits, meats, yeasts and grains. Various ways of food preparation and storage may alter the chromium contents of food, as in the case of food stored in steel tanks or cans leading to enhanced chromium concentrations. Chromium (VI) is dangerous mainly for people who work in the steel and textile industry. Inhalation of hexavalent chromium compounds can result in ulceration and perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis, and edema.

Respiratory symptoms may include coughing and wheezing, shortness of breath and nasal itch. Chromium and most trivalent chromium compounds (calcium chromate, chromium trioxide, lead chromate, strontium chromate, and zinc chromate) have been listed by the National Toxicology Program (NTP) as having inadequate evidence for carcinogenicity in experimental animals.

2.7. Conventional technologies for heavy metal removal

Metal removal processes are carefully considered not only toxic heavy metal removal in environmental aspects, but also precious metal recovery in industrial aspects. Those metals considered environmentally hazardous, or which are of technological importance, strategic significance or economic value must be removed or recovered at their source using appropriate treatment systems. Although many processes for heavy metal removal or recovery have been studied, more efficient process are needed for recycle of water, strict regulation for the effluent concentration of heavy metals, and the reduction of operating cost. Each treatment process has their own advantages and disadvantages and to know these factors is useful for selection and application to the specific case.

2.7.1. Chemical Precipitation

Chemical precipitation is widely used process for removal of heavy metals from solution. The conventional process of heavy metal removal from industrial wastewater involves chemical precipitation of metals usually by lime, followed by settling of the metal precipitates in a pond or a clarifier. The most commonly used precipitation technique is hydroxide treatment due to its relative simplicity, low cost of precipitant, and ease of automatic pH control. Carbonate precipitation and sulfide precipitation has also been used for the treatment of metal containing waste water. Generally, precipitation has been widely used for its simplicity, but has two drawbacks: it usually results in a net increase in the total dissolved solids of the wastewater being treated, and large amount of sludge requiring treatment, which, in turn, may contain toxic compounds that may be difficult to treat (Lawrence k, 2010).

2.7.2. Ion exchange

Ion-exchange resins have recently found a niche in the market of water and waste-water treatment. Also, they are an effective means of removing heavy metals from wastewater. When the resins are saturated, they must be regenerated with an acid or alkaline medium to remove the metal ions from the resin bed. Ion exchange is efficient in removal of dissolved solids from normally dilute spent rinse waters; it is well suited for use in water purification and recycles, capable of treating for high purity heavy metal solution and sequential operation. However, it

requires pretreatment process to reduce suspended solid concentration in solution to prevent fouling or channeling. However, apart from their cost, which can be prohibitive especially to smaller processing plants, resins are vulnerable to oxidation by chemicals, are affected by the presence of magnesium or calcium ions in solution, and are prone to fouling by precipitates and organics.

2.7.3. Reverse osmosis

Reverse osmosis (RO) may be applied in plating processes removing sodium chloride. RO system requires high-quality feed for efficient operation, thus wastewater must be treated to remove solids prior to RO treatment. Application of membrane technology to metal-bearing waste streams has several major drawbacks. Apart from the expense, membranes are also unable to resist certain types of chemicals and pH values and are prone to deterioration in the presence of microorganisms. Membrane fouling, compaction, scaling, limited life of membranes, dissolution of the membrane by oxidized agents, solvents and other organic compounds, and applicability only to feed streams with low concentrations of metal ions are major limitations associated with the use of membrane technologies.

2.7.4. Flocculation and Coagulation

The coagulation–flocculation processes facilitate the removal of suspended solids, colloidal particles. It is used in the final stage of solids–liquids separation. Coagulation is the destabilization of colloidal particles brought about by the addition of a chemical reagent called coagulant. The addition of another reagent called flocculants or a flocculants aid may promote the formation of the floc. Flocculation is the slow stirring or gentle agitation to aggregate the destabilized particles and form a rapid settling floc. This technique has been known to be capable of removing heavy metals from solution.

2.7.5. Flotation

Flotation has nowadays found extensive use in wastewater treatment. Flotation has been employed to separate heavy metal from a liquid phase using bubble attachment, originated in mineral processing. Dissolved air flotation, ion flotation, and precipitation flotation are main

flotation process for the removal of metal ions from solution. Ion flotation has been shown that a promising methods for the removal of heavy metal ions from wastewaters (Fenglian Fu and Qi. Wang, 2011)

2.7.6. Electro dialysis

Electrolytic metal recovery is one of a number of technologies capable of removing metals from wastewater. Electrolytic industrial processes for metals include the production of metals themselves from their compounds, which is called the electro winning of metals; the electrolytic purification of metals; and the deposition or electroplating of metals on conducting surfaces. This process is a highly energy dependent and labor-intensive process. Electro dialysis is a process that efficiently maintains a low metal ion concentration in the anodizing bath solution by transporting metal ions from the bath solution through a selective membrane into a capture media using an electrical current to induce flow. In the electro dialysis process, ionic components of a solution are separated through the use of semi permeable ion-selective membranes (Lawrence k, 2010).

2.8. Heavy metal removal using bio sorption

The conventional heavy metal removal processes have several disadvantages such as less effective removal of metal ion, high reagent requirement, high costs, the generation of toxic sludge's, and the problem of the safe disposal of the materials. Compared with conventional methods for removal of toxic heavy metals, bio sorption process offers the advantages of low cost, minimization of the volume of chemical and biological sludge to be disposed of, high efficiency in detoxifying very dilute effluents, and high metal selectivity. The advantages of bio sorption are cost effective, metal selective, regenerative, minimization of sludge generation, metal recovery, and competitive performance.

2.9. Adsorption

Adsorption is a surface phenomenon and is defined as the increase in concentration of a particular component at the surface or interface between two phases. Compound (pollutant) that sticks or adheres to the solid surface is called adsorbate and the solid surface is known as an adsorbent. adsorption is affected by temperature, the nature of adsorbate and adsorbent, the presence of other

pollutants and atmospheric and experimental conditions like pH, concentration of pollutants, contact time and particle size of the adsorbent. Bio sorption of heavy metals from aqueous solutions is a relatively new process that has been confirmed a very promising process in the removal of heavy metal contaminants. The major advantages of biosorption are its high effectiveness in reducing the heavy metal ions and the use of inexpensive biosorbents. Biosorption processes are particularly suitable to treat dilute heavy metal wastewater (Fenglian Fu and Qi Wang, 2011)

Adsorption can be a potential alternative to traditional treatment processes of metal ions removal (Ayhan, 2008; Mckat et al., 2000;Mohsen,2007). The phenomenon of adsorption has been described in a wide range of non-living biomass like potato peel waste (Mohammed and Devi, 2009), untreated Cocos Nucifera (Prasad and Satya, 2010), orange peel (Ferda and Selen, 2012), crab shell (Vijayaraghavan et al., 2005), untreated coffee grounds(Azouaou et al., 2010), as well as of living biomass like, microbial cell (Gopal et al., 2002), moss (Lee and Low,1989),yeast (Can and Jianlong, 2008), fungi (Sudha and Emilia, 2002), algae (Dumitru and Laura, 2012; Gupta and Rastogi, 2008; Mohammad Mehdi et al., 2011) orange peel (Ferdaand Selen, 2012).

Adsorption has been proved to be an excellent way to treat industrial waste effluents, offering significant advantages like the low-cost, availability, profitability, easy of operation and efficiency (Demirbas, 2008).

The use of microbial biosorbents for removal of toxic heavy metals from waste waters offers a relatively low cost method with potential for metal recovery. Adsorption has distinct advantages over the conventional methods: the process does not produce sludges requiring further disposal, it could be highly selective, more efficient, easy to operate, can handle large volumes of waste waters containing low metal concentrations. The metal sequestering ability of microorganisms such as yeast, bacteria, fungi and algae have been investigated and reported. Adsorption technology based on the utilization of dead biomass offers certain major advantages such as lack of toxicity constraints, non requirement of nutrient supply, and recovery of bound metal species by desorption (Gadd, 1990).

2.10. Types of Adsorbents

In the last few decades, alternative sorbents for the treatment of heavy metal contamination have been investigated (Abdelwahab, 2007; Amany, 2007; Bayat, 2002; Cetin and Pehlivan, 2007; Mustafa, 2008; Nuria et al., 2010; Srinivasan and Viraraghavan, 2010; Wan and Hanfiah, 2007). There is a large volume of literature relating to the performance of different biosorbents for the removal of variety of heavy metals (Larous et al., 2005; Uysal and Ar, 2007; Qi. and Aldrich, 2008; Atalay et al., 2010). The agricultural residues seem to be preferred (Pollard et al., 1992; Nasernejad et al., 2005; Johnson et al., 2002; Horsfall et al., 2006) and green coconut shells are a most appropriate example for the adsorption removal of inorganic and organics (Crisafully et al., 2007) pollutants. Plant materials are mainly comprised of cellulose materials that can absorb heavy metal cations in aqueous solution. Numerous waste biomass sources are available in nature in which some experimental adsorption properties have been reported e.g rice husk (Kishore et al., 2008), saw dust (AjayKumar et al., 2008; Mehmet et al., 2007; Bin et al., 2000), tea and coffee waste (Amir et al., 2005; Amarasinghe and Williams, 2007), orange peel (Ferda and Selen 2012) peanut shells (Qin et al., 2007), activated carbon (Kadirvelu et al., 2001; Gulnaziya et al., 2008) dry tree leaves and barks (Benhima et al., 2008; King et al., 2006; Venkateswarlu et al., 2007). In literatures, studies were conducted using banana peel for As(III) (Suantak et al., 2012) and watermelon rind for Ni(II) and Co(II) (Lakshmi pathy and sarada, 2013). Azouaou et al. (2010) studied the effect of various parameters on adsorption capacity using untreated coffee grounds as adsorbent. They found that the adsorption process is a function of the adsorbent concentration, pH, metal ion concentration and temperature. Mishra and Pate (2009) examined the role of low cost adsorbents on lead and zinc ions removal from waste water. Venkateswarlu et al. (2006) carried out investigations on *Azadirachta indica* (neem) leaf powder as an adsorbent on chromium removal from aqueous solution. The results indicated that the adsorption capacity is strongly depends on equilibrium pH. Waleska et al. (2008) used the untreated coffee husks as adsorbents for the removal of heavy metal ions such as Cd(II), Cu(II) and Zn(II) from aqueous solution. The results indicated that the highest adsorption capacity occurred at distinct pH values for each metal ion.

2.11. Adsorption Mechanisms

The complexity of the adsorbent structure implies that there are many ways for the metal to be captured by the cell. Adsorption mechanisms are therefore various and in some cases they are still not very well understood.

Metal adsorption and biosorption onto agricultural wastes is a rather complex process affected by several factors. Mechanisms involved in the biosorption process include chemisorption, complexation, adsorption-complexation on surface and pores, ion exchange, microprecipitation, heavy metal hydroxide condensation onto the biosurface, and surface adsorption (Demirbas, 2008; Semerjian, 2010) They may be classified by the following different criteria.

