# ADDIS ABABA UNIVERSITY
# SCHOOL OF GRADUATE STUDIES
# SCHOOL OF CHEMICAL AND BIOENGINEERING
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# Investigation of Brewery Spent Grain as Adsorbent for Removal of Heavy Metals from Wastewater

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***A thesis Submitted to the Research and Graduate School of Addis Ababa University, Addis Ababa Institute of Technology, School of Chemical and Bio Engineering in partial fulfillment of the requirements for the attainment of the Degree of Masters of Science in Chemical Engineering under Environmental Engineering Stream.***

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As members of Examining Board of the Final M.Sc. thesis open defense, we certify that we have read and evaluated the thesis prepared by Hunegnaw Baylie, entitled “Investigation of Brewery Spent Grain as Adsorbent for Removal of Hevy Metals from Wastewater” and recommended that it can be accepted as fulfilling the thesis requirements for the Degree of Master of Science in Chemical Engineering (Environmental Engineering).

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## Declaration

I, the undersigned, declare that this thesis entitled "*Investigation of Brewery Spent Grain as Adsorbent for Removal of Heavy Metals from Wastewater*" is my original work, and has not been presented by any other person for an award of a degree in this or any other University, and that all resources of materials used for this thesis have been duly acknowledged.

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Date of submission July, 2016

This thesis has been submitted to the University with my approval as the University Advisor.

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# ACRONYMS AND NOMENCLATURES

| | |
|---|---|
| AA | Amino acids |
| AAS | Atomic absorption spectrophotometer |
| APHA | American Public Health Association |
| BSG | Brewery spent grain |
| $C_e$ | Concentration of the sorbate at equilibrium (mg/L), |
| Cti | Chitin, |
| Cto | Chitosan |
| FTIR | Furrier transmitter infrared radiation |
| $K_f$ | Freundlich adsorption capacity (mg/g) |
| $K_L$ | Langmuir equilibrium constant (l/mg). |
| $k_f$ | Pseudo first order rate constant |
| $k_s$ | Pseudo second order rate constant |
| LPS | Lipo polysaccharides |
| n | Sorption intensity |
| PG | Peptidoglycan |
| PL | Phospholipids, |
| PS | Polysaccharides, |
| $q_e$ | Amount of sorbate sorbed at equilibrium per unit mass (mg/g), |
| $q_m$ | Monolayer sorption capacity at equilibrium (mg/g) |
| SPS | Sulfated polysaccharides, |
| TA | Teichoic acid, |
| UA | Uranic acids |
| UV | Ultraviolet |

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## ABSTRACT

Heavy metals are considered a major cause for environmental problems. Several conventional treatment methods have been developed for removal of toxic metal ions from wastewaters. Currently biological materials have received attention for heavy metal removal and recovery due to their good performance, low cost and availability. Among the broad lists of biosorbent materials, brewery spent grain has utilized for this study to remove, lead and chromium from wastewater. BSG was modified with 1M NaOH and afterward it was washed, dried and grinded to have particles sizes of 250-500μm. Lead (II) and Chromium (VI) stock solutions were prepared and from which different concentrations were obtained by serial dilution. Batch adsorption of Lead (II) and Chromium (VI) onto BSG was studied. The results indicated that the maximum percentage removal of lead and chromium was found to be 96.53% and 79.47% at pH= 4 and pH=2 respectively.

The adsorption data of metal ions have been described by the Freundlich and Langmuir isotherm models. The sorption process conformed to both Langmuir and Freundlich isotherms with maximum sorption capacities of 26.3 and 10.75 mg/g for lead and chromium, respectively. Sorption kinetics for lead and chromium(VI) followed pseudo second order with regression coefficients of 0.9999 and 0.9998 respectively. Optimum operating conditions of 10 g/l adsorbent dose, 120 minutes and pH=2 for Cr(VI) and pH= 4 for Pb(II) solution were applied to remove lead and chromium ions from real electroplating wastewater. The results showed that brewery spent grain reduced lead ions from its initial concentration of 82 mg/l to 38.37 mg/l while chromium ion was reduced from 156.9 mg/l to 88.73 mg/l. Therefore, it can be concluded that modified spent grain as a new effective adsorbent has potential for Pb(II) and Cr(VI) removal from aqueous solutions.

**Basic terms:** Brewer's Spent Grain, Lead, Chromium (VI), sorption, Isotherm, Kinetics, wastewater

# 1. INTRODUCTION

## 1.1. Back ground

Heavy metals occur in immobilized form in sediments and as ores in nature. However due to anthropogenic activities these metals are mobilized and released and natural biogeochemical cycles are disrupted causing increased deposition of heavy metals in terrestrial and aquatic environment (Alluri et al., 2007 and Holant, 1995). Because of their non-biodegradable and persistent nature, heavy metals pollution poses a significant threat to the environment (Mahamood, 2010 and Fu & Wang, 2011). These toxic metals may be generated from different activities such as mining operations, refining ores, sludge disposal, fly ash from incinerators, the processing of radioactive materials, metal plating, or the manufacture of electrical equipment, paints, alloys, batteries, pesticides or preservatives (Kanamadi, 2003).

Heavy metals are very harmful because of their non-biodegradable nature, long biological halflives and their potential to accumulate in different body parts. Heavy metals such as lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, gold, silver, copper and nickel are given concerns and found in wastewaters (Kanamadi, 2003). Most of them (such as Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn, etc.) are well known toxic and carcinogenic agents and when discharged into the wastewater represent serious threat to receiving water bodies and cause adverse effects on the environment (Orhan et al., 2006 and Ahluwalia & Goyal, 2007), even low concentrations of heavy metals have damaging effects to man and animals because there is no good mechanism for their elimination from the body. Nowadays heavy metals are ubiquitous because of their excessive use in industrial applications (Arora et al., 2008).

The conventional treatment methods are commonly used for removal of metal ions from aqueous streams. This treatment includes chemical precipitation, ion exchange, reverse osmosis, membrane filtration, and activated carbon adsorption. However, these conventional technologies are providing expensive due to non-regenerable materials used, high cost, generation of toxic sludge often ineffective particularly for the removal of heavy metal ions at low concentrations as below 50 mg/l (Holan & Volesky, 1995, Ahluwalia & Goyal, 2007 and Shoba, 2013). Existing technologies for heavy metals' removal from wastewaters are often ineffective, expensive and unavailable in developing countries. The need to find alternative inexpensive and effective methods for heavy metals abetment from wastewaters becomes inevitable (Opeolu et al., 2010).

Adsorption in comparison with other methods appeared to be preferable in terms of its efficiency and ease with which it can be applied in its application in the removal of heavy metals in wastewater. An adsorbent can be considered as cheap or low-cost if it is abundant in nature, requires little processing and is a byproduct of waste material from waste industry. Plant wastes are inexpensive as they have no or very low economic value (Bailey, 1999). Today, in this regard, biosorption is one of the main components of environmental and bio-resource technology due to its economical and efficient in removing of very diluted metal concentrations from waste water (Holan & Volesky, 1995).

Most developing nations continuously produce abundant agro-industrial residues such as brewer's spent grain (BSG), which are underexploited (Aliyu & Bala, 2011). Brewers' spent grain (BSG) is the major byproduct of the brewing industry, representing around 85% of the total by-products generated (Mussatto et al., 2006). The brewing industry generates relatively large amounts of byproducts and wastes; spent grain, spent hops and yeast being the most common. However, as most of these are agricultural products, they can be readily recycled and reused (Mussatto et al, 2006).

Efforts have been made to use the cheapest and unconventional adsorbents to adsorb heavy metals from aqueous solution such as brewer's spent grains (Qin et al., 2007). Brewery's spent grain (BSG) is often considered as solid wastes of agro industry and widely available. In this research, brewery's spent grain (BSG) has been used as an adsorbent to remove lead(II) and Chromium(VI) from wastewater. Metals of interest to be removed for this study were chromium (VI) and lead (II). They were chosen based on their vast industrial applications and potential pollution impact on the environment after discharging without proper treatment. A series of batch experiments have been performed to characterize heavy metals adsorption equilibrium on modified brewery's spent (BSG).

This research reveals the significance of Pb(II) and Cr(VI) removal from wastewater streams and discusses the adsorption potential of brewery's spent grain (BSG), at different operation conditions such as pH, dose required, initial concentration of metal ions (Pb(II) and Cr(VI)) and contact time. In addition, sorption isotherms, sorption kinetics as well as models used to characterize biosorbent sorption have been investigated.

## 1.2. Problem statement

Rapid urbanization and industrialization generates enormous volumes of partially treated and untreated wastewater which consists of heavy metals. These heavy metals have potential health risks associated with metal uptake via food chain, dermal absorption or inhaling. High levels of exposure to heavy metals have been known to cause cancer, organ damage, joint diseases, and in extreme cases, death (Holan & Volesky, 1995).

To alleviate the problem of health risk of waste water associated with contaminated heavy metals, different treatment options such as chemical precipitation, chemical redox reactions, electrochemical treatment, membrane processes and ion exchange have been employed. But those technologies are extremely expensive, inefficient to very low concentrations, further toxic wastes, and creating yet another disposal problem. On the other hand, biosorption, the passive uptake of pollutants such as heavy metals by biological materials, can be both highly efficient and cost effective.

Among the broad lists of biosorbent materials, brewery spent grain is the most widely accepted industrial byproduct in different fields of applications due to its physico-chemical characteristics. However, high moisture content of BSG (80 to 85%) together with polysaccharide and protein makes it particularly susceptible to microbial growth and subsequent spoilage in a short period of time (7 to 10 days) (Aliyu & Bala, 2011). To utilize fully this plenty of bio-resource, attentions should be drifted to use it as biosorbent of metal ions sequestration from waste water. Because it possesses the reactive functional groups such as hydroxyl, amine and carboxyl, it is cheaper and readily available alternative resources so as to substitute the costly treatment methods.

Using this abundant biosorbent material, lead and chromium are targeted to be removed. They were chosen based on their vast industrial applications and potential pollution impact on the environment and health effect such as anemia, nervous system disorders, decreased hemoglobin synthesis, cardio vascular diseases, epigastric pain, nausea, vomiting, severe diarrhea, corrosion of skin, respiratory tract, lungs carcinoma.

## 1.3. Study objectives

### 1.3.1. Main objective

The aim of this study is to investigate the possibilities of brewery spent grains as adsorbent for selected heavy metals removal from waste water.

#### 1.3.2. Specific objectives

The specific objectives are:

- Preparation and characterization of adsorbent (brewery spent grain)
- Batch adsorption of heavy metal ions specifically lead (II) and hexavalent chromium using BSG as adsorbent.
- Determination of the left over metal ions in hypothetical wastewater and real wastewater after adsorption process.
- Investigation of the effect of different operating conditions such as pH, reaction time metal ions initial concentration and sorbent dosage on sorption efficiency and removal capacity of BSG.
- Explore the adsorption capacity and determine the model that better fits the adsorption system or process.

## 1.4. Significance of the study

The major motives for the removal of heavy metals from contaminated wastewater are to ensure safety on environmental hazards and human health problems that result from the direct emissions produced from different industrial activities. The outcome of this study benefits industrial sectors as the research provides cheap treatment method to treat their wastes before discharging it to the environment.

In many metal processing industries, tannery, lead battery manufacturing, and mining operation the brewery spent grain adsorbent can be applied as cheap metal removal mechanism to generate a low level of effluent, which continuously meets a stringent quality standard. The other benefits of this study is that utilizing considerable amount of brewery spent grain as adsorbent promotes solid waste management for brewery factories.

## 1.5. Thesis structure

This thesis is structured in five chapters. Chapter one is a brief introduction about the research topic, the problem statement, objectives of the present study and its significance. Chapter two includes an extensive literature review about heavy metal sources, their toxic effects, conventional metal ions removal methods, biosorbent and low cost adsorbents, metal ions uptake mechanism, factors affect the sorption pattern, spent grain generation and its physicochemical characteristics, the use of spent grain as adsorbent and related researches about it, adsorption Isotherms and kinetics.

Chapter three presents the experimental procedure followed in the lab to perform the sorption of chromium and lead experiments by brewery spent grain. This chapter summarizes the instruments and chemicals used for analyzing the adsorption process. Chapter four examines the effect of different factors, the equilibrium and kinetics studies of chromium(VI) and lead adsorption using the brewery spent grain sorbent. Two kinetic models: pseudo first-order and pseudo second-order are tested to follow the adsorption processes. Two isotherm equations, Langmuir and Freundlich, are used. Adsorption of lead and chromium for real waste water is performed. Furthermore, data analysis is presented by design expert 7.0 software. Chapter five concludes the whole works and findings, and recommendations are suggested for further researches.

# 2. LITERATURE REVIEW

## 2.1. Source of heavy metals and their toxicity

Heavy metals exist in rocks, as ores, such as sulphides (iron, arsenic, lead, lead, zinc, cobalt, gold-silver and nickel sulphides), oxides (aluminum, manganese, gold, selenium and antimony) and both sulphides and oxides from which they are recovered as minerals (Duruibe, 2007). This anthropogenic activity in recovery of minerals causes drastic change in geological and biochemical balance (Sudhakar et al., 2012).

Basically there are two main sources of heavy metals in wastewater to be occurred. These are natural and human sources. The natural factors include soil erosion, volcanic activities, urban run offs and aerosols particulate (Akpor et al., 2014). The human factors include effluents from textile, leather, tannery, electroplating, galvanizing, pigment and dyes, battery manufacturing, metallurgical and paint industries and other metal processing and refining operations at small and large scale sector contains considerable amounts of toxic metal ions (Ahluwalia & Goyal, 2007 and Lu & Gibb, 2008).

Electroplating process, such as, electro less depositions, conversion coating, anodizing cleaning, milling, and etching generate heavy metals (such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver, and titanium). Printed Circuit Board (PCB) process generates tin, lead, and nickel solder plates are the most widely used resistant over plates. Others sources for the metal wastes include; the wood processing industry where a chromatid copper-arsenate wood treatment produces arsenic containing wastes; inorganic pigment manufacturing producing pigments that contain chromium compounds and cadmium sulfide; petroleum refining which generates conversion catalysts contaminated with nickel, vanadium, and chromium; and photographic operations producing film with high concentrations of silver and Ferro cyanide (Barakat, 2011).

The generation of heavy metals from different industrial activities mentioned above, in the environment is of major concern because of their toxicity, bio-accumulating tendency, and threat to human life and the environment through a process of bio magnification, they further accumulate in food chains (Abia, 2006 and Alluri et al., 2007). Heavy metals sources, and their adverse effects to humans and other forms of life, are presented in table 2.1 reviewed from different researchers.

Table 2.1 Common type of heavy metals and their toxic effects of human beings

| Heavy metals | Major sources | Toxic effect | References | WHO limits (ppm) |
|---|---|---|---|---|
| Lead | Mining, paint, pigments, electroplating, manufacturing of batteries, burning of coal | Anemia, mental deficiency, nervous system disorders, decreased hemoglobin synthesis, cardio vascular diseases, disorders in bone metabolism, renal function and reproduction. | (Low et al., 2000)<br>(Ravikumar & K, 2013 and Holan & Volesky, 1995) | 0.1 |
| Copper | Printed circuit board manufacturing, electronics plating, plating, wire drawing, copper polishing, paint manufacturing, wood preservatives and printing operations | Reproductive and developmental toxicity, neurotoxicity, and acute toxicity, dizziness, Diarrhoea | (Farooq et al 2010) | 0.05 |
| Cadmium | Electroplating, smelting, alloy manufacturing, pigments, plastic, mining, refining | Itai-itai disease, causes high blood pressure, sterility among males, kidney damage, flu disorders | (Ravikumar & K, 2013 and Farooq et al., 2010) | 0.05 |
| Zink | Galvanization, paint, batteries, smelting, fertilizers and pesticides, fossil fuel combustion, pigment, polymer stabilizers, etc., | Zinc fumes have corrosive effect on skin, cause damage to nervous membrane | (Sao et al., 2014) | 15 |
| Nickel | Porcelain enameling, nonferrous metal, paint formulation, electroplating | headache, dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, | (Deepa & Suresha, 2014) | 0.05 |

Table 2.1 Continued

| | | | | |
|---|---|---|---|---|
| Chromium | plastic coatings, electroplating, leather tanning and finishing, pigments and wood preservative, metal finishing, and chromate preparation | Epigastric pain, nausea, vomiting, severe diarrhea, corrosion of skin, respiratory tract, lungs carcinoma | (Sobhanardakani et al., 2013 and Venkateswarlu et al., 2007) | 100 µg/L (EPA) |
| Arsenic | Pesticides, fungicides, metal smelters | Bronchitis, dermatitis | (Sao et al., 2014) | 0.05 |
| Mercury | metallurgical industries, chemical manufacturing and metal finishing industries | In the vapor form mercury attacks the lungs, kidneys and the brain. The vapor crosses the blood-brain and blood stream. It also causes blindness, mental and emotional deterioration, involuntary mobilization, loss of consciousness, etc. | (Igwe et al., 2008 and Shafeeq et al., 2012) | 0.001 |

The presence of copper, zinc, cadmium, lead, mercury, iron, nickel and others metals, has a potentially damaging effect on human physiology and other biological systems when the tolerance levels are exceeded (Demirbas, 2008). Hence, there is the need for proper understanding of the conditions, such as the concentrations and oxidation states, which make them harmful, and how biotoxicity occurs (Duruibe, 2007).

Exposure to some metals, such as mercury and lead, may also cause development of autoimmunity, in which a person's immune system attacks its own cells. This can lead to joint diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, nervous system, and damaging of the fetal brain (Barakat, 2011). The poisoning effects of heavy metals are due to their interference with the normal body biochemistry in the normal metabolic processes (Duruibe, 2007).

## 2.2. Conventional removal methods of heavy metals

Methods for removing metal ions from aqueous solution mainly consist of physical, chemical and biological technologies. Conventional technologies, such as chemical precipitation, lime coagulation, solvent extraction, membrane filtration, reverse osmosis, on exchange and adsorption, are being used for the removal of heavy metal ions from aqueous wastes (Holan & Volesky, 1995). The process description of each method is presented below (Kanamadi, 2003 and Zabochnicka-świątek & Krzywonos, 2014)

i. **Reverse osmosis:** It is a process in which heavy metals are separated by a semi-permeable membrane at a pressure greater than osmotic pressure caused by the dissolved solids in wastewater. The disadvantage of this method is that it is expensive.

ii. **Electrolysis:** In this process, the ionic components (heavy metals) are separated through the use of semipermeable ion selective membranes. Application of an electrical potential between the two electrodes causes a migration of cations and anions towards respective electrodes. Because of the alternate spacing of cation and anion permeable membranes, cells of concentrated and dilute salts are formed. The disadvantage is the formation of metal hydroxides, which clog the membrane.

iii. **Ultra-filtration:** They are pressure driven membrane operations that use porous membranes for the removal of heavy metals. The main disadvantage of this process is the generation of sludge.

iv. **Ion exchange:** An ion exchanger is a solid capable of exchanging either cations or anions from the surrounding materials held by electrostatic forces on the exchange resin. Commonly used matrices for ion exchange are synthetic organic ion exchange resins. The disadvantages include; high cost, partial removal of certain ions, and it cannot handle concentrated metal solution as the matrix gets easily fouled by organics and other solids in the wastewater.

v. **Chemical precipitation:** Precipitation of metals is achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers. The large amount of sludge containing toxic compounds produced during the process is the main disadvantage.

vi. **Phytoremediation:** Phytoremediation is the use of certain plants to clean up soil, sediment, and water contaminated with toxic metals. The disadvantages include that it takes a long time for removal of metals and the regeneration of the plant for further biosorption is difficult.

Due to the disadvantages mentioned above, like incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require cost effective alternative technologies or adsorbents for the treatment of metal containing wastewaters are needed. Natural materials that are available in large quantities, or certain waste products from agricultural operations, may have potential as inexpensive adsorbents. Due to their low cost, after these materials have been expended, they can be disposed of without regeneration. (Kadirvelu et al., 2001 and Kanamadi, 2003)

The adsorption process is being widely used by various researchers for the removal of heavy metals from waste streams and activated carbon has been frequently used as an adsorbent (Khan et al., 2004). Activated carbon is used as adsorbent material but it is expensive, therefore, research interest into production of cheaper adsorbents. Recently, apart from activated carbon various low cost adsorbents, derived from agricultural waste, industrial byproduct, natural material, or modified biopolymers, have been developed and applied for the removal of heavy metals from metal contaminated wastewater (Barakat, 2011).

Adsorption process can be utilized in various processes such as technological, environmental and biological. This process has been applied practically in industry and environmental protection. The adsorption of substrates is the first stage in many catalytic processes. During the last 15 years' new classes of solid adsorbents have been developed, such as activated carbon fibers and carbon molecular sieves, fullerenes and hetero fullerenes, microporous glasses and nanoporous both carbonaceous and inorganic materials (Dabrowski, 2001).

Porous sorbent particles follow three steps during sorption process (Lazaridis & Asouhidou, 2003). The first step is (i) external mass transfer (boundary layer or film diffusion) between the external surface of the sorbent particles and the surrounding fluid phase. The driving force is the concentration difference across the boundary layer around each particle; (ii) Intraparticle transport within the particle, which may be limited by pore and solid diffusion; (iii) Reaction kinetics at phase boundaries. In general, there are three main steps involved in pollutant sorption onto solid sorbent: (Barakat, 2011).

(i) The transport of the pollutant from the bulk solution to the sorbent surface;
(ii) Adsorption on the particle surface; and
(iii) transport within the sorbent particle.

Generally, for adsorption to occur there must be forces that attract the adsorbate to the solid surface in a solution. One is due to force of physical nature called van der waals force. This adsorption is relatively weak and plays an important part in connection with surface reactions, since they are not sufficiently strong to influence appreciably the reactivity of the molecule adsorbed. The second type is chemisorption which is much stronger than the first one. In this case the adsorbed molecules are held to the surface by valence force of the same type as those occurring between bound atoms in molecules (Abia, 2006).

## 2.3. Biosorption

Biosorption can be defined as concentrating of sorbents in the biomass (Chojnacka, 2010). It exhibits this property, acting just as chemical substance, as an ion exchanger of biological origin (Ahluwalia & Goyal, 2007). From these biological origins abundant naturally existed materials, particularly of cellulosic nature, have been suggested as potential biosorbents for heavy metals (Holan, 1995). According to (Volesky, 2001) biosorption is the passive process of binding and removal of heavy metals from polluted streams (aqueous solution) by dead and inactive biomass. This implies that the removal mechanism is not metabolically controlled (Davis et al., 2003). Figure 2.1 shows the main steps of biosorption process for removal of heavy metal ions from aqueous solution.

Metals can be removed and concentrated from solutions by using biomass material whereby the metal is adsorbed by chemical sites naturally present and functional dead, inactive or plant based biomass (Volesky, 2001 and Sulaiman, 2015). A vast array of biological materials, especially bacteria, algae, yeasts and fungi have received increasing attention for heavy metal removal and recovery due to their good performance, low cost and large available quantities. The biosorbent, unlike mono functional ion exchange resins, contains variety of functional sites including carboxyl, imidazole, sulphydryl, amino, phosphate, sulfate, thioether, phenol, carbonyl, amide and hydroxyl moieties (Wang & Chen, 2009).

According to different researchers on this area, their work revealed that dead cells have shown ability to bind metal ions through various physico-chemical mechanisms this resulted in an increase in the number of new potential applications (Zabochnicka et al., 2014) The advantage of biosorption is in using biomass raw materials which are either abundant seaweeds or wastes from other industrial operations fermentation wastes (Volesky, 2001).

Biosorption have several applications in different industries especially the heavy metals processing ones, which include metal plating, metal processing, mining, battery manufacturing and metal finishing operations (Sulaiman, 2015). Applying biotechnology in controlling and removing metal pollution has been paid much attention, and gradually becomes hot topic in the field of metal pollution control because of its potential application (Holan & Volesky, 1995).

Generally, metal ions removal by biosorption process is more advantageous than conventional treatment methods because of the following reasons (Khan et al., 2004, Kanamadi, 2003 and Ahluwalia & Goyal, 2007);

- Low investment and low operational cost
- It requires little processing
- It is abundant in nature
- It is a byproduct or waste material from another industry
- High removal efficiency, reducing residual metals to below 1 ppb in many cases
- Minimization of chemical and/or biological sludge
- No additional nutrients requirement that cause disposal and space problems
- Regeneration of biosorbent and
- Possibility of metal recovery.

The regeneration of biosorbent is important part of biosorption process that decrease the cost of biosorbent utilized for further treatment and in opening the possibility of recovering the metals extracted from the liquid phase. For this purpose, it is desirable to desorb the sorbed metals and to regenerate the biosorbent material for another cycle of applications. The desorption process should yield the metals in concentrated form. And it should restore the biosorbent close to the original state for effective reuse with undiminished metal uptake and no physical change or damage to the biomass. Dilute mineral acids have been used for removal of metal from biomass (Mahamood, 2010).

While the regeneration of the biosorbent may be accomplished by washing the metal-laden one with an appropriate solution, the type and strength of this solution would depend on just how the deposited metal has been bound. In batch tests of desorbing solutions, one has to realize that the desorbed sorbate metal ions stay in the solution and a new equilibrium is established between that and the one remaining (Volesky, 2001).

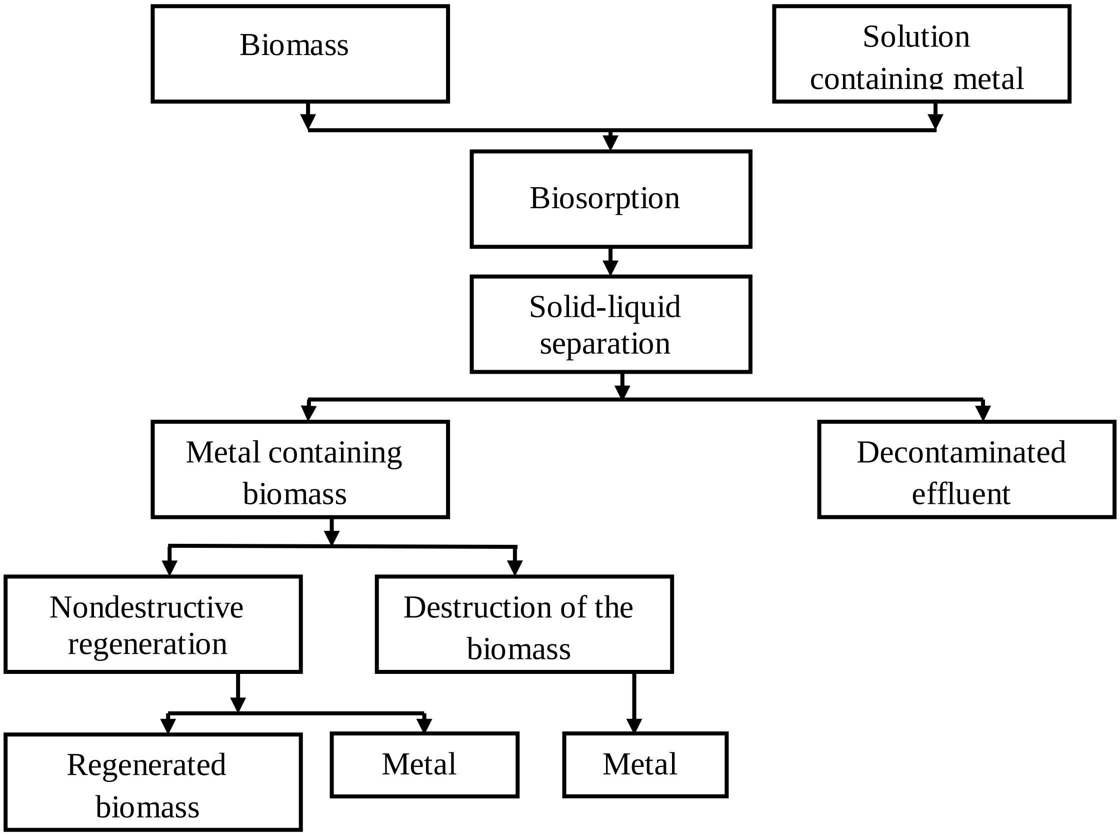


Figure 2.1. Main steps in biosorption process (ZabochnickaŚwiątek, 2014)

### 2.3.1. Biosorbent materials

Biosorbent materials can be categorized under the following biomaterials such as activated charcoal, algae, bacteria, fungi, animal products, agricultural wastes and cellulose based materials (Opeolu et al., 2010), (Abdelghani & Elchaghaby, 2014 and Abbas, 2014).

**Agricultural wastes and cellulose based materials**

They are composed of lignin and cellulose, as well as other polar functional groups containing compounds, which include alcohols, aldehydes, ketones, carboxylates, phenols and ethers which have an ability to bind metal ions from solutions (Khan et al., 2004 and Lesmana et al., 2009). Agricultural byproducts such as rice husk (Ajmal et al., 2003, Wong et al., 2003 and Sobhanardakani et al., 2013), tea waste (Thakur & Parmar, 2013 and Dwivedi, 2014), ground nut shell (Prabha & Udayashankara, 2014), lemon and peel (Husoon, 2013), moringa oleifera (Ravikumar, 2013 and Mataka et al., 2010), neem leaf powder (Venkateswarlu et. al, 2007 and Sharma & Bhattacharyya, 2005), coconut shell (Okafor et al., 2012), saw dust (Yu et al., 2001) etc. are some typical examples investigated as metal ions adsorbent by researchers.

### Bacteria, fungi, yeast and algae

They have been exhibited high sorption capacity of metal ions from aqueous solutions as reported by different researchers. they can treat high volume and low concentration complex wastewaters containing heavy metal(s) in the order of 1 to 100 mg/L (Wang & Chen, 2006). Biomass of Aspergillus Niger, Penicillium chrysogenum, Rhizopus nigricans, Ascophyllum nodosum, Sargassum natans, Chlorella fusca, Oscillatoria anguistissima, Bacillus firmusand Streptomycessp have highest metal adsorption capacities ranging from 5 to 641 mg/g mainly for Pb, Zn, Cd, Cr, Cu and Ni (Ahluwalia & Goyal, 2007).

According to the work of (Wilke et al., 2006) on metal ions (cadmium, lead, nickel and zinc) adsorption by thirty strains of algae were examined for their biosorption abilities from aqueous solutions. The adsorption capacity for lead was high among the metal ions. Algae have certain advantages over other biomass and microbes that as they are autotrophs, their nutrient requirement is low and produce large biomass (Das et al., 2008).

(Kumar, 2009) verified adsorption of Cd, Hg and Pb by taking five green marine macroalgae (Cladophora fasicularis, Ulva lactuca, Chaetomorphasp, Caulerpa sertularioides and Valoniopsis pachynema) at various conditions. The Cd uptake values in the different species were in the order Chaetomorphasp > C. sertularioides >Fasicularis>V.pachynema >U. lactuca. Hg uptake values followed the sequence C. sertularioides > U. lactuca>C.fasicularis>V. pachynema > Chaetomorphasp. The metal uptake values for Pb displayed the order V. pachynema> Chaetomorphasp> C. fasicularis> U. lactuca >C. sertularioides.

The common filamentous fungi can sorb heavy metals (Zn, Cd, Pb, Fe, Ni, Ag, Th, Ra, and U) from aqueous solution and their sorption capacity under different environmental conditions were higher than commercial ion exchange resins, carbon and metal oxides (Bishnoi, 2005). Mullen examined sorption of capacity of four bacteria strains, Bacillus cereus, B. subtilis, Escherichia coli, and Pseudomonas aeruginosa, for the ability to remove Ag+, Cd2+, $Cu^{2+}$, and $La^{3+}$ from solution by batch adsorption. The bacterial removal capacity of metals was shown in the order Ag > La > Cu > Cd; and the result indicated that bacterial cells are capable of binding large quantities of different metals (Mullen et al., 1989). On the other hand, biosorption of lead, chromium and copper ions by bacterium (staphylococcus saprophyticus) was examined by Ilhan (Ilhan et al., 2004).