2.11.1 Physical adsorption

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

2.11.2. Ion exchange

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

1982). Alginates of marine algae usually occur as natural salts of K^+ , Na^+ , Ca^+ and Mg^{2+} . These metallic ions can exchange with the counter ions such as Co^{2+} , Cu^{2+} , Cd^{2+} and Zn^{2+} resulting in the biosorptive uptake of the metals (Kuyucak and Volesky 1989). Ion exchange was proposed to be the mechanism of copper biosorption by fungi *Ganoderma lucidum* (Muraleedharan and Venkobacher, 1990) and *Aspergillus niger*. Yasemin and Zeki (2007) also hypothesized that adsorption of Ni(II), Cd(II) and Pb(II) from aqueous solution by shells of hazelnut and almond take place through ion exchange. The major components of the polymeric material in shell are lignin, tannins or other phenolic compounds. Based on the structure of the phenolic compounds a possible mechanism of ion exchange could be considered as a divalent heavy metal ion (M^{2+}) that attaches itself to two adjacent hydroxyl groups and two oxy groups which could donate two pairs of electrons to metal ions forming four coordination number compounds and releasing two hydrogen ions into solution.

2.11.3. Complexation

The metal removal from solution may also take place through complex formation on the cell surface after interaction between the metal and active groups. Metal ions can bind to unidentate (single).ligands or to chelates (Cabral, 1992; Tsezos and Volesky, 1982) proposed that adsorption by *Rhizopus arrhizus* has a mechanism not only based on physical adsorption, but also on metal complexation with nitrogen of the chitin cell wall network. Cabral (1992) also hypothesized that metal complexation was found to be the only mechanism responsible for calcium, magnesium, cadmium, zinc, copper and mercury accumulation by *Pseudomonas syringes*.

2.11.4 Precipitation

Precipitation of the metals may take place both in solution and on the cell surface. Furthermore, it may be either dependence on the cellular metabolism if, in the presence of toxic metals, the microorganisms produce compounds, which favor the precipitation process. In case where precipitation is not dependent on the cellular metabolism, it may be a consequence of the chemical interaction between the metal and the cell surface. This phenomenon is the terminal step of uranium biosorption by *Rhizopus arrhizus* (Tsezos and Volesky, 1982) the formation of the complex uranium–chitin, mentioned above, is followed by the complex hydrolysis and the

precipitation of the hydrolysis product uranyl hydroxide in the cell wall. Holan and Volesky (1994) proposed that an additional mechanism, such as entrapment of metals in the form of insoluble micro deposits, could greatly contribute to cadmium adsorption by the biomass marine algae.

2.12. Factors affecting adsorption process

2.12.1. Contact time

The removal efficiency increased with an increase in contact time before equilibrium is reached. The amount adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under the operating conditions (Samna et al., 2013).

2.12.2. Concentration

Different initial metal concentration and a fixed concentration of biomass were used to calculate adsorption capacity. The removal efficiency decreased with increasing initial concentration. The initial and final concentrations of were measured by atomic absorption spectrophotometer (Adhena et al., 2014)

2.12.3. Adsorbent dose

The adsorbent dosage is an important parameter because this determines the capacity of an adsorbent. The removal of metal ions increases with an increase in the adsorbent dosage. The effect of adsorbent dosage on adsorption was studied by varying the amount of adsorbents and keeping the other parameters constant (Dakiky et al., 2002; Azouaou et al., 2010)

2.12.4. pH

For biosorption of heavy metal ions, pH is one of the most important environmental factors. The pH value of solution strongly influences not only the site dissociation of the biomass surface, but also the solution chemistry of the heavy metals: hydrolysis, complexation by organic or inorganic ligands, redox reactions, precipitation, the speciation and the bio sorption availability of the heavy metals. The pH of the solution was clearly an important parameter that controlled the adsorption process (Jianlong et al., 2006)

3. Materials and Methods

Laboratory experiments presented in this chapter were carried out in order to evaluate the adsorption efficiency of the coffee husk. A series of experiments were conducted to determine the removal efficiency of heavy metals; namely, Cr(VI) and Pb (II) using coffee husk. The experiments utilized with coffee husk on adsorption processes. In addition to the adsorption experiments, a material physical characteristics experiments were carried out in order to know the surface characteristics of the coffee husk used in these experiments Therefore, the purpose of this section is to mention the chemicals, material, and instruments used and methodology followed to achieve the objectives of the study.

3.1 Materials

3.1.1 Apparatus and equipments used

In this experiment the apparatus and equipment were required to set up the continuous tests and to analyze the samples. Beaker, volumetric flasks, graduated cylinder, funnel, tube, pipettes, plastic and glass bottles, Plastic stirrer, peristaltic pump and magnetic stirrer are some of the apparatus were used during continuous tests. 2% formaldehyde treated coffee husk sample was dried in hot air oven at 105°C for 12 hrs to 24hrs depending on the amount of coffee husk in the oven and electrical furnace was used to determined ash content and volatile content of the samples. Fourier transform infrared (FTIR) spectra were recorded using (Perkin Elmer, Spectrum 65FT-IR spectrophotometer) to analyze the functional groups present in the adsorbent. Solution pH was adjusted using pH meter. Atomic absorption-spectrophotometer was used to evaluate the initial and final Cr (VI) and Pb (II) ions concentration.

3.1.2 Chemicals used

All chemicals used in this study were analytical reagent grade and were used without further purification. Analytical grade of potassium dichromate ($K_2Cr_2O_7$) and Lead nitrate ($Pb(NO_3)_2$) salts was dissolved separately in distilled water for stock solution preparation to simulate the industrial wastewater, 2% formaldehyde solution was used in treatment of coffee husk in order to reduce biodegradation of organic compounds and avoid mould formation during continuous

sorption (Chen, 2005), 0.1MNaOH and 0.1MHCl were used to adjust the solution pH of the experiments.

3.2. Methods

The treatment process has been done at Addis Ababa Institute of Technology; laboratory room particularly environmental laboratory of school of Chemical and Bio-engineering and the concentration analysis before and after treatments were done at Addis Ababa University College of natural and computational science and Ethiopian geological survey laboratories using Atomic absorption spectrophotometer.

3.2.2. Adsorbent preparation (Bio-sorption material)

Coffee husk collected from local coffee processing unit was used in this study as adsorbent. Then the collected coffee husk sample was grinded by using electrical mill and allowed to pass through different mm sieves (2, 1 mm) as shown in plate-1 and 2 at appendix-IX and the grinded and sieved coffee husk was washed with plenty of distilled water to remove dirt and boiled for about three hours by string with electrical stirrer(Motor agitator) at 100rpm to remove color. Then it was filtered and dried at 105 °C for 12 h to 24h depending on the amount of coffee husk in a convection oven. Finally, it was treated with 2% formaldehyde solution in order to reduce biodegradation of organic compounds and avoid mould formation during continuous sorption (Chen, 2005) and then air dried .

3.2.3 Characterization of coffee husk

The moisture content and ash content of the coffee husk were determined by gravimetric techniques using drying oven and muffle furnace (Sheffield, S302RR, England), respectively. Bulk density was determined using measuring cylinder. The porosity of the grinded coffee husk to a size of $1 \leq X < 2$ was determined based on the particle density and bulk density of the coffee husk according to (Nimmo, 2004).

3.2.3.1. Proximate analysis

3.2.3.1.1. Determination of porosity

The porosity was determined using bulk density and particle density of the Coffee husk. After obtaining these two densities then the values introduced to equation (1).

$$\text{Porosity (\%)} = \left(1 - \frac{\text{bulk density}}{\text{particle density}}\right) \times 100 \text{-----(1)}$$

3.2.3.1.2. Determination of bulk density

The bulk density was determined according to ASTM D2854-96 method that 100cm³ cylinder was weighed and a coffee husk sample was packed by repeatedly tapping the cylinder in order to fill up to the marked level of the cylinder. The cylinder was then weighed and the difference in the weight gave the weight of coffee husk taken in the cylinder. The bulk density of the prepared coffee husk was calculated by taking the ratio of weight of the prepared coffee husk taken in the measuring cylinder to the tapped volume of the measuring cylinder.

$$\text{Bulk density (g/m}^3\text{)} = \frac{\text{weight of dry sample (g)}}{\text{volume of packed sample (m}^3\text{)}} \text{----- (2)}$$

3.2.3.1.3. Determination of moisture content

Moisture content was determined using ASTM D2867-91 method. A crucible was weighed and 5g of coffee husk was taken and after then the crucible was placed in an electric hot air oven maintained at 105⁰C for 3 hour. According to Nwabanne and Mordi (2009). Then the crucible was taken out, cooled in a portable desiccators and weighed again. Heating and weighing was continued until obtaining value and the loss in weight of the prepared coffee husk gave percentage of the moisture content in the sample of coffee husk used for adsorption. Then percent of moisture content was determined using (equation 3). Moisture content (%) = loss in weight on drying (g)/initial sample weight (g) x100.

$$\text{Moisture content} = \frac{((W_1+W_2) - (W_1 + W_3))}{W_2} \times 100 \text{-----(3)}$$

Where, W_1 = weight of dish

W_2 = weight of sample

W_3 = weight of residue after drying

3.2.3.1.4. Determination of volatile matter

About 2.5g of the prepared and dried coffee husk was taken in previously weighed crucible. The crucible was placed in a muffle furnace maintained at about 925⁰C, according to David et al., (2006). It was taken out exactly at 10 minutes. The crucible was cooled in desiccators and weighed again. The result was calculated using equation 4 in order to obtain the percent of volatile matter.

$$\text{Volatile matter (\%)} = \frac{\text{weight of volatile components (g)}}{\text{Oven dried weight (g)}} \times 100 \text{-----(4)}$$

3.2.3.1.5. Determination of ash content

Ash content determination was done according to the ASTM D2866-94 method. 2.5g The residual coffee husk after loss of the moisture was placed in a porcelain crucible and transferred into a preheated muffle furnace at a temperature of 550 °c for 5 hour. The crucible was cooled in a desiccators and weighed again. The heating, cooling and weighing cycle was repeated until constant weight was obtained, then the weight lost was recorded as the ash content of the coffee husk sample. The percent ash content (dry basis) was calculated as:

$$\text{Ash (\%)} = (\text{Wight of ash/oven dry Wight}) \times 100$$

$$\text{Ash content} = \frac{((W_1 + W_3) - W_1)}{W_2} \times 100 \text{----- (5)}$$

Where W_1 = weight of dish

W_2 = weight of sample

W_3 = weight of residue after igniting

3.2.3.1.6. Fixed carbon determination

The fixed carbon content of the coffee husk is the carbon found in the material which is left after volatile materials are driven off. This differs from the ultimate carbon content of the coffee husk

because some carbon is lost in hydrocarbons with the volatiles. Fixed carbon is used as an estimate of the amount of charcoal that will be yielded from a sample of coffee husk. Fixed carbon was determined by removing the mass of volatiles determined by the volatility test, ash test, and moisture test above, from the original mass of the coffee husk sample (Baier *et al.*, 2006). The fixed carbon content was determined using the formula in the Eq. (6).

$$C_F (\%) = 100 - V_c - A_c - M_c \text{-----} \quad (6)$$

Where, C_F is fixed carbon, V_c is volatile content, A_c is ash content and M_c is moisture content

3.2.3.2. Infrared spectroscopic analysis

The Fourier transform infrared (FTIR) spectrometer (Model 65 spectrometer, USA) was used to identify the functional groups present in the coffee husk in the wave number range of 400 – 4000 cm^{-1} . For this purpose 1mg of coffee husk was placed on KBr disk and dissolved with 10 drops of paraffin. Then the KBr disk with the sample was immediately put into sample holder.

Then FTIR spectra were recorded. Coffee husk was analyzed before and after metals ions (Cr^{+6} and Pb^{2+}) adsorption for each using Fourier transform infrared spectrometer to see the functional groups that might involve in the sorption of chromium and lead metal ions. Samples of 1mg KBr disks containing 1% finely ground powder ($<20\mu\text{m}$) samples were prepared for this study. Samples of the adsorbent were subjected to Fourier transform infrared spectrometer (FTIR).

3.2.4 Adsorbate preparation

Stock solutions of lead (II) and Cr(VI) were prepared by dissolving 1.6g of lead nitrate and 2.83g of potassium dichromate respectively in 1000ml distilled water in different 2000ml beakers. About 20mg/l concentrations of metal ions were prepared by diluting 100ml of the stock solutions to 5000ml separately in different 5000ml beakers. The pH was maintained using 0.1M HCl and 0.1M NaOH solutions to desired level for the treatment to be continued and investigated the effect of varying P^{H} on adsorption of chromium (VI) and Pb (II) by coffee husk. In this study synthetic waste water have been selected due to the absence of the intended heavy metals to significant level or concentration in the waste water samples taken from B-CONNECTED INDUSTRIAL which found in Dukem eastern industrial zone and performing the activities of

printing only while the textile industries particularly DONGFANG SPINNING PRINTING AND DYEING PLC which is located in the same industrial zone as B-CONNECTED INDUSTRIAL was not willing to give the industry effluents (textile waste water which may contain metals like Pb, Cr, etc. that have alarming pollution impact on the environment).

3.2.5 Peristaltic pump calibration

The calibration of peristaltic pump was done by measuring the volume of the synthetic waste water pumped per minute at different speed of the pump. As it is summarized in Table-1 (Appendix-X), the lower and higher flow rate of the pump was calibrated at a speed of 2.5 and 5.8 rpm, respectively.

3.2.6 Experimental setup

The detail information of experimental setup that was used in this research is presented below.

3.2.6.1 Continuous Adsorption Experiment

The wastewater samples were percolated through the 250ml buret glass with pieces of almost inert plastic (bush) which is placed at the bottom and serves as a bed as indicated in appendix IX plate- 9(a) and then 10-30g coffee husk having particle size 'X' where $1\text{mm} \leq X < 2\text{mm}$ was filled which acts as adsorbent as shown in appendix IX plate- 9(b). The wastewater samples were passed through this 250ml buret glass at different levels of adsorbent dose, flow rate and P^H . All concentration measurements before and after adsorptions were performed in two replicate, and mean values were considered in data analysis.

3.2.7 Experimental factors and responses

3.2.7.1 Study factors

The effects of the factors listed below on the removing efficiency of coffee husk were studied in continuous experiments. Study factors in continuous experiment are Flow rate, Adsorbent dose and pH. The three factors in continuous experiments were analyzed against three levels for each variable and analysis was done to know their effect on the removing efficiency of coffee husk.

3.2.7.2. Factors and the Corresponding Ranges and levels

Table 2 Factors and the corresponding ranges and Levels in continuous experiments

Factors	Range	Levels
pH	3-12	3,7.5 and 12
Adsorbent dose	(10-30) gm/100 ml	10,20, and 30
Flow rate	5-15ml/min	5,10 and 15

3.2.7.3. Experimental response

The degree of removal of heavy metals (Cr and Pb) or removing efficiency of coffee husk is the response of this research or experiment and shown in the Appendix VI; Table 1 & 2 for Cr(VI) and Pb (II) respectively.

3.2.8. Data Analysis

The basic statistical analysis of generated data was done by Microsoft excel and inferences was drawn using Design-Expert 7.0.0 and Origin 6.0.

4. Results and discussion

4.1. Characterization of coffee husk

4.1.1. Proximate analysis of coffee husk

The preliminary investigation of proximate analyses for coffee husk was done to understand the performance of coffee husk for further studies. The obtained values are presented in Table (2).

Table 3: The proximate analysis result of coffee husk samples

Parameter Test	Result of Coffee husk
porosity	74%
Bulk density	0.43g/ml
Moisture content	14.59%
Volatile content	82.70%
Ash content	2.36%
Fixed carbon	0.35%
Percentage of dry matter	85.41 %

4.1.1.1. Bulk density of coffee husk

On evaluation of surface characteristics of coffee husk, it was observed that coffee husk had a bulk density of 0.43 g/ml. Bulk density is an important physical parameter especially when an adsorbent is to be investigated for its filterability. Higher density provides greater volume activity and normally indicates high quality adsorbent (Kundu; Gupta, 2006).

That is, it would be able to filter more liquid volume before available cake space is filled and it can be stable or without degraded with the solution (Bai. *et al*, 2006).

4.1.1.2 Dry matter and moisture content of coffee husk

The laboratory results of the moisture content of coffee husk were determined to be 14.59%, whereas dry matter content of sample was determined to be 85.41% as shown in Table(2). The moisture content of a sample refers to the percentage of water content of the sample. These gave

a tangible and substantial amount of organic matter needed for removal. Hence, the results obtained for coffee husk samples were good since the yield and quantity of the coffee husk produced can be enhanced by removal of moisture.

4.1.1.3 Ash content of coffee husk sample.

On investigation the proximate analyses of coffee husk as presented in Table (2) showed that Coffee husk contains small amount of inorganic constituents and large amount of volatile organic compound. When coffee husk is exposed to water, mostly some inorganic matters in coffee husk may be leached out in water. Inorganic matter exists in two forms. One is the inherent mineral matter within the coffee husk particles, and the other is adventitious inorganic material remaining external to the coffee husk particles (Chenet *et al.*,1999). The percentage of ash content for coffee husk samples was found to be 2.36 % .The obtained value for coffee husk was favorable because the ash content serves as interference during the adsorption. The lower the ash content the better the starting material for adsorption (Khan *et al.*,2009).

4.1.1.4 Volatile content of coffee husk sample.

The percentage of volatile content for coffee husk samples was 82.70 % as shown in Table (2). The higher volatile content of coffee husk showed that some of organic molecules of the material was attacked and it is stable for adsorption experiment of Cr (VI) and Pb (II) ions from aqueous solution.

4.1.2. FTIR analysis

The result of FTIR study of an adsorbent before and after loaded with metal is presented in Fig 1. As it can be seen from the figure there are different peaks and there was a change after the adsorbent loaded with metals. In the figure the broad absorption peak between 3200 - 3500 cm^{-1} was indicative of alcohols and H-bonded phenols (O-H stretching). The dominant adsorption peak between 2850-3000 cm^{-1} indicates the presence of alkanes and aldehydes (C-H stretching). The medium adsorption peak between 1620-1680 cm^{-1} indicates -C=C- stretch alkenes.

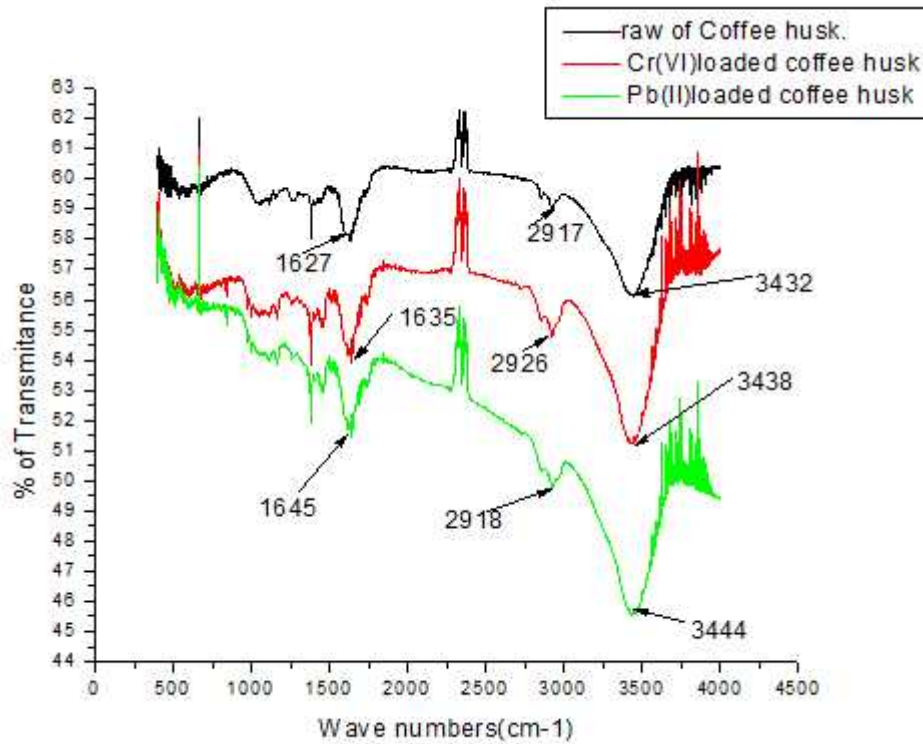


Figure 1: FTIR spectrum of coffee husk

Table 4: Frequencies and respective functional groups present on the surface of coffee husk.

Frequencies(Cm-1)	Bond	Functional group
3500-3200	O-H stretch, H-bonded	Alcohols, phenol
3000-2850	C-H Stretch	Alkanes and Aldehydes
1680-1620	-C=C- stretch	Alkenes

Fig 1 shows the spectrum of coffee husk displayed a number of sorption peaks, indicating the complex nature of the material investigated.

The FTIR Spectroscopic analysis indicated broad bands at 3448 cm^{-1} , 3438 cm^{-1} and 3432 cm^{-1} representing bonded $-\text{OH}$ groups rather than $-\text{NH}$ group. This is because of the peak of O-H stretching is broad with rounded tip but the peak for bonded-NH group is a broad peak with two sharp spikes (primary amines), a broad peak with one sharp spike (secondary amines) or no signal (tertiary amine). The bands observed at about $2955\text{--}2852\text{ cm}^{-1}$ shows the presence of C-H stretching which are related to the asymmetric stretching of C-H bonds of methyl ($-\text{CH}_3$) group in the caffeine molecule and can be successfully used to develop predictive models for quantitative analysis of caffeine (Paradkar and Irudayaraj, 2002). But, there is no aldehydic C-H because the aldehydic C-H stretching vibration occurs in the region of $2830\text{--}2700\text{ cm}^{-1}$ with the appearance of two intense bands.