The maximum biosorption value were found to be 88.66 mg $Cr^{6+}$/l, 100 mg $Pb^{2+}$/l, 44.9 mg $Cu^{2+}$/l. (Deng & Wang, 2012) verified Hg sorption capacity using marine bacteria, strains of $S_1$, $S_2$ and $S_3$ exhibited a maximum Hg tolerance of 120 mg/l and a maximum Hg uptake capacity of 133 mg/g, was isolated by bacterium strain one, $S_1$ at pH 4–10. The effect of co-ions depended on the ratio of remaining bioaccumulation capacity. Among several functional groups, carboxyl groups contributed to Hg uptake and were the most important.

The performance of the yeast Saccharomyces Cerevisiae to remove heavy metals from aqueous solutions was studied by (Farhan & Khadom, 2015). The study was undertaken by considering different environmental conditions such as the effect of pH, temperature, initial concentration, contact time, and biosorbent dosage on biosorption capacity. The results showed that metal uptake is a rapid process at pH values (5.0–6.0), and the order of accumulated metal ions is Pb>Zn>Cr>Co>Cd>Cu. The biosorption process obeys Freundlich and the Langmuir adsorption isotherms. The kinetics of metal ions biosorption could be described by Lagergren and Ho models.

Infante studied the sorption of mercury, lead and nickel onto Saccharomyces Cerevisiae by considering different environmental conditions and the interaction effects influenced the biosorption process. The result revealed that the biomass of Saccharomyces cerevisiae removed a higher percentage of lead (86.4%) as compared to mercury and nickel (69.7 and 47.8% respectively) (Infante, 2014).

**Industrial wastes/residues**

Industrial waste is also one of the potentially low cost adsorbent for heavy metal removal. It requires little processing to increase its sorptive capacity. Generally industrial wastes are generated as byproducts. Since these materials are locally available in large quantities, they are inexpensive (Babel & Kurniawan, 2003).

Industrial wastes, such as, fly ash, waste slurry, blast furnace slag and sludge, black liquor lignin, red mud, sugar beet pulp, tea industry waste, and, etc. are currently being investigated as potential adsorbents for the removal of the heavy metals from wastewater. It was found that modified industrial wastes showed higher adsorption capacity. The application of certain modified low cost industrial waste materials has demonstrated high removal capacities for the heavy metal laden with wastewater (Ahmaruzzaman, 2011).

### Animal wastes

Animal wastes such as cow dung and bones have been investigated as good adsorbent for removal of heavy metals. (Agarwal & Gupta, 2015) found that animal bone charcoal (ABC) produced from animal bones was used as adsorbent to remove Cr(VI) from its aqueous solution. The result showed that at pH 2 and initial concentration of 100 mg/L, the removal efficiency of Cr(VI) was found to be 92%.

Removal of lead (II) from aqueous solutions fish bones was studied by (Kizilkaya & Tekinay, 2014) and the maximum adsorption capacity for Pb (II) was found to be 323 mg/g at optimum conditions. On the other hand, the use of cow dung and its promising adsorbent in the removal of heavy metals from waste waters and environment was reviewed by (Ojedokun & Solomon, 2016). The other biosorbent materials are also mentioned in Table 2.2.

Table 2.2 Types of biological materials that have been used for preparing biosorbents

| Category | Examples |
|---|---|
| Bacteria | ➢ Gram-positive bacteria (Bacillus sp., Corynebacterium sp., etc.).<br>➢ Gram-negative bacteria (Eschrichia sp., Pseudomonas sp., etc.). and<br>➢ Cyanobacteria (Anabaena sp., Synechocystis sp., etc.) |
| Fungi | ➢ Molds (Aspergillus sp., Rhizopus sp., etc.)<br>➢ Mushrooms (Agaricus sp., Trichaptum sp., etc.). and<br>➢ Yeast (Scaccharomyces sp., Candida sp., etc.) |
| Algae | ➢ Micro algae (clorella sp. Chamydomonas sp., etc.) and<br>➢ Macro algae (green seaweed (Enteromorphasp., Codiumsp., etc.)<br>➢ brown seaweed (Sargassum sp., Ecklonia sp., etc., and<br>➢ Red seaweed (geildium sp., Porphyra sp., etc.)) |
| Industrial waste | ➢ Fermentation wastes, Food/beverage wastes,<br>➢ Activated sludges, anaerobic sludge, etc. |
| Agricultural waste | Fruit/Vegetable wastes, rice straws, wheat bran, soybean halts, etc. |
| Natural residues | Plant residues, sawdust, tree barks, weeds, etc. |
| Others | Chitosan driven materials, cellulose driven materials, etc. |

Source; (Abbas, 2014)

### 2.3.2. Biosorption metal uptake mechanism

Technically biosorption process involves a solid biosorbent phase and a liquid phase; often water which contains a dissolved species to be sorbed (sorbate, a metal ion) till equilibrium is established (Alluri et al., 2007 and Mosbah & Sahmoune, 2013). Due to higher affinity of the sorbent for the sorbate species the latter is attracted and bound with different mechanisms such as ion exchange, complexation, precipitation, chelation, coordination, reduction and physical adsorption (Tsezos et al., and Kanamadi, 2003).

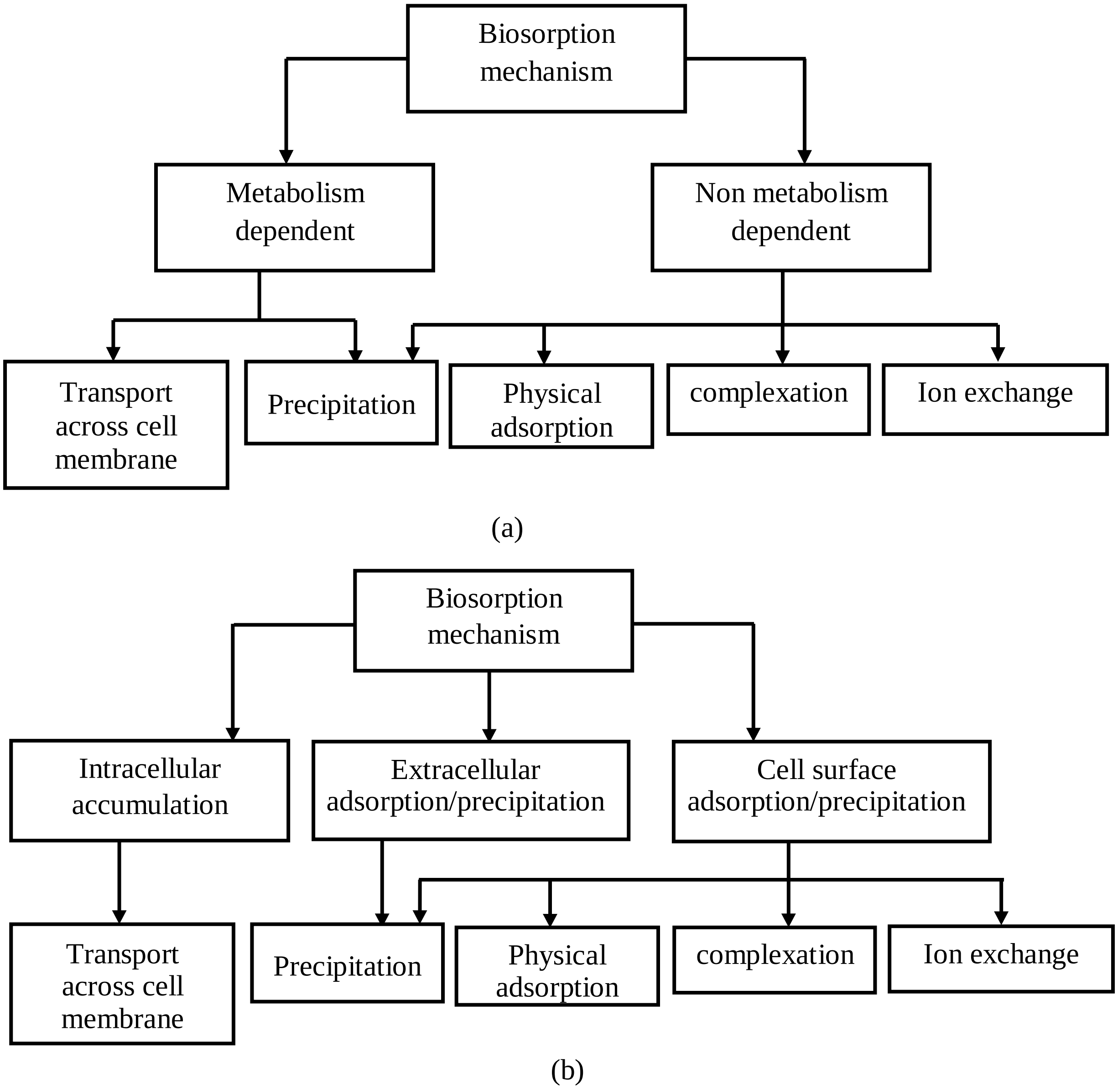
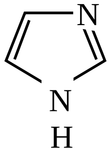
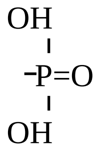
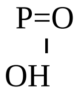


Figure 2.2 Biosorption mechanisms (Veglio & Beolchini, 1997) according to (a) cellular metabolism and (b) location where the metal removed are found.

Generally, biosorption mechanisms can be classified based on various criteria (Alluri et al., 2007 and Kanamadi, 2003). On the basis of cell's metabolism, biosorption mechanisms can be metabolism dependent and non-metabolism dependent. On the other hand, according to the location of sorbet species biosorption can be classified as extracellular accumulation/ precipitation, cell surface sorption/precipitation and intracellular accumulation.

Table 2.3 Major binding/ functional groups of biosorption

| Binding group | Structural formula | pKa | Ligand atom | Occurrence in selected bio molecules |
|---|---|---|---|---|
| Hydroxyl | -OH | 9.5-13 | O | PS, UA, SPS, AA |
| Carbonyl/ketone) | C=O | | O | Peptide bond |
| Carboxyl | -COOH | 1.7-4.7 | O | UA |
| Sulfhydryl thiol | -SH | 8.3-10.8 | S | AA |
| Sulfonate | $-SO_3$ | 1.3 | O | SPS |
| Thioether | -S | - | S | AA |
| Amine | $-NH_2$ | 8-11 | N | Cto, AA |
| Secondary amine | -NH | 13 | N | Cti, PG, AA |
| Amide | -NH-C=O | - | N | AA |
| Imine | =NH | 11.6-2.6 | N | AA |
| Imidazole |  | 6 | N | AA |
| phosphonate |  $-\overset{OH}{\underset{OH}{P}}=O$ | 0.9-2.1<br>6.1-6.8 | O | PL |
| Phosphodiester |  $\underset{OH}{P}=O$ | 1.5 | O | TA, LPS |

where; PS: polysaccharides, UA: uronic acids, SPS: sulfated PS, AA: amino acids, Cto: chitosan, Cti: chitin, PG: peptidoglycan, PL: phospholipids, TA: teichoic acid, LPS: lipo, PS.

Source: (Abbas, 2014)

Cell membranes play an important role in the process of sorption because of the availability of various functional groups such as carboxylic, hydroxyl phosphate amine which can be considered as a complex ion exchanger similar to commercially available resins (Zabochnicka et al., 2014). Metal ions are adsorbed and transported across the membrane in the same mechanism by which metabolically important ions such as potassium, magnesium, and sodium are conveyed (Alluri et al., 2007). The term adsorption can be used as a general term and includes several passive, i.e. non-metabolic, mechanisms such as: complexation; chelation; co-ordination; ion exchange; precipitation; reduction (Tsezos et al., 2007).

**Complexation**: Complex formation of metal ions with organic molecules involves ligand centers in the organic species i.e. the presence of an atom or atoms having lone pair electrons to donate. Complexation may be electrostatic or covalent and the simplest case is complexation by a mono-dentate ligand such as $RNH_2$. To approach and elucidate biosorption mechanisms, a significant part of the recent advances in biosorption are based on the classification of elements according to the hard-soft acid-base classification (Pearson's classification). "Hard acids", metals such as Na, K, Ca, Mg, often essential nutrients for microbial growth, bind preferentially to oxygen containing "hard bases", ligands such as $OH^-$, $HPO_4^{2-}$, $CO_3^{2-}$, $R\text{-}COO^-$, and =C=O. Soft acids, metals such as the precious metals Ag, Au, Pt, Pd are bound covalently to the cell wall by "soft bases", ligands containing nitrogen or sulfur.

**Chelation:** Organic molecules containing more than one functional group with donor electron pairs can simultaneously donate these to a metal atom. This can result in the formation of a ring structure involving the metal atom a process termed 'chelation'. Chelated compounds are more stable than complexes involving mono-dentate ligands. Stability tends to increase with the number of chelating sites available on the ligand.

**Anion Exchange:** Anion exchange on biopolymers can take place on a variety of organic nitrogenbased groupings. In proteins, amino (lysyl side chain and N-terminal) imidazole (histidyl) and guanidine (arginyl) groupings are common centers of positive charge. Centers of positive charge in nucleic acids will occur with protonation of amino groups on purine or pyrimidine rings or with protonation of heterocyclic nitrogen atoms. Polysaccharides as a group are acidic or neutral macromolecules with basic functional groups being rare and arising as unacetylated amino sugars.

**Coordination:** Metal atoms have preferences for specific donor atoms ("hard/hard" / "soft/soft") and the stereo chemical arrangements that play an important role in the binding with the available ligands on the microbial cell.

**Cation Exchange:** In biopolymers the most likely cation binding invisible groups to be involved, are: carboxyl, organic phosphate and organic sulfate. Carboxylic acids are widely distributed in biopolymers being most commonly found as side-chain constituents of proteins, the uranic, neuraminic and muramic acids, and related substituted monosaccharides of polysaccharides. Phosphodiester links impart negative charge to the nucleic acid backbone while both diester and monoester groupings are found most commonly in bacterial polysaccharides and related macromolecules. Lipoprotein and lipopolysaccharides are also likely to contain phosphodiester as part of the lipid moiety.

Sulphate esterified to carbohydrate hydroxyl groups is common in connective tissue and algal polysaccharides and is for most purposes likely to provide the greatest negative charge density, at very low pKa, among the charged biopolymers. Ester sulfate and phosphomonoester groupings also occur in proteins. Hydroxyl groups of serine, threonine and tyrosine are available for specific translational modifications. Phenolic hydroxyl is also capable of providing weak negative charge and binding potential.

**Precipitation:** Metal precipitation is also involved in biosorption process. The precipitates may be formed and remain in contact with or inside the microbial cells or may be independent of the solid phase of the microbial cell. In the latter case, the presence of the solid phase-microbial cell or biofilm also plays a favorable role in the phenomenon of precipitation. metal precipitates may also be formed.

This may be more easily understood when metals are bound to Extracellular Polymeric Substances (EPS) excreted by some prokaryotic (bacteria, archaea) and eukaryotic (algae, fungi) microorganisms. Purified products from isolated cells such as glucan, mannan, and chitin accumulate greater quantities of cations than the intact cells, proving that biomolecules can form metal precipitates. Further, it may be dependent on the cell's metabolism if, in the presence of toxic metals, the microorganism produces compounds that favour the precipitation process. Precipitation may not be dependent on the cells' metabolism, if it occurs after a chemical interaction between the metal and cell surface.

### 2.3.3. Factors affecting biosorption

The most important factors that should be taken into account when considering biosorption are: (i) the type and nature of the biomass; (ii) initial solute concentration; (iii) biomass concentration (biosorbent dosage/solution volume) in solution; (iv) physicochemical factors like temperature, pH, and ionic strength (Chimie, 2014). Apart from the physico-chemical factors such as pH, the presence of other anions and cations, metal speciation, pollutant solubility and form, etc. may also have an influence. With living cell systems, the provision of nutrients and optimal growth conditions is an obvious requirement (Gadd, 2009).

**Effect of solution pH:** The pH of the metal ion solution is an important parameter for adsorption of metal ions because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate (Ii et al., 2011). Therefore, pH of solution influences the nature of biomass binding sites and metal solubility; Metal biosorption has frequently been shown to be strongly pH dependent in almost all systems examined, including bacteria, cyanobacteria, algae, and fungi (Holan & Volesky, 1995).

It has been generally reported that in highly acidic medium ($pH\approx2$) the removal of metal ions is almost negligible and it increases by increasing the solution pH up to a certain limit (Abdelghani & Elchaghaby, 2014). This can be explained that decreasing of biosorption levels by lowering pH can be due to competition between protons and metal ions for the capturing same sites (Igwe, 2006). On the other hand, too high pH value can cause precipitation of metal complexes, so it should be avoided during experiments. For different biosorption system of metal ions, the optimal pH is different. (Wang & Chen, 2006).

**Effect of temperature:** Temperature influence has more effect in a situation where by metal uptake increases within a temperature range of about 20-30$^0$C, but decreases with an increase of temperature above a critical value (Sulaiman, 2015). Increase in temperature probably weakens the bond formed between the metal ions and the adsorption sites on the adsorbent thereby resulting in an increase in the amount of metal ions adsorbed on the adsorbent. At high temperature, adsorption is expected to decrease due to the increased tendency of the metal ion to escape from the surface of the adsorbent to the solution phase, hence there will bound to be weak adsorption interactions between the adsorbent and the adsorbate (Ojedokun & Solomon, 2016).

**Initial solute concentration:** It is generally agreed that the biosorption capacity increases as the initial metal ion concentration in the solution increases, whereas the metal removal percentage (also called removal efficiency) decreases by increasing the metal ion initial concentration (Abdelghani & Elchaghaby, 2014). As a rule, increasing the initial metal concentration results in an increase in the biosorption capacity because it provides a driving force to overcome mass transfer resistance between the biosorbent and biosorption medium (Pahlavanzadeh et al., 2010).

**Biosorbent dosage:** The amount of biomass added in the solution during sorption process also affects the specific metal uptake. In principle, with more biosorbent present, the available adsorption sites or functional groups also increase (Mosbah & Sahmoune, 2013). At low biomass dosage, the number of ions adsorbed per unit adsorbent weight is high. Adsorption capacity is reduced when the biomass dosage increases as a result of lower adsorbate to binding site ratio where the ions are distributed onto larger amount of biomass binding sites (Ojedokun & Solomon, 2016).

**Other factors:** Biosorption is mainly used to treat wastewater where more than one type of metal ions would be present; the removal of one metal ion may be influenced by the presence of other metal ions (Kanamadi, 2003). Wastewaters are contaminated with various contaminants, including different kinds of metals at the same time, which has an effect on biosorption dynamics. The presence of other substances dissolved in a solute on can inhibit biosorption of metals. This is due to competitiveness between ions of metals that are removed and other ions for binding spots on the surface of cells (ZabochnickaŚwiątek, 2014).

The age of biomass can influence the properties of cell walls that are crucial for adsorption of heavy metals. According to numerous observations the relationship between the age of biomass and adsorption of heavy metals is not fully understood (ZabochnickaŚwiątek, 2014). Growth and nutrition of the biomass, and age can also influence biosorption due to changes in cell size, wall composition, extracellular product formation, etc. The surface area to volume ratio may be important for individual cells or particles, as well as the available surface area of immobilized biofilms. The type and nature of the biomass or derived product can be very important including the nature of its application as, e.g. freely-suspended cells or biomass, immobilized preparations, living biofilms, etc. (Gadd, 2009).

## 2.4. Biosorption Equilibrium model

Biosorption equilibrium is the basic requirement for designing a biosorption system (Chimie, 2014). The biosorption isotherms describe the relationship between the mass of the adsorbed component per biosorbent mass the concentration of this component in the solution. Modeling equilibrium sorption is important for industrial applications of biosorption; it yields data that facilitates designing and optimizing the process. (Abdelghani & Elchaghaby, 2014).

The classical Langmuir and Freundlich sorption isotherm models consider sorption by free binding sites rather than ion exchange. Sorption isotherms are useful in quantitatively evaluating and predicting the process performance of the binding capacity and affinity for different metal concentrations and sorbent dosages (Isabel et al., 2014). These models can be applied only at a constant pH. These models are the most widely used for the modelling of biosorption equilibrium in the presence of one metal. These are plotted in a 2D plane, where the specific uptake, q, is reported as function of the metal residual concentration, $C_e$. In the case of multi metal systems, models should be modified in order to take into account all the metals (Veglio & Beolchini, 1997). Equilibrium studies are described by sorption isotherm characterized by certain constants whose values express the surface properties and affinity for the sorbent.

### 2.4.1. The Langmuir Model

According to Langmuir, the sorption occurs at the surface of the sorbent in a homogeneous way and the atoms/ions form a mono-layer, having no mutual interactions, on the sorbent surface. Although it gives no information about the mechanism, it is still used to obtain the uptake capacities of the sorbents (Farooq et al., 2010). The Langmuir isotherm which hints on homogeneity describes the monolayer coverage of a sorbate on a sorbent surface at constant temperature (Adelagun, 2014). The linear form of the Langmuir equation can be expressed in terms of equilibrium concentration and adsorption capacity as:

$$Ce/q_e = 1/K_l q_m + C_e/q_m \qquad (1)$$

Where: $C_e$ is the concentration of the sorbate at equilibrium (mg/L), $q_e$ is the amount of sorbate sorbed at equilibrium per unit mass (mg/g), $q_m$ is the monolayer sorption capacity at equilibrium (mg/g) and $k_l$ is the Langmuir equilibrium constant (l/mg). The values of maximum sorption capacity, $q_m$ and k are obtained from the slope and intercept respectively of the plot of straight line graph of $C_e/q_e$ against $C_e$.

### 2.4.2. The Freundlich Model

The Freundlich model is used in the process of sorption on heterogenic surface, i.e. energy heterogenic surface. Typical property of heterogenic surface is that the areas where adsorption occurs differ in terms of adsorption energy. In consequence, adsorption places with the highest adsorption energy are covered first, and then the places with lower energy are covered (Zabochnickaświątek & Krzywonos, 2014). The Freundlich isotherm, which is empirical in nature, can be interpreted to adsorption onto surfaces supporting sites of varied affinities, and has been used widely to fit experimental data of liquid-phase adsorption (Oubagaranadin & Murthy, 2010).

The Freundlich isotherm has also been employed to quantify equilibrium biosorption systems. Like the Langmuir isotherm, the extent of adsorption/sorption is determined as a function of the equilibrium concentration of the metal in solution, without reference to pH or other ions in the same aqueous system (Davis et al., 2003). The Freundlich isotherm is regarded as an empirical isotherm. It indicates the surface heterogeneity of the sorbent. The linearized form of Freundlich equation is given by:

$$\mathrm{Ln}(q_e) = (1/n)\ \ln(C_e) + \ln(K_f) \qquad (2)$$

where $K_f$ and n are Freundlich adsorption constants, related to adsorption capacity and sorption intensity respectively obtained from the plot of $\ln(q_e)$ against $\ln(C_e)$ which gives a straight line graph with 1/n as slope and $\log(K_f)$ as intercept.

### 2.5. Kinetics of sorption

The prediction of the biosorption rate gives important information for designing batch biosorption systems (Abdelghani & Elchaghaby, 2014). The efficiency of the adsorbent is evaluated by studying adsorption kinetics. Kinetics is an adsorption dynamic which describes the solute uptake rate and evidently control the resident time of adsorbate and possibilities of desorption. The kinetic properties of adsorbate uptake are used in selecting optimum operating conditions for the full scale batch process. Several kinetic models have been applied to fit the biosorption data of different metal ions onto various biosorbents. These models include the pseudo first order, pseudo second order, Elovich, intraparticle diffusion, etc. (Abdelghani & Elchaghaby, 2014).

### 2.5.1. Pseudo first order model

The Lagergren rate equation is one of the most widely used sorption rate equations for the adsorption of a solute from a liquid solution (Holan & Volesky, 1995). The pseudo-first-order equation is given as:

$$dq_t/d_t = k_f (q_e - q_t) \tag{3}$$

where $q_t$ is the amount of adsorbate adsorbed at time t (mg/g), $q_e$ is the adsorption capacity at equilibrium (mg/g), $K_f$ is the seudo first order rate constant ($min^{-1}$), and t is the contact time (min). The integration of the above equation with for the boundary conditions; t = 0 to t = t and $q_t$ = 0 to $q_t = q_t$, gives:

$$\log (q_e - q_t) = \log(q_e) - (K_f/2.303) * t \tag{4}$$

The values of adsorption rate constant ($K_f$) for metals adsorption on SBG will be determined from the plot of $\log(q_e - q_t)$ against t.

### 2.5.2. Pseudo-second-order model

The pseudo-second-order model is given as:

$$(dq_t/d_t) = K_s(q_e - q_t)^2 \tag{5}$$

Where $K_s$ is the pseudo-second-order rate constant (g/mg min), $q_e$ is the amount of metal ion adsorbed at equilibrium (mg/g), and $q_t$ is the amount of metal ion adsorbed at time t (mg/g). Integrating for the boundary conditions t = 0 to $t = t$ and $q_t = 0$ to $q_t = q_t$ gives

$$q_t = \frac{{q_e}^2 * K_{s*t}}{1 + q_e K_s * t} \tag{6}$$

Eq. (5) is the integrated rate law for a second order reaction and can be rearranged to obtain

$$q_t = \frac{t}{\frac{1}{K_s {q_e}^2} + \frac{t}{q_e}} \tag{7}$$

This has a linear form of

$$\frac{t}{q_t} = \frac{1}{K_s {q_e}^2} + \frac{1}{q_e} t \tag{8}$$

The initial adsorption rate, *h* (mg/g min) is defined as:

$$h = k_s {q_e}^2 \tag{9}$$

The rate parameters $k_s$ and $q_e$ can be directly obtained from the intercept and slope of the plot $(t/q_t)$ against t.

## 2.6. Brewery spent grain as adsorbent

Beer is the fifth most consumed beverage in the world next to tea, carbonates, milk and coffee and it continues to be a popular drink with an average consumption of 23 liters/person per year by population aged above 15. The brewing industry has an ancient tradition and is still a dynamic sector open to new developments in technology and scientific progress (Fillaudeau et el., 2006 and Olajrie 2012).

The brewing process uses malted barley and/or cereals, unmalted grains and/or sugar/corn syrups (adjuncts), hops, water, and yeast to produce beer (Olajire, 2012). Most brewers use malted barley as their principal raw material. From this process, various byproducts are generated. The three most common byproducts are spent grains, spent hops and surplus yeast, which are generated from the main raw materials. These three brewery byproducts are available in large quantities throughout the year, but their use has still been limited., being basically sold to local dairy farmers to be used as cattle feed, or simply as a land fill (Mussatto, 2009 and Gupta & Abughannam, 2010).

Spent grains are resulted from mashing process and obtained after rendering the malt and cereal grain content soluble in water. After extraction, the spent grains and wort (water with extracted matter) are called mash and need to be separated (Fillaudeau et al., 2006). The separated, brewers' spent grain (BSG) amount consists about 85% of the total byproducts (Tang et al., 2009).

Brewers' spent grain (BSG) is a readily available, high volume low cost byproduct of brewing and is a potentially valuable resource for industrial exploitation. Although BSG is the main byproduct of the brewing process, it has received little attention as a marketable commodity, and its disposal is often an environmental problem (Li et al., 2009).

However, for several years it has been utilized and sold as livestock feed (Fillaudeau et al., 2006) and, being basically sold to local dairy farmers, or simply as a land fill (Mussatto, 2009). Several attempts have been made in utilizing BSG in animal feeds, production of value added compounds (xylitol, lactic acid, among others), micro-organisms cultivation, or simply as raw material for extraction of compounds such as sugars, proteins, acids and antioxidants (Aliyu & Bala, 2011).

### 2.6.1. Composition of brewery spent grains (BSG)

Brewery spent grain is considered as a lignocellulosic material rich in protein and fiber, which account for around 20% and 70% of its composition, respectively. Microscopic examination of brewery spent grain shows the presence of numerous fibrous tissues from the surface layers of the original barley grain. The main components of these fibrous tissues are arabinoxylan, lignin (a polyphenolic macromolecule), and cellulose (a linear homopolymer of glucose units) (Gupta & Abughannam, 2010).

Chemical composition of brewery spent grain varies with types of barley used, harvesting time, characteristics of hops and adjuncts added, and brewery technology (Santos et al., 2003). According to (Huige, 1994) Minerals, vitamins, and amino acids are also found in brewery spent grain. The mineral elements include calcium, cobalt, copper, iron, magnesium, manganese, phosphorus, potassium, selenium, sodium, and sulfur, all in concentrations lower than 0.5% each. The vitamins include (in ppm): biotin (0.1), choline (1800), folic acid (0.2), niacin (44), pantothenic acid (8.5), riboflavin (1.5), thiamine (0.7), and pyridoxine (0.7); protein bound amino acids include leucine, valine, alanine, serine, glycine, glutamic acid, and aspartic acid in the largest amounts, and tyrosine, proline, threonine, arginine, and lysine in smaller amounts. Cysteine, histidine, isoleucine, methionine, phenylalanine, and tryptophan also present in minor quantity (Huige, 1994).

Brewery spent grain basically consists of the husk–pericarp–seed coat layers that covered the original barley grain. Depending on the evenness of malting more or less starchy endosperm and walls of empty aleurone cells may also remain. The starch content will be negligible, and some residues of hops introduced during mashing will be present depending on the brewing regime used. Thus, the major components of brewery spent grain will be the walls of the husk–pericarp–seed coat, which are rich in cellulose and non-cellulosic polysaccharides and lignin, and may contain some protein and lipid (Huige, 1994).

Chemically, BSG is rich in polysaccharides, protein and lignin. Residual starch can contribute up to 13% of the dry weight and brewery spent grain from lager malts has higher protein content than that from ale. In general, at the point of production, brewery spent grain is a relatively uniform chemical feedstock available for industrial upgrading (Robertson, 2010). Different components of brewer spent grain (BSG) is shown in table 2.4 cited from different researchers.