The peaks around 1645 cm^{-1} correspond to the $\text{C}=\text{C}$. These types of functional groups are important sorption sites to participate in metal binding (Ahalya *et al.*, 2006).

4.1.3 XRD Characterization

X-ray diffraction (XRD) is a material characterization technique that can be useful for analyzing the lattice structure of a material. It investigates crystalline properties of a synthesized material. The XRD patterns of the adsorbents are presented in Figures 2. Low and high intensity Bragg diffraction peak were observed for the adsorbents. The XRD showed no peaks from impurities, indicating high purity of the adsorbents. The X-ray diffraction (XRD) analysis of coffee husk before adsorption and coffee husk after adsorption of hexavalent chromium and lead showed peaks that are amorphous in nature of biomass. The crystallinity parts give sharp narrow diffraction peaks and the amorphous component gives a very broad peak (halo).

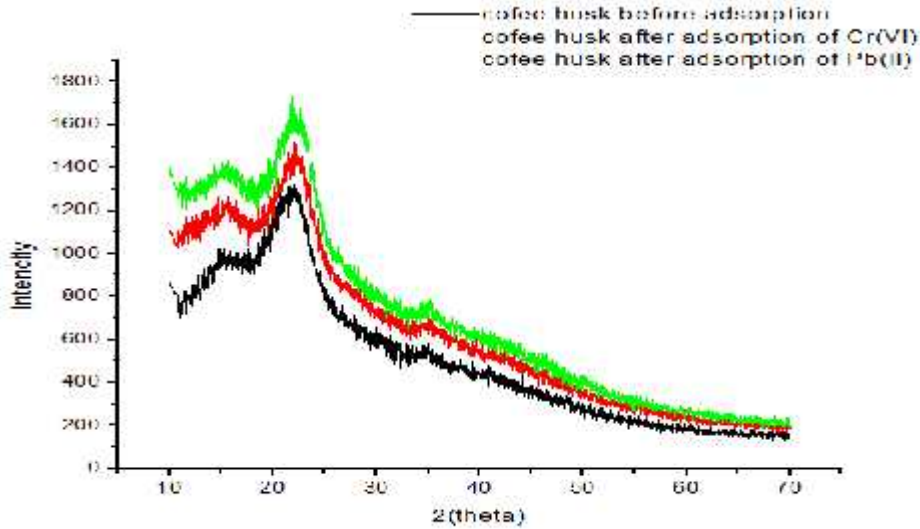


Figure 2: comparison of powder x-ray diffraction (PXRD) pattern for coffee husk

4.2. Analysis of variance (ANOVA) for the design model

A total of 60 experiments(27 experiments for Cr(VI), 27 experiments for Pb(II) and 6 experiments. with the bed(bush).The 6expts. were done at different PH and low flow rate(5ml/min) to see the effect during the experiments. The six experimental results revealed that the bed (bush) has no significant effect(0.00015 and 0.000083 mg/l) on adsorption of Cr(VI) and Pb(II) respectively. Replication of three measurements was done to see precision of the measurements. The single dependent output response of percentage removal (Y1) was obtained from the independent input variables for general full factorial design (GFFD) and is presented in Appendix VI.The quadratic effects of three independent variables adsorbent dosage, solution pH and flow rate each with three levels were chosen as independent variables with designated factors as A, B, and C, respectively, and the variables are presented in Table 4.

Table 5: Variables designed for the adsorption of Cr(VI) and Pb(II).

Independent Variables	Factors	Range & Level Variables		
		Low Level	Medium Level	High Level
1. Adsorbent dosage (g)	(A)	10	20	30
2. PH	(B)	3	7.5	12
3. Flow rate(ml/min)	(C)	5	10	15

The ‘Statistics’(ANOVA) on Cr(VI) and Pb(II) ions percentage removal using coffee husk value with low probability P value ($P < 0.0001$) indicating that the model suggested by the software was highly significant. The Model F value of 48.3 and 34.82 implies that significant for percentage removal. In this case for percentage removal A, B, C, AB, BC, B², C² and A,B,C,AB,AC,B² for Cr(VI) and Pb(II) respectively are statistically significant ($P < 0.05$) model terms at the 95% confidence level. The ANOVA summary is given in Table 5 and 6 for Cr(VI) and Pb(II) respectively.

Table 6 Analysis of variance(ANOVA) for percentage removal of Cr(VI) ions.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Significance
Model	808.63	9	89.85	48.3	< 0.0001	significant
A-dose	174.66	1	174.66	93.90	< 0.0001	
B-PH	308.10	1	308.101	65.64	< 0.0001	
C-Flo rate	224.0	1	224.01	120.43	< 0.0001	
AB	9.21	1	9.21	4.95	0.0399	
AC	3.675E-003	1	3.675E-003	1.976E-003	0.9651	
BC	66.84	1	66.84	35.93	< 0.0001	
A ²	0.094	1	0.094	0.050	0.8250	
B ²	10.43	1	10.43	5.61	0.0300	
C ²	15.30	1	15.30	8.22	0.0107	
Residual	31.62	17	1.86			
Cor Total	840.25	26				

Table 7 Analysis of variance (ANOVA) for percentage removal of Pb(II) ions.

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F	Significant
Model	611.45	9	67.94	34.82	< 0.0001	Significant
A-CH. dose(grams)	376.45	1	376.45	192.95	< 0.0001	
B-PH	138.03	1	138.03	70.75	< 0.0001	
C-Flow rate(ml/min.)	35.46	1	35.46	18.17	0.0005	
AB	9.42	1	9.42	4.83	0.0421	
AC	12.61	1	12.61	6.47	0.0210	
BC	0.28	1	0.28	0.14	0.7091	
A ²	2.24	1	2.24	1.15	0.2994	
B ²	36.89	1	36.89	18.91	0.0004	
C ²	0.069	1	0.069	0.036	0.8526	
Residual	33.17	17	1.95			
Cor Total	644.62	26				

4.3. Interaction effects of process variables on Cr (VI) and Pb (II) removal

The interaction effect of process variables for percentage removal of Cr(VI) and Pb (II) ions using coffee husk were visualized through contour and 3D plots of three dimensional views of response surface as a function of two independent variables, maintaining all other variables at fixed or different level. These plots can be helpful in understanding both the main and interaction effects of the independent variables on the response variable.

4.3.1. The interaction effect of adsorbent dosage and pH (AB)

The interaction effect of adsorbent dosage and pH value on percentage removal of Cr (VI) and Pb(II) ions using coffee husk is shown in Contour (a) and 3D (b) for Cr(VI) and (C) and 3D(d) plot of Pb(II) as shown in Figure 26 below. The maximum percentage removal of Cr(VI) ion using coffee husk was obtained at lower pH and higher adsorbent dosage whereas the maximum percentage removal of Pb (II) ion was obtained at high PH and adsorbent dose. The graph shows that the maximum adsorption (99.8%) occurs under acidic conditions, pH 3 and adsorbent dose of 30 g. Increasing the solution pH from 3 to 12, decreasing removal to 87.9 % for Cr (VI) and increase the removal from 79.5 to 99.45 for Pb (II). This may be due to the surface positive

oxygen-containing functional groups of the coffee husk adsorbent carried the oxyanions (negatively charged) of Cr(VI) ions by electrostatic force of attraction. At higher pH, the increased negative charges on the adsorbent surface decreased the attraction of oxyanions of Cr(VI) ion and increase the attraction of Pb(II) cation on the adsorbent.

Design-Expert® Software

Removing efficiency

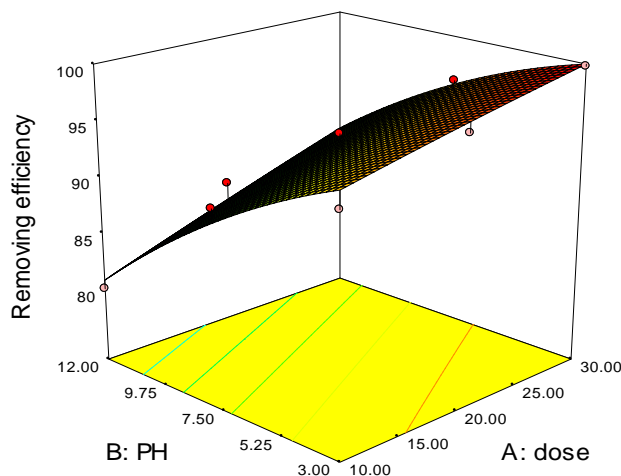


X1 = A: dose

X2 = B: PH

Actual Factor

C: Flo rate = 5.00



(a)

Design-Expert® Software

%Removing efficiency of Pb(II)

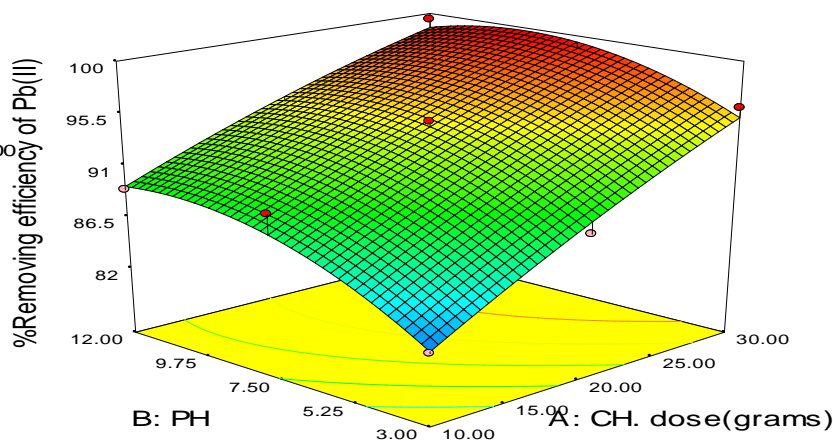


X1 = A: CH. dose(grams)

X2 = B: PH

Actual Factor

C: Flow rate(ml/min.) = 5.00



(b)

Figure 3 3D (a) and 3D (b) plot of the interaction effect of adsorbent dosage and PH (AB) on percentage removal of Cr(VI(a)) and Pb(II)(b) ions using coffee husk respectively.

4.3.2. The interaction effect of pH and Flow rate (BC)

Figure(4) (a), (b) represents the 3D plot of the combined effect of pH value and Flow rate (BC) on percentage removal of Cr(VI) ions using coffee husk. The percentage removal of Cr(VI) ions was decreased with increased both p^H value and flow rate. 87 % Cr(VI) removal was achieved at $p^H= 12$ and flow rate of 15ml/min at constant adsorbent dose of 30 g. But, at the same dosage (30 g), the Cr(VI) removal was increased to 99.8 % by decreasing the p^H value to 3 and flow rate to 5ml/min. The decreased in percentage removal due to increased in P^H may be due to the increased negative charges on the adsorbent surface that decreases the attraction of oxyanions of Cr(VI) ion of the same charge as adsorbent surface.

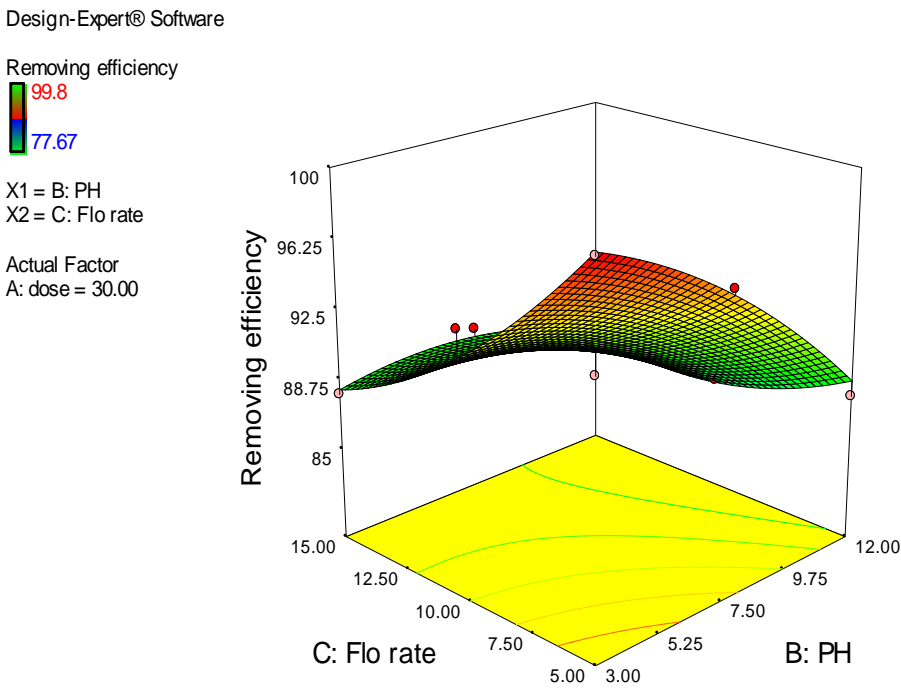


Figure 4: 3D plot of the interaction effect of PH and flow rate (BC) on percentage removal of Cr(VI)ions using coffee husk.

4.3.3. The interaction effect of adsorbent dosage and Flowrate (AC)

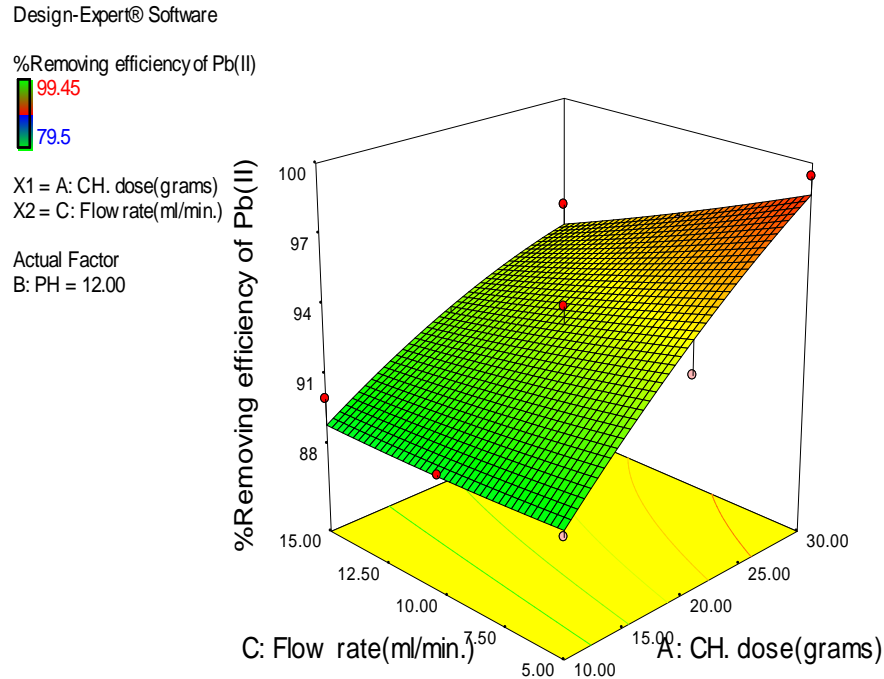


Figure 5: 3D plot of the interaction effect of Adsorbent dose and flow rate(AC) on percentage removal of Pb (II)ions using coffee husk.

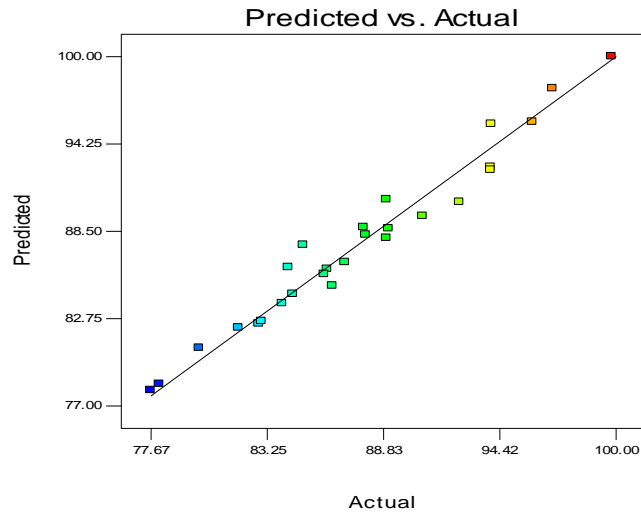
4.4. Development of regression model analysis

Based on the quadratic effect of the model designed from input variable, the comparison of response surface methodology (RSM) model of actual and predicted plots for percentage removal of Cr (VI) and Pb (II) ions using coffee husk was estimated as shown in Figure-6a and b. The relationship between actual values and predicted values indicate that the actual values are distributed relatively near to the straight line, indicating good fitness of the model. Again in Figure-7a and b, the plot of studentized residuals versus run order was tested and the residuals

were scattered randomly around ± 3.72 . This was an indication of better fitting of the model with the experimental data for Cr (VI) and Pb (II) respectively.

Design-Expert® Software
Removing efficiency

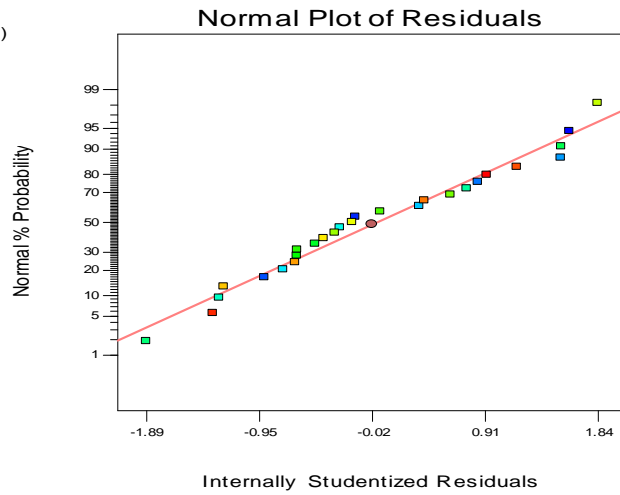
Color points by value of
Removing efficiency:



(a)

Design-Expert® Software
%Removing efficiency of Pb(II)

Color points by
Design ID

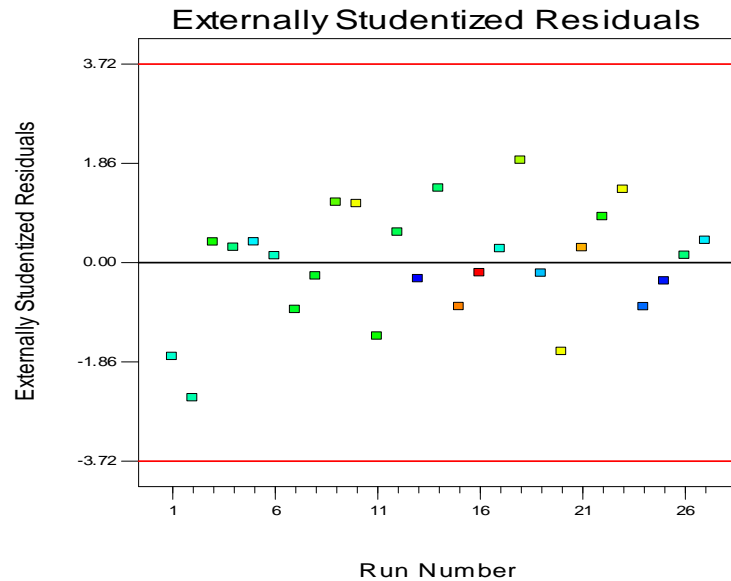


(b)

Figure 6: The actual and predicted plot for percentage removal of Cr(VI) (a) and Pb(II)(b) ions using coffee husk.

Design-Expert® Software
Removing efficiency

Color points by value of
Removing efficiency:



(a)

Figure 7:Plot of Studentized residuals versus experimental run number for Cr(VI)(a) and Pb(II)(b)

The goodness of fit of the model was checked by the determination coefficient (R^2) as shown in the Table-7. The R^2 value provides a measure of how much variability in the observed response values can be explained by the experimental variable and their interaction. The R^2 value is always between 0 and 1. The closer the R^2 value is to 1, the stronger the model is and the better it predicts the response. In this case, the value of the determination coefficient ($R^2=0.9624$) indicates that 96 % of the variability in the response could be explained by the model. In addition, the value of the adjusted determination coefficient (Adj $R^2=0.9424$) is also very high to advocate for a high significance of the model. Also higher the value of correlation coefficient ($R^2=0.9126$) justifies an excellent correlation between the independent variables. The response surface contour and 3D plots of percentage removal of Cr(VI) and Pb (II) versus the interactive of adsorbent dosage (g), pH and flow rate are shown in the Figure (19) and (20).

Table 8 Model summary statistics for percentage removal of Cr(VI) ions using coffee Husk

Std. Dev. = 1.36	R-Squared = 0.9624
Mean = 87.70	Adj R-Squared = 0.9424
C.V. % = 1.56	Pred R-Squared = 0.9126

4.5. Optimum conditions for Cr(VI) and Pb (II) removal

According to RSM, the optimum conditions for the removal of Cr(VI) from synthetic waste water using coffee husk are obtained at adsorbent dose of 30g/100mL, pH-3.00, and flow rate- 5ml/min while pH is 12 for Pb (II). At these conditions, the maximum removal of Cr(VI) and Pb (II) were found to be 99.8 % and 99.45 % respectively.

4.6. Evaluation of adsorption capacity of coffee husk using optimum Condition

4.6.1 Adsorption capacity of coffee husk at different adsorbent dosages

The study on the effect of the amount of adsorbent on the process of adsorption were carried out by varying adsorbent dose from 10 to 30g in the 20mg/l concentration of Cr(VI) solution of 100ml at p^H 3 and flow rate 5ml/min and Pb(II) solution of 100 mL at PH=7.5 and flow rate 5ml/min. The adsorption capacity of Cr(VI) and Pb(II) ions on coffee husk decreases from 0.18806 to 0.05743 mg/g and 0.18 to 0.0613 respectively; when the amount of coffee husk increases from 100 to 300g/L. This seems to be due to the increase in surface area of the adsorbent because of adhesive force and hinder it's active site.