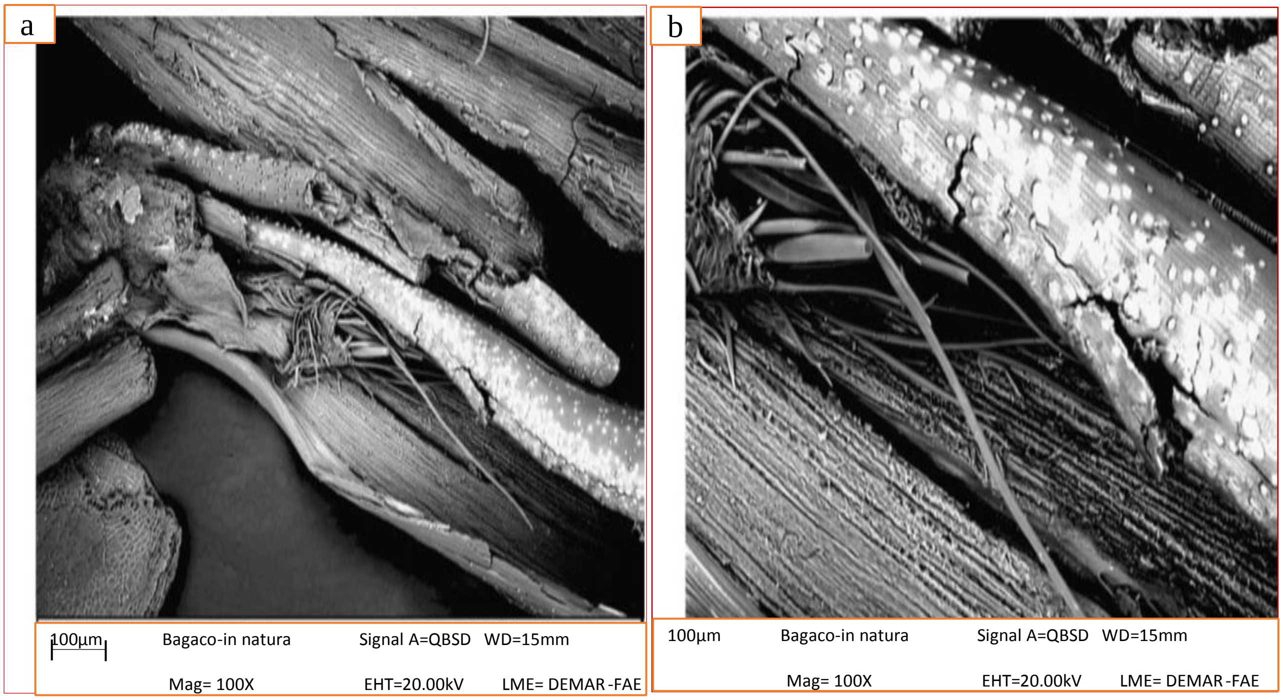


Figure 2.3 Scanning electron microscopy of BSG particles. (a) Magnification 100 fold; (b) magnification 300 fold: source (Mussatto, 2006)

Table 2.4 Chemical composition of brewers' spent grain (BSG)

| Components | Kanauchi et al. 2001 | Mussatto and Roberto,2005 | Santos et al., 2006 | Huige, 1995 | Itodo et al., 2014 |
|---|---|---|---|---|---|
| Cellulose | 25.4 | 16.8 | - | - | 28.4 |
| Arabinoxyl | 21.8 | 28.4 | - | - | - |
| Lignin | 11.9 | 27.8 | - | - | 27.8 |
| Protein | 24 | 15.2 | 24.2 | 14 – 15 | 15.2 |
| Fat | - | - | 3.9 | - | - |
| Phenol | - | - | 18.7 | - | - |
| Lipid | 10.6 | - | - | - | - |
| Ash | 2.4 | 4.6 | 3.4 | - | 4.6 |

### 2.6.2. General uses of spent grain

The main current application of BSG is as cattle feed, where it can be utilized directly in wet form (as separated from the mashtun) or as dry material (Mussatto, 2014). Animal growth in terms of body weight gain were reported by (Kaur & Saxena, 2004) due to supplementation of brewery spent grain in their diet. The addition brewery spent grain in the cow's diet also increases milk yield, and milk TS concentration (Tsirgogianni, 1996).

Since BSG is derived from materials utilized for humans, it can be incorporated into so many human diets, such as breads and snacks; especially where there is need to boost the fiber contents (Aliyu & Bala, 2011). According to the study of (Waters et al., 2012) it revealed that wheat flour incorporating BSG had increased water absorption and improves its texture and nutritional value. Also, incorporation of BSG into monogastric diets is beneficial for intestinal digestion, alleviating both constipation and Diarrhoea. Such effects were attributed to the content of glutamine-rich protein, and to the high content of non-cellulosic polysaccharides and smaller a mounts of β-glucans (Tang et al., 2009).

In energy perspective several alternatives have been investigated for BSG use in energy production, such as thermochemical conversion (pyrolysis, combustion) (Mahmood, Brammer, Hornung, Steele, & Poulston, 2013), biogas production (Tewelde et al., 2012) and ethanol production (Olugbenga & Ibiyemi, 2011). Due to the energy crisis today, BSG has preferred to produce alternative energy sources because of its large availability, chemical composition and low cost (Mussatto, 2014). Generally, the following benefits of brewery spent grain are summarized in the areas of food, energy production and in chemical and biotechnological processes (Mussatto, 2014 and Aliyu & Bala, 2011).

I. Food ingredient
    ✓ Animal nutrition
    ✓ Human nutrition
II. Energy production (bioethanol, biogas, thermochemical conversion) III. Charcoal production
IV. As a brick component V. Economic benefits
VI. Environmental benefits

VII. BSG use in chemical processes
  - ✓ Extraction of valuable compounds by chemical processes
  - ✓ Raw material for pulp and paper production
  - ✓ Adsorbent material

VIII. Biotechnological processes
  - ✓ Extraction of valuable compounds by enzymatic processes
  - ✓ Substrate for cultivation of microorganisms
  - ✓ Substrate for enzyme production
  - ✓ Additive or carrier in brewing
  - ✓ Source of added-value products

## 2.7. Metal adsorption by brewery spent grain

Adsorption processes must be fast, efficient, and use cheap adsorbents to compete with other techniques. Due to its low cost and easy availability, BSG has been tested as an adsorbent for several types of compounds (Mussatto et al., 2006). Brewery spent grain adsorption capacity depends on initial treatment method (Lu & Gibb, 2008 and Low et al., 2000). Modified spent grain(MSG), uses as adsorbent, since it has a large specific surface area and small size, with hollow and layered structures containing many functional groups such as carboxyl, hydroxyl and amine that are responsible for the binding of metal ions (Qingzhu et al., 2008).

Pretreatment methods using different kinds of modifying agents such as base solutions (sodium hydroxide, calcium hydroxide, sodium carbonate) mineral and organic acid solutions (hydrochloric acid, nitric acid, sulfuric acid, tartaric acid, citric acid, thioglycollic acid), organic compounds (ethylene diamine, formaldehyde, epichlorohydrin, methanol), oxidizing agent (hydrogen peroxide), etc. ( Ngah & Hanafiah, 2008).

Brewery spent grain adsorbent treated with NaOH greatly enhanced adsorption of Cd(II) and Pb(II) ions with sorption capacities of 17.3 and 35.5 mg/g respectively as a result of the increase in the amount of galactouronic acid groups after hydrolysis of O-methyl ester groups, whereas HCl treated brewery spent grain adsorbent has lower adsorption capacity than the untreated spent grain (Low et al., 2000). On the other hand, the highest measured uptake of lead onto HCI and NaOH treatment was 28.57 mg/g at 0.33 g/mg/minute with removal efficiency of 95.45% (Isabel et al., 2014).

The work of (Itodo et al., 2014) showed that results of the studies on Zn and Cd metal ions were favorably adsorbed on untreated brewery spent with a removal efficiency of 94.46% and 77.81% and adsorption capacity of 32.2 mg/g and 20.4 mg/g respectively. In the case of sorption of trivalent chromium onto alkali treatment(NaOH) brewery spent grain, it does not improve spent grains uptake performance (Ferraz et al., 2015). The removal of Cu(II) ions from aqueous solutions using unmodified brewery spent grain was studied. The experimental data fitted the Langmuir isotherm and the maximum adsorption capacity of spent grain was determined to be 10.47 mg/g dry weight (pH 4.2) (Lu & Gibb, 2008). Table 2.5 summarizes different researchers work on brewery spent grain metal uptake capacity when it is used as chemically treated and untreated.

Table 2.5 Summarized metal ions uptake capacity of chemically treated and untreated brewery spent grain

| Adsorption capacity(mg/g) | Low et al., 2000 | Isabel et al., 2014 | Itodo et al., 2014 | (Qingzhu Li et al., 2009) | Lu & Gibb, 2008 | Low et al., 2001 | Feeraz et al., 2001 |
|---|---|---|---|---|---|---|---|
| Lead | 35.5[2] | 28.57[2] | - | 35.04[4] | - | - | |
| Copper | - | - | - | - | 10.47[1] | - | |
| Zink | - | - | 32.2[1] | - | - | - | |
| Chromium (VI) | - | - | - | - | - | 18.94[3] | |
| Chromium (III) | - | - | - | - | - | | 18.94[3] |
| Cadmium | 17.3 [2] | - | 20.4[1] | - | - | - | |

1-untreated BSG
2-NaOH treated BSG
3-HCI treated BSG
4- NaCl treated BSG
-undetermined

# 3. MATERIALS AND METHODS

## 3.1. Equipment and Materials

The major raw material used for adsorbent during the experimental works was spent brewery grain (SBG). Analytical reagent grade chemicals used were 0.1M sodium hydroxide, 3M sulphuric acid**,** concentrated $HNO_3$, 0.1M hydrochloric acid, lead nitrate ($Pb(NO_3)_2$), 2,5-diphenylcarbazide, potassium dichromate, distilled water and ethanol, bought from different chemical stores in Addis Ababa.

The equipment used during the experimental works were Atomic Absorption Spectrophotometer, AAS (AAS nova 400plus), orbital shaker (Excella E24R), pH meter, UV spectrophotometer (lambda 950), FTIR (spectrum 65 FTIR), electronic balance, oven, magnetic stirrer, different size conical and Erlenmeyer flasks, beakers, measuring cylinders, burette, zipper plastic bags, whatman number 42 filter paper, different mesh size sieves and centrifuge mill.

The experimental work began in January 2016 and ended in May 2016; a total of five months were spent for the laboratory works. Lead metal analysis was done at Addis Ababa University; College of Natural Science, Environmental Science Postgraduate Laboratory. And chromium analysis was conducted at School of Chemical and Bio Engineering Laboratory, AAiT. Real waste water samples for batch adsorption test were obtained from Metal and Engineering Corporation (METEC) located in Addis Ababa, Ethiopia.

## 3.2. Experimental methods

### 3.2.1. Preparation of Spent Brewery Grains (BSG)

Fresh spent grain was obtained from BGI Ethiopia brewery located in Addis Ababa. It was successively washed with distilled water to remove impurities, and then dried at 75°C. Afterward it was treated with a sodium hydroxide solution of 0.5M for 4 hours at room temperature to enhance its metal sorption capacity (Mussatto et al., 2006). The excess of alkaline solution was removed by washing spent grains with distilled water until it was completely free from the base in successive washings, according to the procedure described by (Low, et al. 2000). This material was designated as TSG (Treated Spent Grains). Then TSG was dried in an oven at 75ºC for 24 h. The dried biomass was grinded and sieved and the particles having sizes of 250-500 μm were used in the tests.

### 3.2.2. Fourier Transform Infrared Spectroscopy (FTIR) analysis of BSG

FTIR analysis was carried out in order to identify the surface property of the adsorbent and functional groups that might be involved in the binding of metal ions. The functional groups of brewery spent grain before and after sorption were determined using FTIR spectrometer at wave number range of 400 – 4000 $cm^{-1}$. 1.0 % sample (BSG) was well mixed into 250 mg fine alkali potassium bromide (KBr) powder and then finely pulverized and put into a pellet-forming die. Force of 10 bar was applied to form transparent pellets.

Air and moisture from the KBr powder were eliminated. Then it was pulverized and dried at approximately 110 °C for two to three hours. After drying the powder was stored in a desiccator. A typical infrared scan was generated in the mid-infrared region of the light spectrum. The midinfrared region is from 400 to 4000 wavenumbers, which equals wavelengths of 2.5 to 25 microns. FTIR analysis was done at Addis Ababa university, College of Natural Science, Chemistry Laboratory.

### 3.2.3. Preparation of stock solution

Lead nitrate $Pb(NO_3)_2$ and Potassium dichromate salts were used in the preparation of the salt stock solutions. Stock Pb(II) and Cr (VI) solutions (1,000 mg/l) were prepared by dissolving accurately weighed amounts of each salts, 1.599g of $Pb(NO_3)_2$ and 2.58g of potassium dichromate in 1000ml distilled water. Working solutions of different concentration were prepared from the stock solution by serial dilution with distilled water. All chemicals used were of analytical reagent grade and bought from different chemical stores in Addis Ababa.

### 3.2.4. Wastewater characterization & sampling

Electro plating wastewater containing Pb(II) and Cr(VI) ions of (50 ml) were digested with 10 ml of concentrated $HNO_3$ at $80^oC$ until the solution became transparent (APHA 2005). These transparent solutions were then filtered through Whatman number 42 filter paper and diluted to 50 ml with distilled water. Working solutions for calibration were prepared by serial dilution of the stock solution. The initial and final concentrations of heavy metal, in the filtrate were determined by using atomic absorption spectrophotometer and UV/VIS spectrophotometer (lambda 950), fitted with a specific wave length of 283.3 nm and 540 nm for lead (II) and Cr(VI) respectively.

### 3.2.5. Batch sorption experiment

Different initial concentrations (30, 65 and 100 mg/l) of each Pb(II) and Cr(VI) ion solutions were prepared by proper dilution from stock (1000 mg/l) metal ions standard solutions. PH (2-6) of the test solution was monitored by adding 0.1M HCl and 0.1M NaOH solution as required. Definite amount (2g) of brewery spent grain was then added to the metal ion solution (200 ml) in a 250 ml stopper conical flask and agitated for the desired contact time using orbital shaker (EXELLA E24R) at 200 rpm. The time (0, 30, 75, 120 and 180 minutes) required for reaching equilibrium condition was estimated by drawing samples at regular interval of time till the equilibrium was reached. The content of the lead(II) ions in the test flask were separated from bio-sorbent (BSG) by filtration through a filter paper and was analyzed by Atomic Absorption Spectrophotometer, AAS (AAS nova 400plus).

Chromium analysis was conducted by using diphenyl method. A 0.25% W/V solution of diphenyl carbazide was prepared in 50% acetone. 15ml each of the sample solutions containing various concentrations of Cr (VI) were pipetted out into 25ml standard flasks. To these samples 2 ml of 3M $H_2SO_4$ was added followed by 1ml of diphenyl carbazide and total volume was made up to 25 ml using deionized, double distilled water. Chromium (VI) concentrations estimated by the intensity of the red brownish color complex formed, was measured using UV/VIS Spectrophotometer (lambda 950) at 540 nm. Amount of metal ions bound during the series of batch investigations was calculated by using the mass balance equation. This can be described as metal ions disappeared from the solution by biosorbent materials. The sorption capacity of metals can be calculated as (Ashraf, Mahmood, & Wajid, 2011):

$$\ldots.\ Q_e = \frac{(C_o - C_e) * V}{m} \qquad (10)$$

where; $Q_e$= adsorption capacity at equilibrium, V = volume of adsorbate solution (ml), m=mass of BSG (g), $C_o$ = initial concentration in mg/L, $C_e$= concentration at equilibrium (mg/L). The removal percentage (R %) is defined as the ratio of difference in metal concentration before and after adsorption ($C_o$–$C_e$) to the initial concentration of the adsorbate in aqueous solution ($C_o$) shown below:

$$\%R = \frac{(C_o - C_e) * 100}{C_o} \qquad (11)$$

where; $C_o$ = initial concentration in mg/L, $C_e$= concentration at equilibrium (mg/L). Figure 3.1 shows the process flow diagram of the experimental works.