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Adsorption capacity(mg/g)

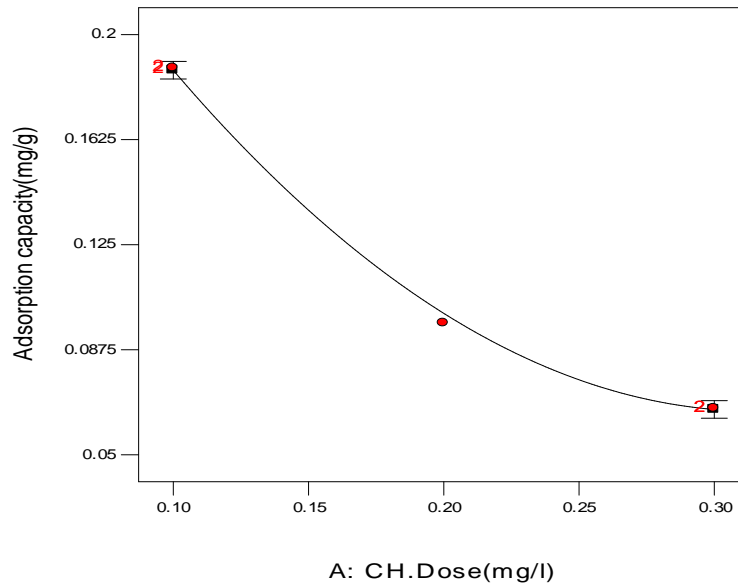
● Design Points

X1 = A: CH.Dose(mg/l)

Actual Factors

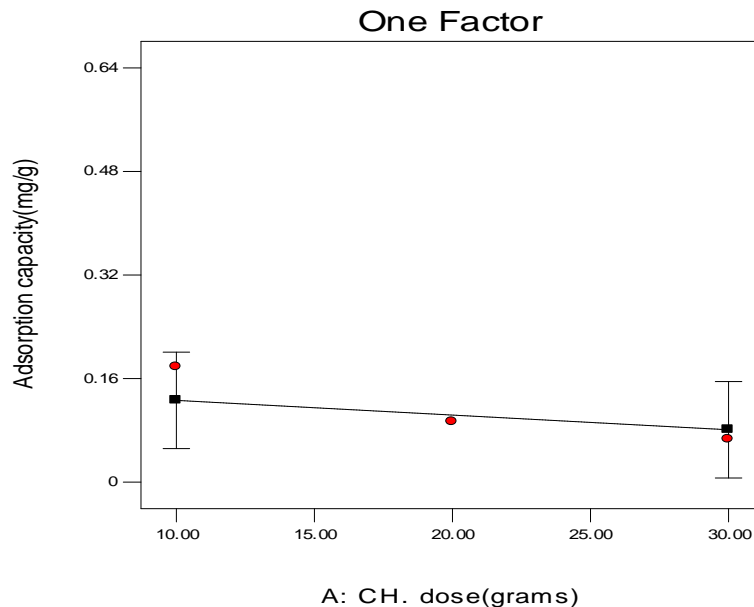
B: PH = 3.00

C: Flow rate(ml/min.) = 5.00



(a)

Design-Expert® Software
 Adsorption capacity(mg/g)
 ● Design Points
 X1 = A: CH. dose(grams)
 Actual Factors
 B: PH = 12.00
 C: Flow rate(ml/min.) = 5.00



(b)

Figure 8: Effect of adsorbent dosage on adsorption capacity of Cr(VI)(a) and Pb(II)(b) ions using coffee husk.

4.7. Adsorption capacity of coffee husk at different pH.

In order to optimize the pH for maximum adsorption capacity of Cr(VI) and Pb(II) ions, adsorption experiment was conducted in the pH range from 3 to 12, adsorbent dose of 10 g to 30g and flow rate of 5ml/min to 15ml/min., as shown in Figure-9. The maximum adsorption capacity of Cr(VI) using coffee husk was obtained at lower pH value whereas it was obtained at slightly basic P^H for Pb(II) ions. The graph shows that the maximum adsorption capacity of 0.18806 mg/g occurs under acidic conditions (pH 3) whereas the maximum adsorption capacity of 0.18mg/g occurs under basic conditions (PH 7.5). Therefore, the optimum pH 3.0 and PH 7.5 were obtained for the highest adsorption capacity of Cr(VI) and Pb(II) respectively. This is due to at lower pH value the surface of the adsorbent becomes highly protonated and favours the uptake of Cr (VI) ions. With increase in pH, the degree of protonation of the surface reduces gradually and attains a negatively charged surface hence adsorption capacity was increased for Pb(II) cations.

Design-Expert® Software

Adsorption capacity(mg/g)

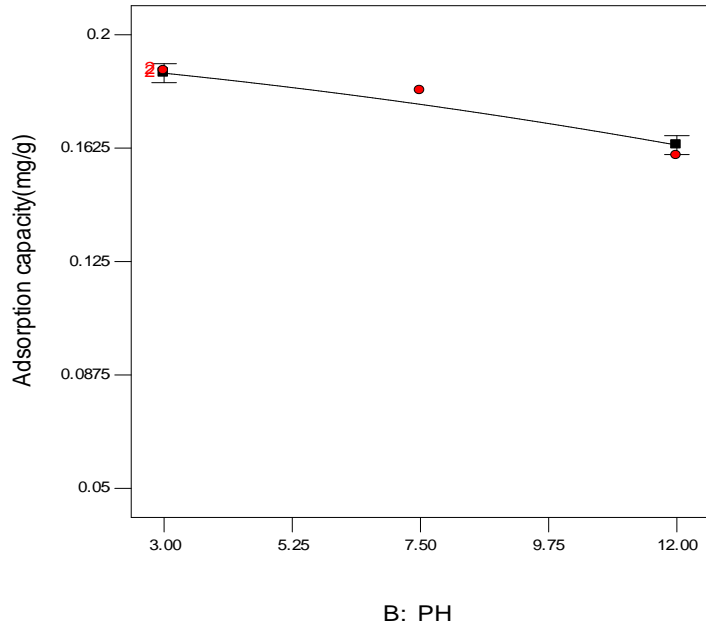
● Design Points

X1 = B: PH

Actual Factors

A: CH.Dose(mg/l) = 0.10

C: Flow rate(ml/min.) = 5.00



(a)

Design-Expert® Software

Adsorption capacity(mg/g)

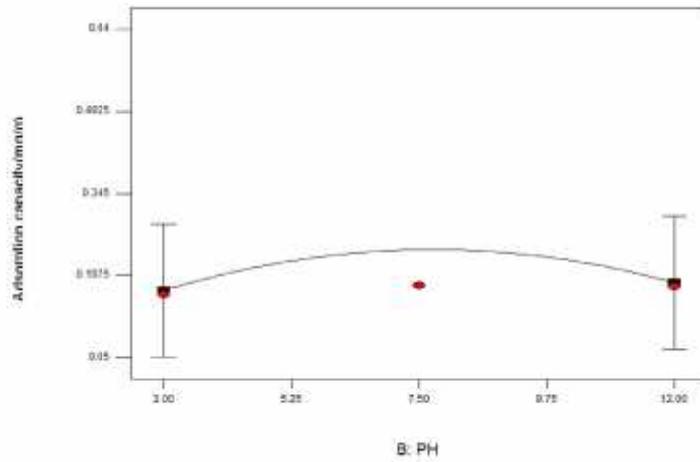
● Design Points

X1 = B: PH

Actual Factors

A: CH. dose(grams) = 10.00

C: Flow rate(ml/min.) = 5.00



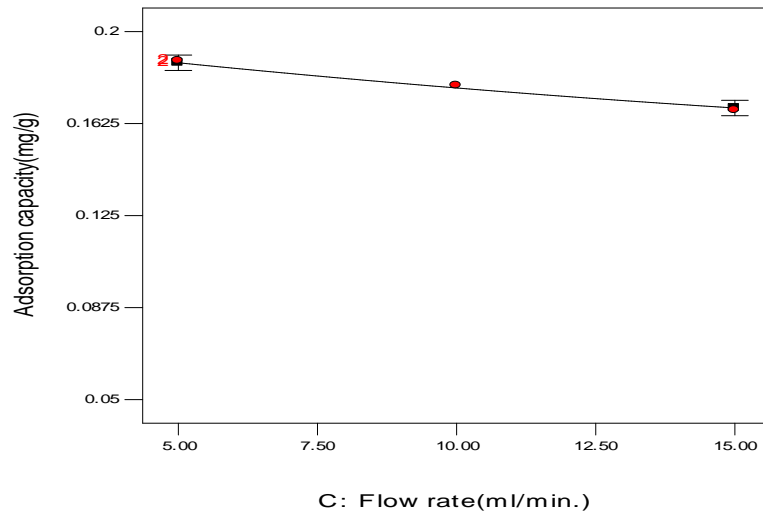
(b)

Figure 9: Effect of pH on adsorption capacity of Cr(VI)(a) and Pb(II)(b) ions using coffee husk

4.8. Effect of Flow Rate

When dealing with the operating conditions of the continuous treatment of wastewater on an industrial scale, the flow rate of such influent wastewater is a very essential parameter to evaluate. In general, the effect of flow rate on adsorption capacity of adsorbent(Coffee husk) by varying the flow rates from 5ml/min to 15 ml/min, was evaluated by keep adsorbent dose(10g) and PH(3) constant. The adsorption capacity of adsorbent (coffee husk), were lowered at higher flow rates,this is shown in figure-10a & b for chromium and lead respectively below. It is clear that rapid uptake is noticed in the initial stages of flow rate and the rate of uptake starts to decrease thereafter and finally reaches saturation. As increasing the flow rate of the pollutant influent solution, the contact time between the adsorbate solutes and the adsorbent is minimized in time, and hence the adsorbate molecules do not have enough time to uptake the binding sites on the adsorbent surface or diffuse into the pores of the adsorbents, causing the adsorbate solutes to leave the column before equilibrium to occur.

Design-Expert® Software
Adsorption capacity(mg/g)
● Design Points
X1 = C: Flow rate(ml/min.)
Actual Factors
A: CH.Dose(mg/l) = 0.10
B: PH = 3.00



(a)

Design Expert® Software

Adsorption capacity (mg/g)

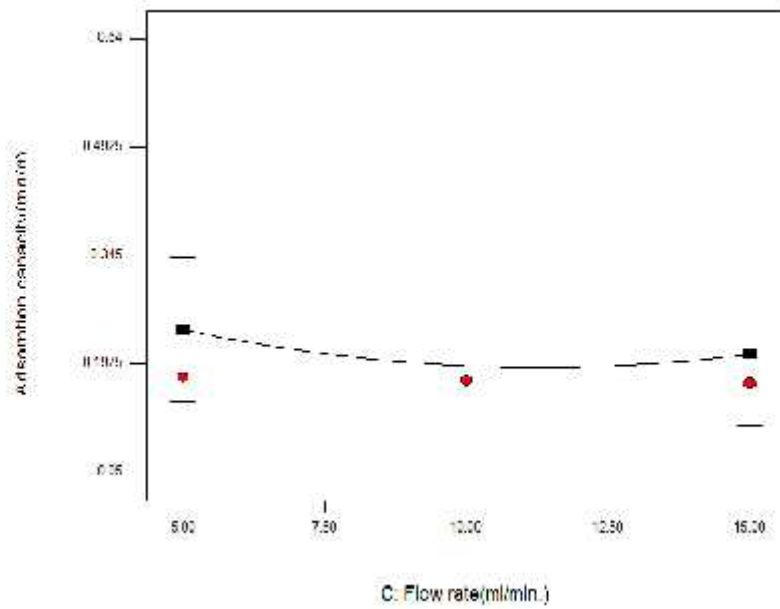
◆ Design Points

X1 = C: Flow rate (ml/min)

Actual Factors

A: CIL dose (grams) = 10.00

B: pH = 7.50



(b)

Figure 10: Effect of flow rate on adsorption capacity of Cr (VI)(a) and Pb (II)(b) ions using coffee husk.

5. Conclusions and Recommendations

5.1 Conclusions

The coffee husk produced from Ethiopian coffee, as newly alternative adsorbent for Cr(VI) and Pb(II) removal was investigated without making any chemical modifications except treatment with 2% formaldehyde solution in order to reduce biodegradation of organic compounds and avoid mould formation during continuous sorption (Chen, 2005). This coffee husk was characterized and utilized for removal of Cr(VI) and Pb(II) from aqueous solution using continuous adsorption techniques. The results indicate that the coffee husk is an excellent adsorbent. Thus Cr(VI) and Pb(II) removal with coffee husk reached 99.8% and 99.45% with dosages of 30g for constant Cr(VI) and Pb(II) concentrations of 20 mg/l in 100mL volume of solutions. Adsorption of Cr(VI) and Pb(II) ions were highly pH-dependent and the results showed that the optimum pH for the removals was found to be strong acidic media (pH 3) for Cr(VI), at which Cr(VI) exists mostly as the most easily adsorbed form, HCrO_4^- whereas it was found to be strong basic media (pH 12) for Pb(II), increasing adsorbent dose and decreasing flow rate were found to increase the percentage removal of Cr(VI) and Pb(II). The FTIR spectra analysis showed that this material contains many functional groups namely: methylene, and hydroxyl groups. These functional groups characteristics of coffee husk shows responsible for chromium and Pb(II) binding onto surface of coffee husk within the pH range (pH 3-12). The development of mathematical model for adsorption of Cr(VI) using statistical design of experiments appears to be a useful tool for prediction and understanding of interaction effects between process variables using general full factorial design.

The studies data presented here inform that the adsorbent, coffee husk is locally available low-cost raw material could be fruitfully employed as adsorbent for removal of chromium and lead from aqueous solution, therefore it can be useful in the treatment of chromium and lead contaminated wastewater before discharge into the aquatic environment without any sludge production.

5.2 Recommendation

In the future the following works should be explored on coffee husk for wastewater treatment:

-) In this study synthetic wastewater was used to evaluate the continuous test adsorption processes. However, in the future, use of real wastewater collected from the industries could be the great potential of the studies as synthetic wastewater does not contain other interfering substances such as other metal ions, micro-organism, and humic acid.
-) Further research is needed to evaluate economic feasibilities on the adsorbent preparation production processes and utilization in the wastewater treatment system which has not been done in this work.
-) Carry out the research on the removal of other toxic heavy metals such as Cd, mercury, Cu, As and so on and the another waste water.
-) The saturated adsorbent which contains Cr(VI) and Pb(II) is not safe for disposal due to the stringent environmental constraints. It is important and appropriate to propose a method for regeneration and reuse of adsorbent and recovery of Cr(VI) and Pb(II) so as to reduce the load on environment in terms of disposal of polluted adsorbent.

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Appendixes

Appendix I: Calculation of Potassium Dichromate Requirement

To Prepare 1000 mg/L of Cr(VI) Stock Solution we have to calculate how much $K_2Cr_2O_7$ is required to get concentration of Cr(VI) stock solution of 1000mg/L [1 g in 1 L solution]. Potassium dichromate ($K_2Cr_2O_7$) has molecular weight = $2*39 + 2*52 + 7*16 = 78 + 104 + 112 = 294$ g/mol, 104 g Cr(VI) is available in 294 g of $K_2Cr_2O_7$. 1 g Cr(VI) in $K_2Cr_2O_7$ is ? 1 g Cr(VI) is available in = $(294/104)*1 = 2.8269$ g of $K_2Cr_2O_7$.

Appendix II: Calculation of Lead nitrate Requirement

Similar to Appendix I, to Prepare 1000 mg/L of Pb(II) Stock Solution we have to calculate how much $Pb(NO_3)_2$ is required to get concentration of Pb(II) stock solution of 1000mg/L [1 g in 1 L solution]. Lead nitrate $Pb(NO_3)_2$ has molecular weight = $207.2 + 2*14 + 6*16 = 207.2 + 28 + 96 = 331.2$ g/mol, 207.2 g Pb(II) is available in 331.2g of $Pb(NO_3)_2$. 1 g Pb(II) in $Pb(NO_3)_2$ is ? 1 g Pb(II) is available in = $(331.2/207.2)*1 = 1.6$ g of $Pb(NO_3)_2$.

Appendix III: Calculation of particle density

Picnometer was used to determine the particle density of coffee husk as follow

$$\text{Mass of picnometer}(W_1) = 23.4898\text{g}$$

$$\text{Mass of coffee husk} + W_1 = W_2 = 35.7858\text{g}$$

$$\text{Mass of water} + W_2 = W_3 = 78.4025\text{g}$$

$$\text{Volume of picnometer} (V_{pic}) = 50\text{cm}^3$$

$$\text{Density of water} (d_w) = 1\text{g/cm}^3$$

$$\text{Mass of water} (W_w) = W_3 - W_2 = 42.6167\text{g}$$

$$d_w = W_w / V_w \text{ where } V_w \text{ is volume of water}$$

$$V_w = W_w / d_w = 42.6167\text{g} / 1\text{g/cm}^3 = 42.6167\text{cm}^3$$

$$\text{Volume of coffee husk}(V_{Ch}) = V_{pic} - V_w = 50\text{cm}^3 - 42.6167\text{cm}^3 = 7.3833\text{cm}^3$$

Mass of coffee husk(W_{Ch}) = $W_2 - W_1 = 35.7858g - 23.4898g = 12.296g$

$$\rho_{Ch} = W_{Ch} / V_{Ch} = 12.296g / 7.3833cm^3 = 1.6654g / cm^3$$

where ρ_{Ch} is particle density of coffee husk

Appendix IV: Dilution of Cr(VI) Stock Solution from 1000 mg/l

Let assume, Initial concentration of stock solution of Cr(VI) or Pb(II), $C_1=1000mg/l$ was diluted to the required working concentrations. Initial volume of stock solution of Cr(VI) or Pb(II), $V_1 = ?$ [have to find out]. Required diluted concentration of Cr(VI) or Pb(II), $C_2= 20mg/l$ Required diluted solution volume of Cr(VI) or Pb(II), $V_2= 2000mL$ [can vary to required volume]. According to the dilution formula below V_1 can be calculated as the following:

Mass of stock solution=Mass of diluted solution

$$C_1 * V_1 = C_2 * V_2 .$$

$$\text{which is } V_1 = (C_2 * V_2) / C_1 ;$$

$V_1 = (20mg/l * 2000mL) / 1000mg/l = 40mL$ Required distilled water= Total volume of solution–Initial Volume of Cr(VI) = $2000 - 40 = 1960 mL$. Then, $V_1=40mL$ of Cr(VI) or Pb(II) stock solution was taken from the Cr(VI) or Pb(II) stock solution and was measured by a micropipette. This V_1 amount of Cr(VI) or Pb(II) stock solution was taken in a 2000mL volumetric flask and then filled up there maining portion (up to 2000mLmarks) of the volumetric flask with distilled water (1960mL).

Appendix V: Generated data in the laboratory

AAS Analysis Results

Chromium

Standard	Conc. (ppm)	Abs.
1	1	0.01810
2	2	0.03616
3	3	0.05487
4	4	0.07186

Lead

Standard	Conc. (ppm)	Abs.
1	1	0.00315
2	2	0.00657
3	3	0.00974
4	4	0.01320

Std	Chromium		Lead	
	Initial concentration(mg/l)	Final concentration(mg/l)	Initial concentration(mg/l)	Final concentration(mg/l)
1	20	1.194	20	3.576
2	20	0.606	20	2.331
3	20	0.04	20	0.784
4	20	1.854	20	2
5	20	1.2	20	1.018
6	20	0.8	20	0.28
7	20	4	20	2.2
8	20	2.72	20	1.37
9	20	2.42	20	0.11
10	20	2.2	20	4.1
11	20	1.5	20	2.088
12	20	1.2	20	1.6
13	20	3.1	20	2.6
14	20	3	20	1.022
15	20	2.2	20	0.77
16	20	4.466	20	2.2
17	20	2.222	20	1.2
18	20	2.77	20	0.81
19	20	3.202	20	3.4
20	20	3.144	20	2.79
21	20	2.4	20	2.07
22	20	3.426	20	2.782
23	20	2.8	20	1.826
24	20	2.18	20	0.987
25	20	4.382	20	2.004
26	20	3.4	20	1.882
27	20	2.6	20	0.988

Appendix VI; Adsorption Efficiency determination

The adsorption efficiency was calculated by Equation 1.

$$E = \left(1 - \frac{C_{\text{final}}}{C_{\text{initial}}}\right) \times 100\% \text{ --- Equation 1}$$

Where E – adsorption efficiency, %; C_{final}– concentration of heavy metals in the eluates, mgL⁻¹; C_{initial} – the concentration of heavy metals in the solution, mgL⁻¹

Appendix VII: Factors, Levels and corresponding response for Cr(VI) and Pb(II)

Table-1: Factors, Levels and corresponding response for Cr(VI)