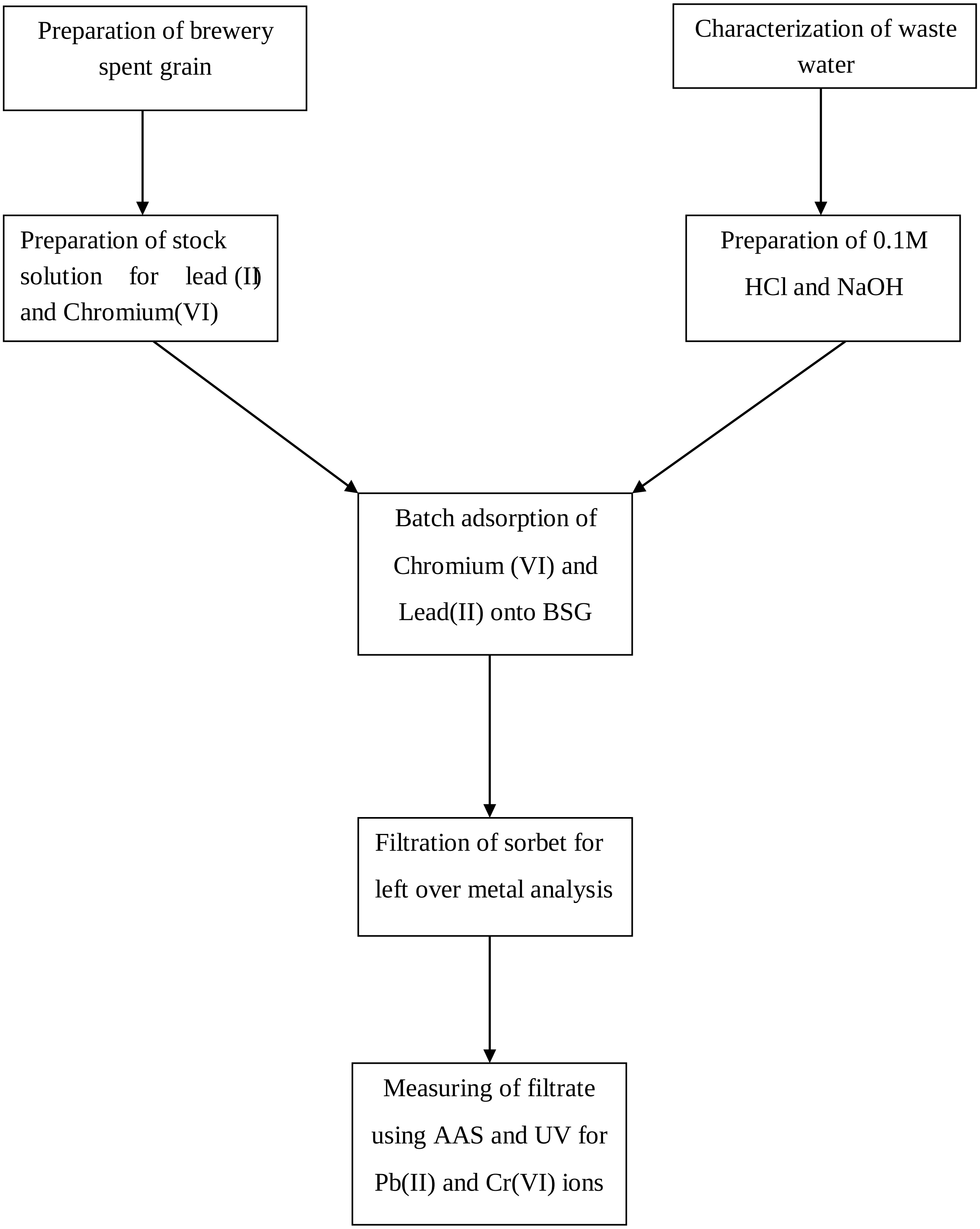


Figure 3.1 Flow diagram for batch sorption of metal ions by BSG

# 4. RESULT AND DISCUSSION

## 4.1. FT-IR analysis and sorption mechanisms of BSG

FTIR analysis was performed to detect information on the nature of the bonds and to identify different functional groups available on the adsorbent surface. As it can be seen from Figure 4.1 brewery spent grains contains functional groups of O-H and C-O stretching vibration of primary alcohol, N-H stretching vibration of amine), C-H stretching and bending vibration of alkane groups, C=O stretching vibration carbonyl, C=C stretching vibrations of alkene, C–F stretching vibrations of alkyl halide. All functional groups, their types of vibrations, wave number and intensity found in brewery spent grain are given in Table 4.1.

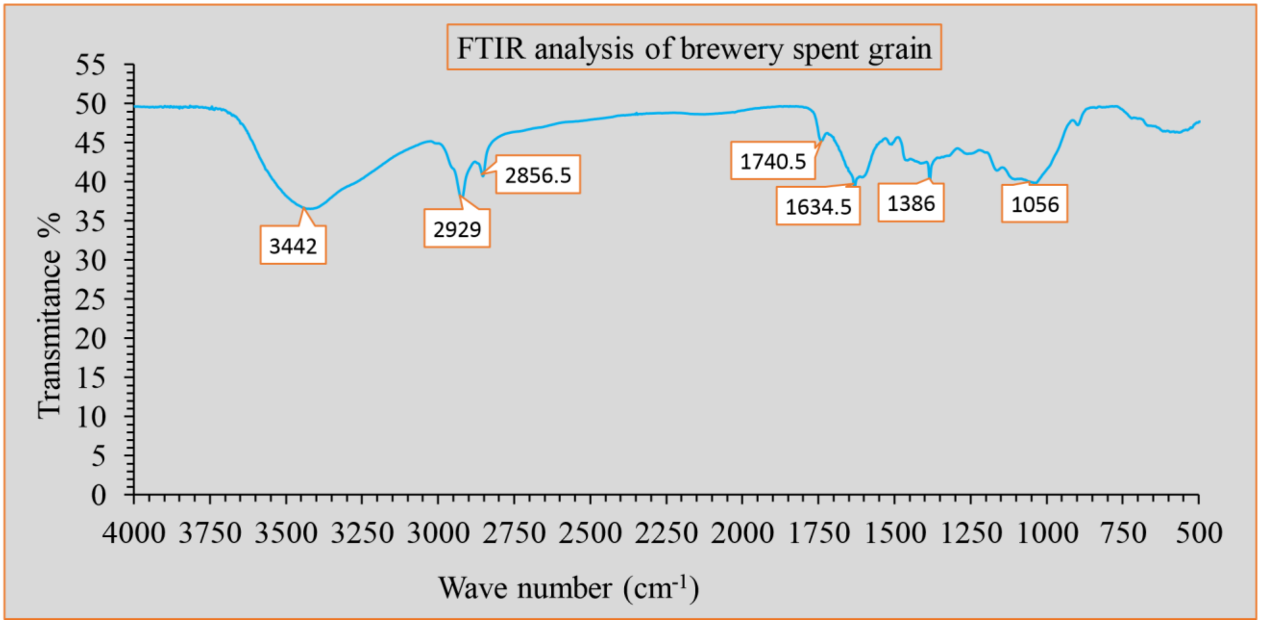


Figure 4.1 FTIR spectra for spent brewery grain before adsorption of metal ions

Table 4.1 Characteristic IR absorption frequencies of BSG functional groups

| Functional groups | Types of vibration | Wave number ($cm^{-1}$) | Intensity |
|---|---|---|---|
| O-H (Alcohol) | Stretch, H-bound | 3442.00 | Strong, Broad |
| N-H (amine) | Stretch | 3442.00 | Medium |
| C-H (Alkane) | Stretch | 2929.00 | Strong |
| C=O (carbonyl) | Stretch | 1740.50 | Strong |
| C=C (alkene) | Stretch | 1634.50 | Variable |
| -C-H (Alkane) | Bending | 1386.00 | Variable |
| C-F (alkyl halide) | Stretch | 1056.00 | Strong |
| C-O (Alcohol) | Stretch | 1056.00 | Strong |

As seen in figure 4.2 broad peak representing hydroxyl and amine groups shifts from 3442 to 3438 cm$^{-1}$ and 3440 cm$^{-1}$ after lead and chromium ion adsorption respectively. The decrease in wave number of this peaks is attributed to the attachment of lead and chromium ions on hydroxyl and amine groups. The peaks at 2929, 1386, 1056 cm$^{-1}$ corresponds C-H stretching vibration of alkane, -C-H bending vibration of alkane, C-O stretching vibration in primary alcohol showed a reduction in wave number for both lead and chromium after adsorption which are attributed to the metal ions attachment. The other constant peak values before and after adsorption are worth nothing that the bond with functional groups were not observed after adsorption of chromium and lead ions.

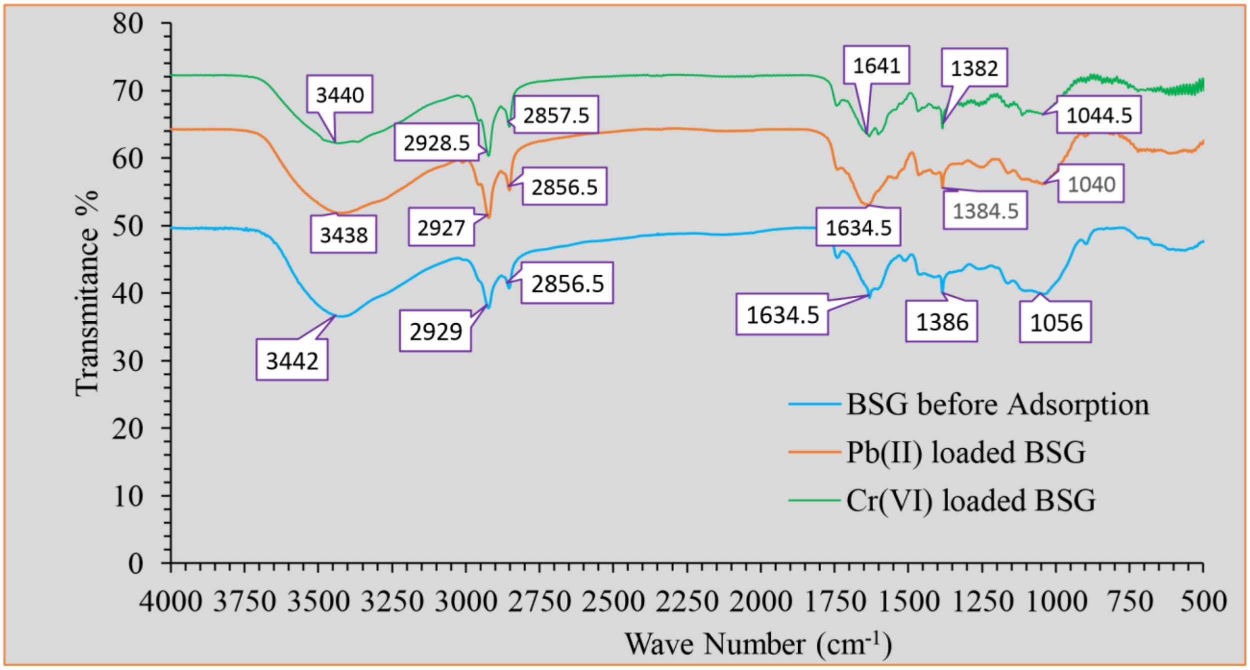


Figure 4.2 FTIR spectra for spent brewery grain before and after adsorption of metal ions

## 4.2. Effect of pH of Adsorbate solution

pH effect on sorption of lead and chromium was conducted between the pH of solutions ranges of 2-6. An increase in pH beyond 6, the amount of hydroxyl ions increased in the solution and metal ions react and precipitate with OH$^-$ ions which results impossible the biosorption process (Chimie, 2014). Lowering the pH below 2 of the solution probably results in decreasing of biosorption levels and this can be explained due to competition between protons and metal ions for the capturing same sites of the adsorbent, which at low pHs, metal ions do not successful (Taghi ganji, 2005).

The influence of pH on the extent of sorption of Pb (II) and Cr(VI) ions by BSG shown in Figure 4.3. From the plot, maximum amount of lead metal ion was adsorbed at pH 4 with maximum percentage removal of 96.53%, while maximum chromium sorption was observed at pH 2 with maximum percentage removal of 79.47%. For sorption of lead, as pH value increases from 4 to 6 slightly diminishing of removal efficiency was observed. This may be attributed to the fact that above optimum pH of 4, $OH^{-}$ions increment causes a decrease in adsorption of metal ions at adsorbent adsorbate interface (Thakur & Parmar, 2013).

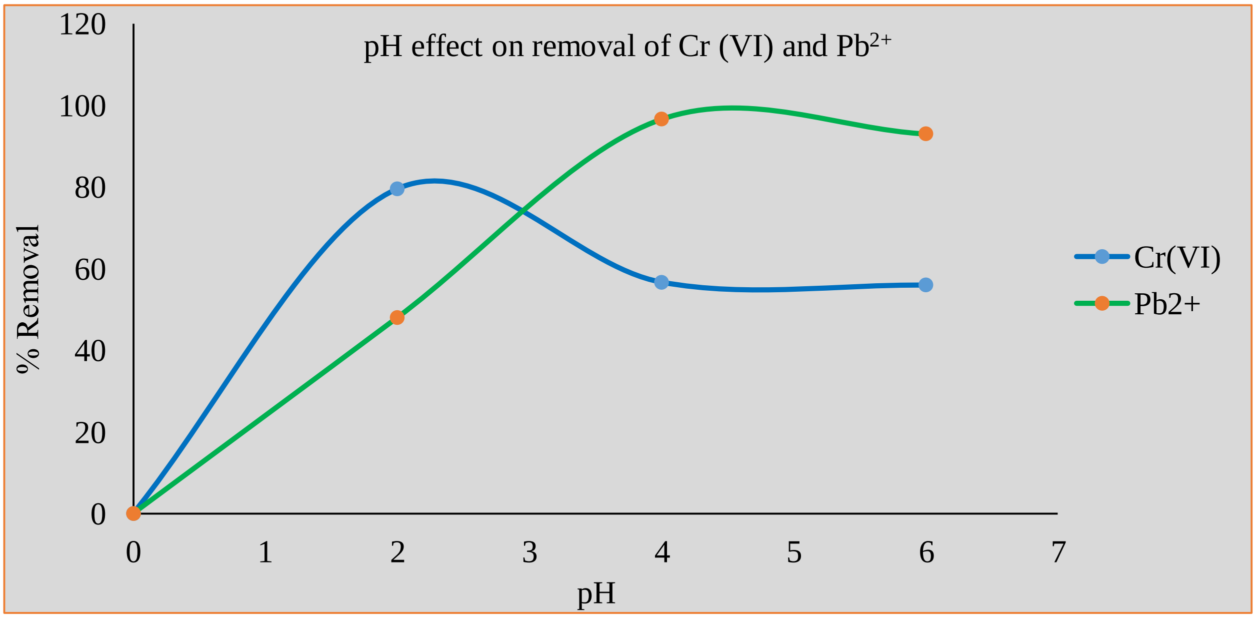


Figure 4.3 Effect of pH on Cr(VI) and $Pb^{2+}$ removal

For chromium sorption onto BSG, maximum adsorption efficiency was obtained at pH 2. But as pH increased from 2 to 6 its removal efficiency was reduced. The maximum adsorption of Cr(VI) was observed at the acidic range because at lower pH there is an increase in $H^{+}$ ions on the adsorbent surface, and the presence of $HCrO^{4-}$ ions resulting in significant strong electrostatic attraction (Agarwal & Gupta, 2015).

## 4.3. Effect of brewery spent grain dosage

The effect of BSG dose (g) on sorptive removal of Pb (II) and Cr(VI) ions was investigated by varying its amount in 200 ml fixed volume of metal solutions. As shown in Figure 4.4 BSG dosage was varied over the range of 2.5-10 gm/l or 0.5-2 gm/200ml. Other factors were kept constant at pH=4 for lead and pH=2 for chromium and contact time of 120 minutes for both metal ions.

The removal efficiency of lead increased from 87.2% to 96.3% and that of Cr(VI) from 41% to 79.47% as the BSG dosage increased from 0.5g to 2g in 200 ml of metal ions solution. This adsorption increment attributed to the fact that the increase in percentage removal of metal ions with increase in adsorbent dose is due to the availability of more and more adsorbent surfaces for the solutes to adsorb (Prabha & Udayashankara, 2014).