Std	Run	Blocks	Factor 1 A CH dose (grams)	Factor 2 B P ^H	Factor 3 C Flowrate	%Removing efficiency of Cr(VI)
1	12	Block 1	10.00	3.00	5.00	94.03
2	17	Block 1	20.00	3.00	5.00	96.97
3	20	Block 1	30.00	3.00	5.00	99.8
4	19	Block 1	10.00	7.50	5.00	90.73
5	11	Block 1	20.00	7.50	5.00	94
6	26	Block 1	30.00	7.50	5.00	96
7	14	Block 1	10.00	12.00	5.00	80
8	18	Block 1	20.00	12.00	5.00	86.4
9	7	Block 1	30.00	12.00	5.00	87.9
10	5	Block 1	10.00	3.00	10.00	89
11	8	Block 1	20.00	3.00	10.00	92.5
12	10	Block 1	30.00	3.00	10.00	94
13	6	Block 1	10.00	7.50	10.00	84.5
14	21	Block 1	20.00	7.50	10.00	85
15	3	Block 1	30.00	7.50	10.00	89
16	25	Block 1	10.00	12.00	10.00	77.67
17	15	Block 1	20.00	12.00	10.00	81.89
18	9	Block 1	30.00	12.00	10.00	86.15
19	16	Block 1	10.00	3.00	15.00	83.99
20	27	Block 1	20.00	3.00	15.00	84.28
21	4	Block 1	30.00	3.00	15.00	88
22	1	Block 1	10.00	7.50	15.00	82.87
23	13	Block 1	20.00	7.50	15.00	86
24	23	Block 1	30.00	7.50	15.00	89.1
25	24	Block 1	10.00	12.00	15.00	78.09
26	2	Block 1	20.00	12.00	15.00	83
27	22	Block 1	30.00	12.00	15.00	87

Table-2: Factors, Levels and corresponding response for Pb(II)

Std	Run	Blocks	Factor 1 A: CH dose (grams)	Factor 2 B: P ^H	Factor 3 C: Flowrate (ml/min)	%Removing efficiency of Pb(II)
1	12	Block 1	10.00	3.00	5.00	82.12
2	17	Block 1	20.00	3.00	5.00	88.34
3	20	Block 1	30.00	3.00	5.00	96.08
4	19	Block 1	10.00	7.50	5.00	90
5	11	Block 1	20.00	7.50	5.00	94.91
6	26	Block 1	30.00	7.50	5.00	98.6
7	14	Block 1	10.00	12.00	5.00	89
8	18	Block 1	20.00	12.00	5.00	93.15
9	7	Block 1	30.00	12.00	5.00	99.45
10	5	Block 1	10.00	3.00	10.00	79.5
11	8	Block 1	20.00	3.00	10.00	89.56
12	10	Block 1	30.00	3.00	10.00	92
13	6	Block 1	10.00	7.50	10.00	87
14	21	Block 1	20.00	7.50	10.00	94.89
15	3	Block 1	30.00	7.50	10.00	96.15
16	25	Block 1	10.00	12.00	10.00	89
17	15	Block 1	20.00	12.00	10.00	94
18	9	Block 1	30.00	12.00	10.00	95.95
19	16	Block 1	10.00	3.00	15.00	83.016
20	27	Block 1	20.00	3.00	15.00	86.048
21	4	Block 1	30.00	3.00	15.00	89.67
22	1	Block 1	10.00	7.50	15.00	86.09
23	13	Block 1	20.00	7.50	15.00	90.87
24	23	Block 1	30.00	7.50	15.00	95.063
25	24	Block 1	10.00	12.00	15.00	89.98
26	2	Block 1	20.00	12.00	15.00	90.59
27	22	Block 1	30.00	12.00	15.00	95.06

Appendix VIII : Adsorption capacity

The adsorption capacity was calculated by Equation 2.

$$Q = (C_0 - C_f)V/m \text{-----Equation 2}$$

Where Q is adsorption capacity(mg/g), C₀ initial concentration of heavy metals in the solution,mg/l. C_f final concentration of heavy metals in the eluates,mg/l; the volume of the sample treated,ml. m is mass of the adsorbent dose

Appendix IX: Effect adsorbent dose at different P^H and Flow rate on Cr(VI and Pb(II) Removal efficiency

1. Effect of adsorbent dose at different p^H and Flow rate on Cr(VI) removal efficiency at different P^H and Flow rate

Table-1: Effect of adsorbent dose at P^H=3 and flow rate =5ml/min

Factor 1 A CH dose	Factor 2 B pH	Factor 3 C Flow rate	%Removing Efficiency
10	3	5	94.03
20	3	5	96.97
30	3	5	99.8

Table-2: Effect of adsorbent dose at P^H=7.5 and flow rate =5ml/min

Factor 1 A CH dose	Factor 2 B pH	Factor 3 C Flowrate	%Removing Efficiency
10	7.5	5	90.73
20	7.5	5	94
30	7.5	5	96

Table-3: Effect of adsorbent dose at P^H=12 and flow rate =5ml/min

Factor 1 A CH dose	Factor 2 B pH	Factor 3 C Flowrate	%Removing Efficiency
10	12	5	80
20	12	5	86.4
30	12	5	87.9

Table-4: Effect of adsorbent dose at P^H=3 and flow rate =10ml/min.

Factor 1 A CH dose	Factor 2 B pH	Factor 3 C Flowrate	%Removing Efficiency
10	3	10	89
20	3	10	92.5
30	3	10	94

Table-5: Effect of adsorbent dose at P^H=7.5 and flow rate =10ml/min

Factor 1 A CH dose	Factor 2 B pH	Factor 3 C Flowrate	%Removing Efficiency
10	7.5	10	84.5
20	7.5	10	85
30	7.5	10	89

Table-6: Effect of adsorbent dose at P^H=12 and flow rate =10ml/min

Factor 1 A CH dose	Factor 2 B pH	Factor 3 C Flowrate	%Removing Efficiency
10	12	10	77.67
20	12	10	81.89
30	12	10	86.15

Table-7: Effect of adsorbent dose at P^H=3 and flow rate =15ml/min

Factor 1 A CH dose	Factor 2 B pH	Factor 3 C Flowrate	%Removing Efficiency
10	3	15	83.99
20	3	15	84.28
30	3	15	88

Table-8: Effect of adsorbent dose at P^H=7.5 and flow rate =15ml/min

Factor 1 A CH dose	Factor 2 B pH	Factor 3 C Flowrate	%Removing Efficiency
10	7.5	15	82.87
20	7.5	15	86
30	7.5	15	89.1

Table-9: Effect of adsorbent dose at P^H=12 and flow rate =15ml/min

Factor 1 A CH dose	Factor 2 B pH	Factor 3 C Flowrate	%Removing Efficiency
10	12	15	78.09
20	12	15	83
30	12	15	87

2. Effect of adsorbent dose at different P^H and Flow rate on Pb(II) removal efficiency at different P^H and Flow rate

Table-1: Effect of adsorbent dose at P^H=3 and flow rate =5ml/min

Factor 1 A CH dose	Factor 2 B pH	Factor 3 C Flowrate	%Removing Efficiency
10	3	5	82.12
20	3	5	88.34
30	3	5	96.08

Table-2: Effect of adsorbent dose at P^H=7.5 and flow rate =5ml/min

Factor 1 A CH dose	Factor 2 B pH	Factor 3 C Flowrate	%Removing Efficiency
10	7.5	5	90
20	7.5	5	94.91
30	7.5	5	98.6

Table-4: Effect of adsorbent dose at P^H=3 and flow rate =10ml/min

Factor 1 A CH dose	Factor 2 B pH	Factor 3 C Flowrate	%Removing Efficiency
10	3	10	79.5
20	3	10	89.56
30	3	10	92

Table-5: Effect of adsorbent dose at P^H=7.5 and flow rate =10ml/min

Factor 1 A CH dose	Factor 2 B pH	Factor 3 C Flowrate	%Removing Efficiency
10	7.5	10	87
20	7.5	10	94.89
30	7.5	10	96.15

Table-6: Effect of adsorbent dose at P^H=12 and flow rate =10ml/min

Factor 1 A CH dose	Factor 2 B pH	Factor 3 C Flowrate	%Removing Efficiency
10	12	10	89
20	12	10	94
30	12	10	95.95

Table-7: Effect of adsorbent dose at P^H=3 and flow rate =15ml/min

Factor 1 A CH dose	Factor 2 B pH	Factor 3 C Flowrate	%Removing Efficiency
10	3	15	83.016
20	3	15	86.048
30	3	15	89.67

Table-8: Effect of adsorbent dose at PH=7.5 and flow rate =15ml/min

Factor 1 A CH dose	Factor 2 B pH	Factor 3 C Flowrate	%Removing Efficiency
10	7.5	15	86.09
20	7.5	15	90.87
30	7.5	15	95.063

Table-9: Effect of adsorbent dose at PH=12 and flow rate =15ml/min

Factor 1 A CH dose	Factor 2 B pH	Factor 3 C Flowrate	%Removing Efficiency
10	12	15	89.98
20	12	15	90.59
30	12	15	95.06

Appendix X: Important plates of the experimental works.



Plate 1 Electrical mill for size reduction.



Plate 2 Sieve separation of grinded coffee husk of x size where 1mm < x < 2mm.



(a)

(b)

Plate 3 Washing of grinded coffee husk with plenty of distilled water (a) and Boiling (b).



(c)

(d)

Plate 4 Dried coffee husk (c) and treated coffee husk with formaldehyde (d)

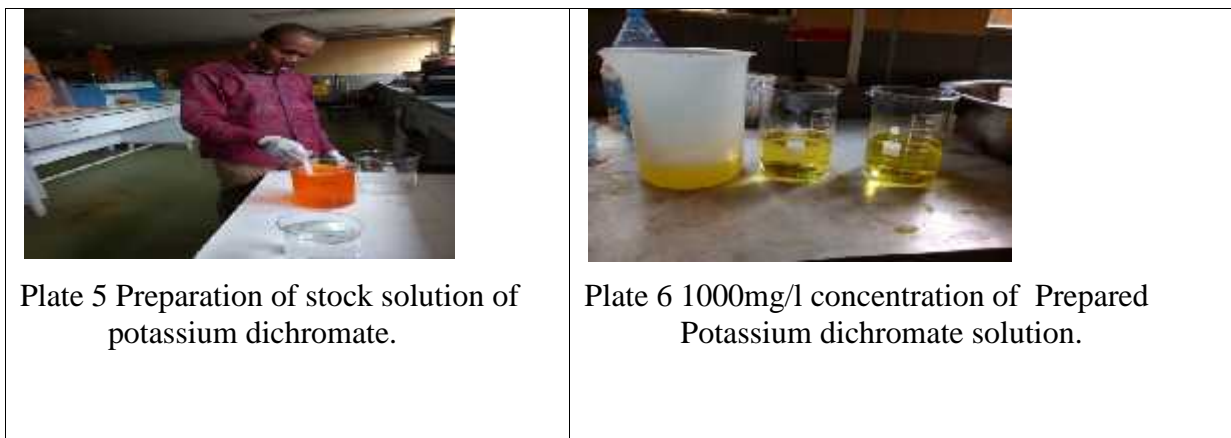


Plate 5 Preparation of stock solution of potassium dichromate.

Plate 6 1000mg/l concentration of Prepared Potassium dichromate solution.



Plate 7 20mg/l concentration of prepared potassium dichromate



(a)



(b)

Plate 8 Setup of the continuous flow heavy metal removal process using bush (a) and with immobilized coffee husk(b).

Appendix-XI Peristaltic pump calibration

Table -1: Calibration of peristaltic pump

Speed of peristaltic pump(rpm)	Flow rate(ml/min)
2.50	5
4.10	10
5.80	15