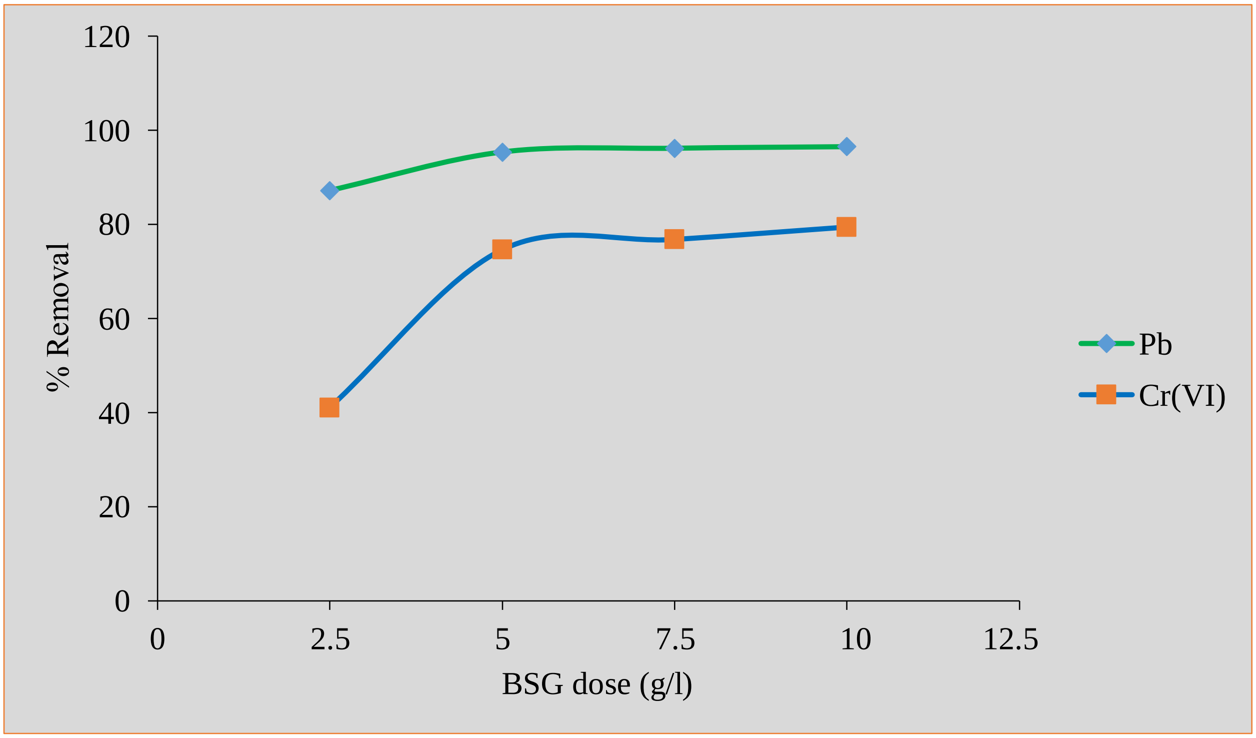


Figure 4.4 Effect of BSG dosage on Cr(VI) and Pb (II) % removal

Up to 5 g/l of adsorbent dosage, both metals removal efficiency was rapid, further addition of BSG dosage did negligible increment on % removal. Optimum dose was chosen for 7.5 g/l of sorbent beyond which negligible change in the amount of metal removal was observed. This constant rate of adsorption is attributed to saturation of the adsorbent binding sites or equilibrium between liquid and solid phase (Deepa & Suresha, 2014).

On the other hand, Figure 4.5 shows that the adsorption capacity of BSG for both metal ions diminished as dose amount increased. This can be justified as that at low biomass dosage, the amount of ions adsorbed per unit adsorbent weight is high. The adsorption capacity is reduced when the biomass dosage increases as a result of lower adsorbate to binding site ratio where the ions are distributed onto larger amount of biomass binding sites (Abdelghani & Elchaghaby, 2014).

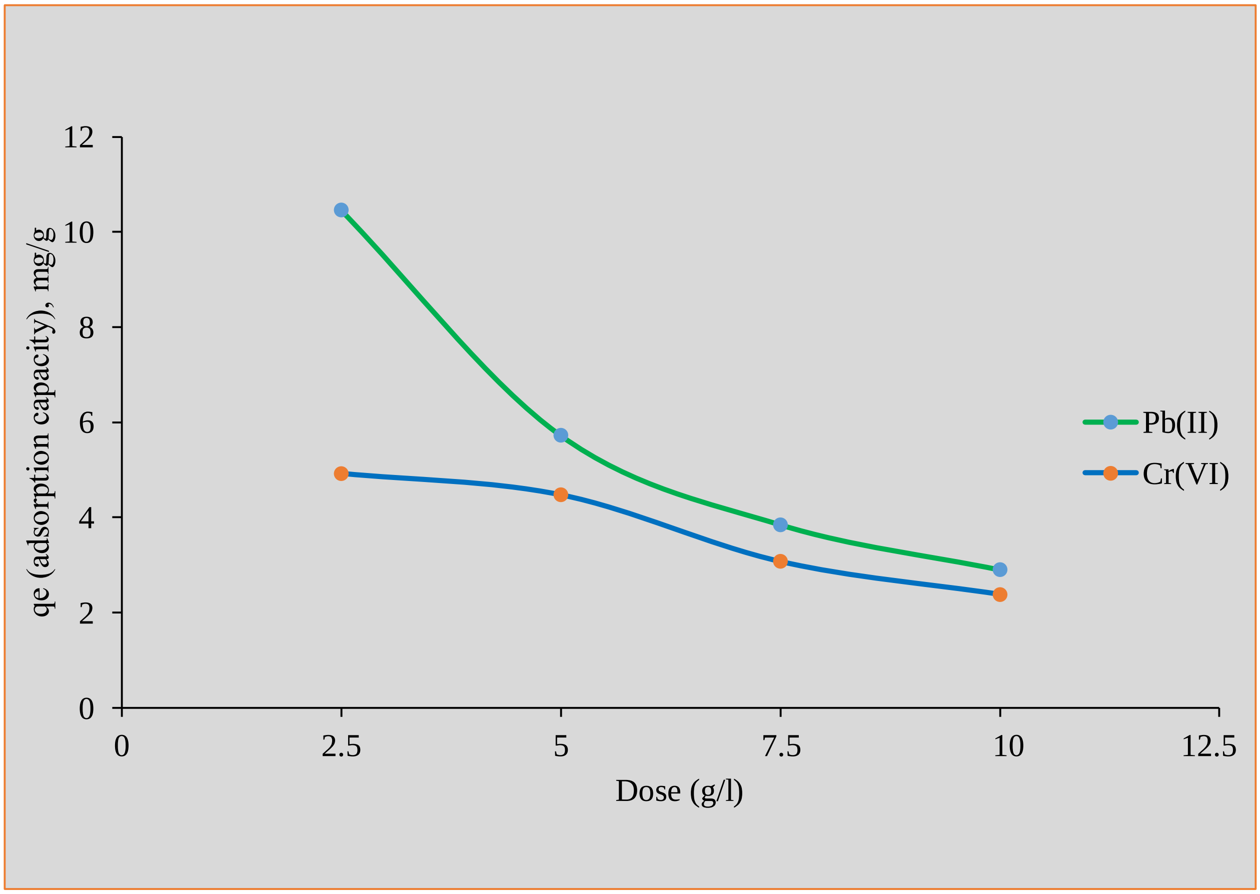


Figure 4.5 Effect of BSG dosage on Cr(VI) and Pb (II) adsorption capacity

## 4.4. Effect of contact time

Figure 4.6 shows the time profiles of brewery spent grain adsorption of Pb(II) and Cr(VI). Adsorption of Pb(II) and Cr(VI) showed an increasing trend up to a reaction time of 30min beyond which adsorption appeared to have approached equilibrium. After 75 min, the adsorption capacity and removal efficiency of Pb(II) and Cr(VI) by brewery spent grain was constant and % removal increment was almost negligible. After 120 min, all reach equilibrium. Contact time required to attain equilibrium was dependent on the initial concentration of heavy metals.

For the same concentration, the percentage removal of heavy metal increases with increase of contact time till equilibrium is attained (Thakur & Parmar, 2013). The result showed that the optimal contact time of Pb (II) and Cr(VI) to attain equilibrium with brewery spent grain adsorbent was 75 minutes with removal efficiency of 96.08% for lead and 78.71% for Chromium (VI) ion. Beyond 75 minutes the removal efficiencies increments were small with maximum equilibrium attainment of 96.3 and 79.47% for lead(II) and chromium (VI) respectively.

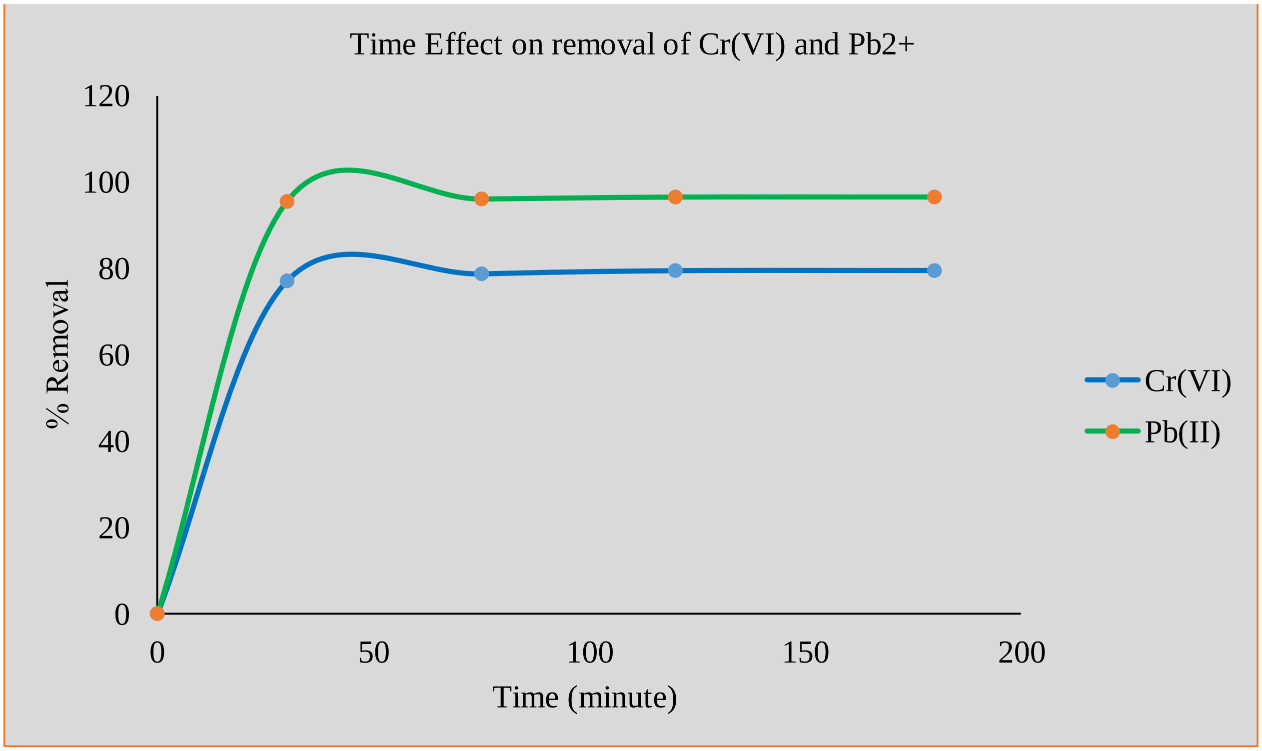


Figure 4.6 Effect of contact time on Cr(VI) and Pb(II) removal at pH=2 and pH=4 respectively

## 4.5. Effect of initial metal ions concentration

As shown in Figure 4.8 adsorption capacity increased with increasing concentration of adsorbate. For Pb(II) ion adsorption there was an increase from 2.9mg/g to 9.59mg/g when initial concentration increased from 30mg/l to 100mg/l and for Cr from 2.59mg/g to 7.77mg/g. For both metal ions adsorption capacity increased as their initial concentrations increased. This may be justified that increase in metal ions concentration results in increase in number of available molecules per binding sites of the adsorbent. Increase in initial metal ions concentration enhances the interaction between the metal molecules and the surface of the adsorbent (Itodo et al., 2014) meaning, it provides a driving force to overcome mass transfer resistance between the biosorbent and biosorption medium.

On the other hand, Figure 4.7 shows that the removal efficiency of the metal ions by BSG decreased with increasing the initial ion concentration. This attributed to the fact that at lower ions concentration in the solution, the ions would interact with the binding sites and thus facilitated almost 100% adsorption whereas at higher concentrations, more ions are left unadsorbed in the solution due to the saturation of the binding sites (Abdelghani & Elchaghaby, 2014).

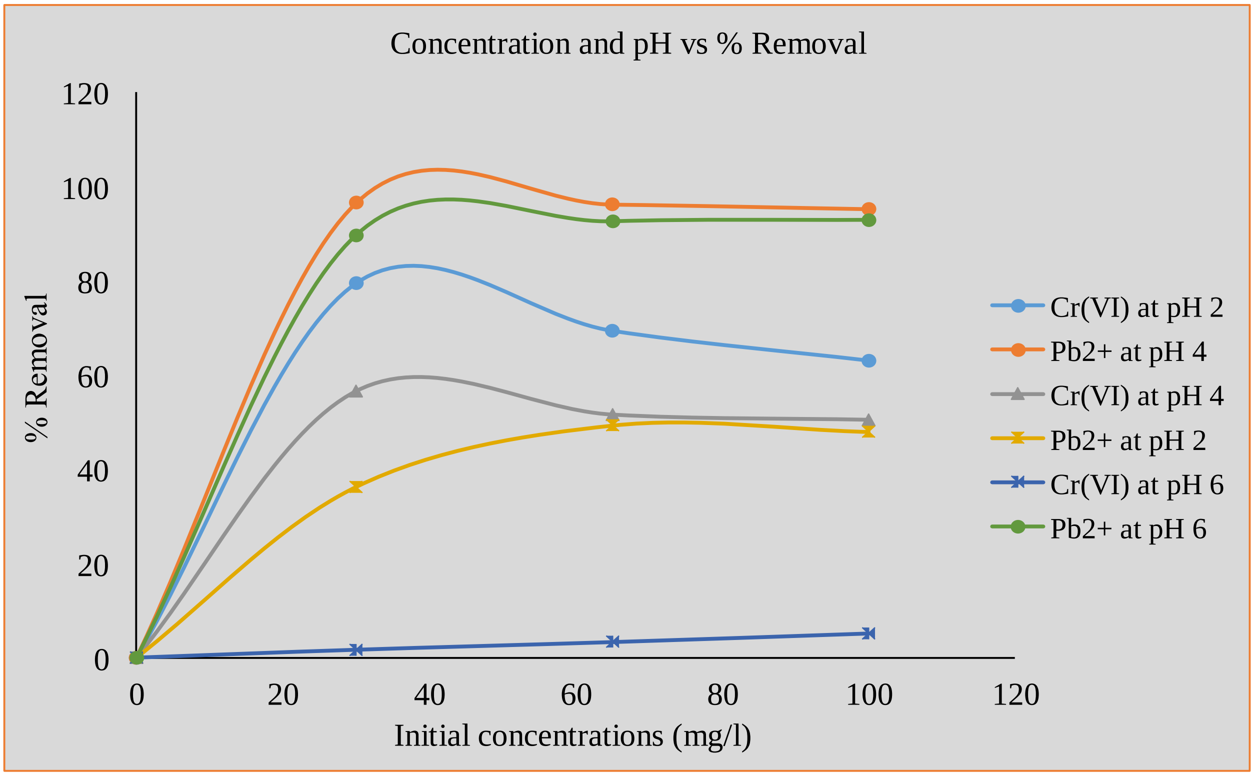


Figure 4.7 Effect of initial metal ions concentration on % removal of Cr(VI) and Pb(II)

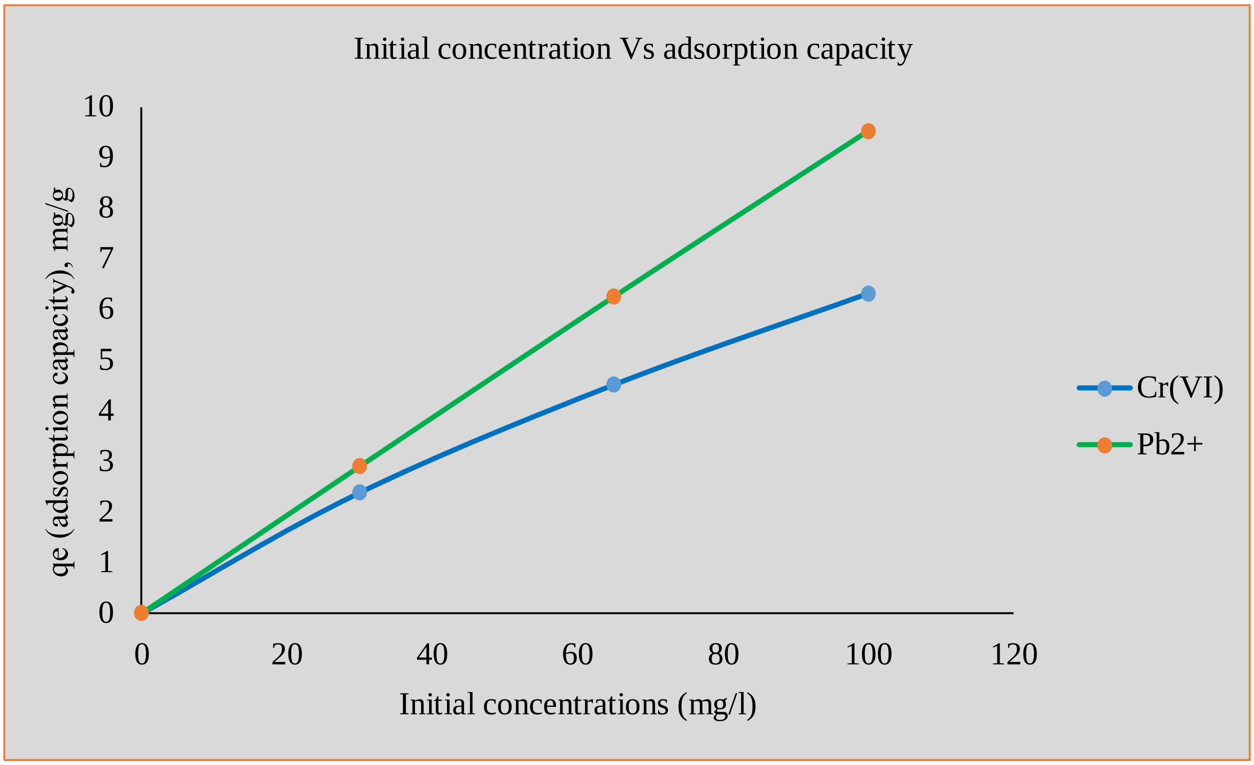


Figure 4.8 Effect of initial metal ions concentration on adsorption capacity of Cr(VI) and Pb(II)

Adsorption capacity and removal efficiency results obtained from the present studies were compared with other works on Pb(II) and Cr(VI) ions removal using different adsorbents. As it can be seen from Table 4.2 adsorption capacity of BSG was 26.3 which was almost comparable with the other mentioned adsorbents. For the case of chromium (VI) adsorption capacity of brewery spent grain is higher than neem leaf powder adsorption capacity. However, ground nut shell shows high sorption capacity for chromium (VI). But its removal efficiency is good for both adsorbents for removal of chromium (VI).

On the other hand, its removal efficiency for both metal ions is almost comparable with the other works as shown in Table 4.2. This can be justified as that the removal efficiency is the reduction of available metal ions from solution whereas adsorption capacity is the property of adsorbent capacity that can adsorb specific adsorbent in mg per one gram of adsorbent.

Table 4.2 Removal efficiency and uptake capacities of different adsorbents for Pb(II) and Cr(VI) ions compared with present study

| Adsorbent | Adsorbet | % Removal | $q_{max}$ (mg/g) | References |
|---|---|---|---|---|
| Lemon & orange peel | Pb(II) | 72.50 | - | Husoon, 2013 |
| Untreated BSG | Pb(II) | 88.24 | 28.57 | Isabel et al., 2014 |
| Neem leaf powder | Cr(VI) | - | 7.43 | Venkateswarlu et al., 2007 |
| | Cr(VI) | 87.00 | - | Sharma & Bhattacharyya, 2005 |
| Ground nut shell | Pb(II) | - | 31.54 | Qaiser & Umar, 2009) |
| | Cr(VI) | - | 30.21 | |
| BSG (NaCl treated) | Pb(II) | - | 31.24 | Qingzhu Li et al., 2009 |
| Animal bone | Cr(VI) | 92.00 | - | Agarwal & Gupta, 2015 |
| BSG (NaOH treated) | Pb(II) | 96.53 | 26.30 | Present study |
| | Cr(VI) | 79.47 | 10.75 | |

## 4.6. Adsorption Isotherms

The adsorption Isotherm for Cr(VI) and Pb (II) ions was studied. The concentrations of the metal ions in their equilibrium phase and that in the BSG at a room temperature was studied to know the maximum sorption capacity of the BSG for the metal ions. To determine this maximum sorption capacity of BSG Langmuir and Freundlich isotherm models were used. Langmuir and Freundlich Isotherm Correlation coefficient and constants of the sorption of Pb (II) and Cr(VI) brewery spent grain were obtained from the slope and intercept of the plot of amount of sorbed metal ions per unit mass, $q_e$ against equilibrium concentration of metal ions remaining in solution, $C_e$ shown in Fig 4.9-4.12. The different isotherm parameters from the different plots are given in Table 4.3.

The correlation coefficients ($R^2$) of Langmuir model for the adsorption of the Pb (II) and Cr (VI) were 0.9801 and 0.9822, respectively, which were slightly higher than the $R^2$ values of Freundlich model for Cr (VI). The result reveals that the adsorption of Cr(VI) on brewery spent grain is well fitted to the Langmuir model, meaning that BSG biomass surfaces are homogeneous sorption patches, on which monolayer coverage of Cr(VI) ions were formed on the outer surface of the biosorbent i.e. BSG. On the other hand, the sorption of lead by brewery spent grain is well fitted to both Langmuir and Freundlich isotherm models with a correlation coefficient ($R^2$) of 0.9801 and 0.9918. respectively.

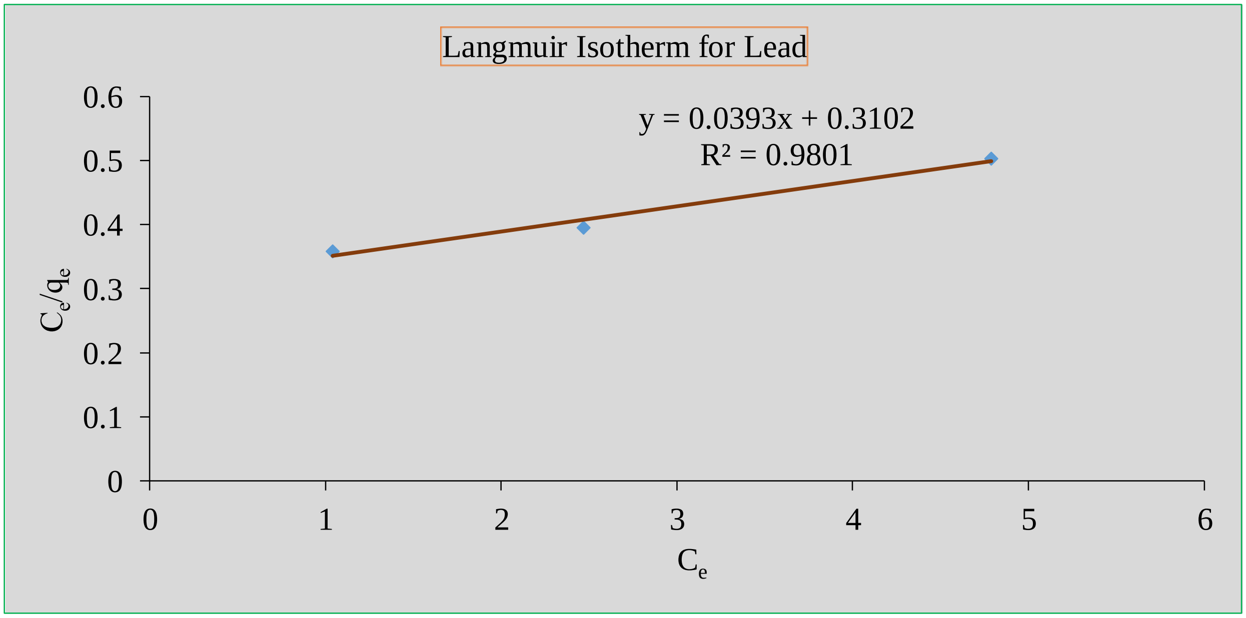


Figure 4.9 Langmuir Isotherm for lead adsorption by BSG

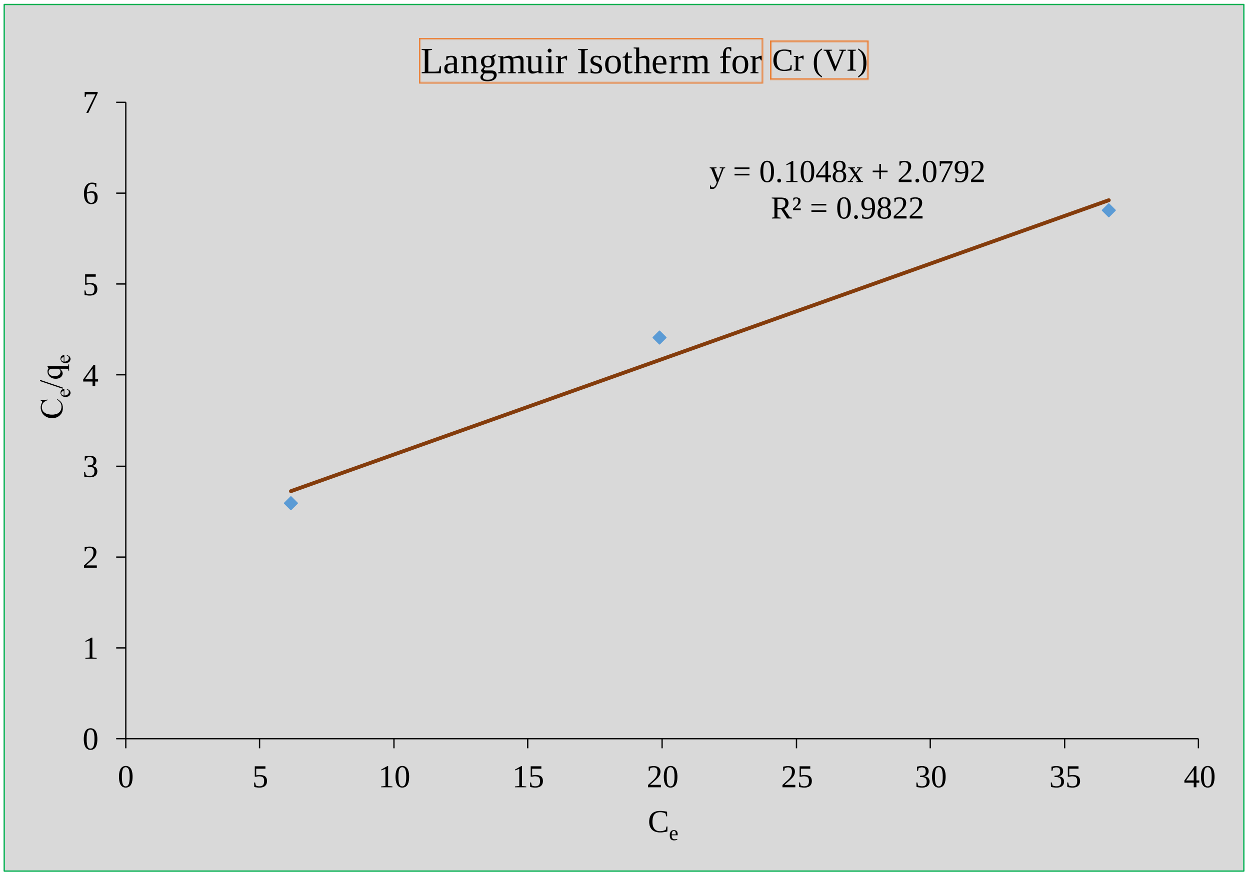


Figure 4.10 Langmuir Isotherm for Cr (VI) adsorption by BSG

Freundlich isotherm model constant parameters, $K_f$ and n were determined by linear regression from the plot of log($q_e$) against log($C_e$). $K_f$ is the degree of adsorption; when $K_f$ value is low it indicates minimal adsorption of heavy metals whereas the higher $K_f$ value suggests greater sorption ability (Oves et al., 2013). For this case, $K_f$ value was highest for Pb (II) ion (2.88 mg/g) and it was lowest for Chromium(VI) ion (1.53mg/g) indicating a favorable adsorption according to Freundlich isotherm.

Adsorption intensity, n from Freundlich Isotherm was determined for both metal ions. When n>1, the adsorbate is favorably adsorbed on an adsorbent and it indicates the situation of adsorption intensity (Itodo et al., 2014). From this it can be conclude that the two metal ions were favorably adsorbed on BSG. The value of n was lower for Pb (II) ion (1.27) but was highest for Cr(VI) ion (1.98) suggesting a maximum biosorption of Cr(VI) and least of Pb (II) according to Freundlich model, but all values favored Freundlich isotherm.

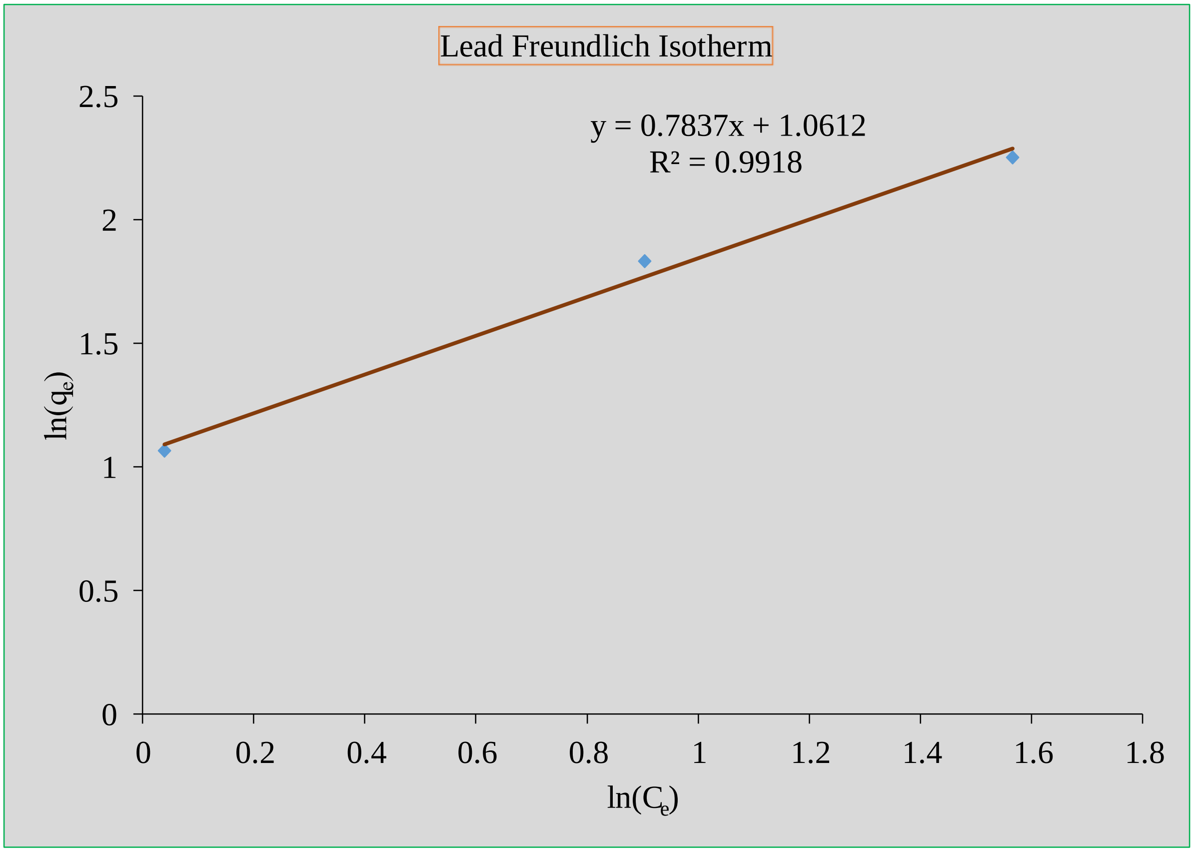


Figure 4.11 Freundlich Isotherm Lead adsorption by BSG

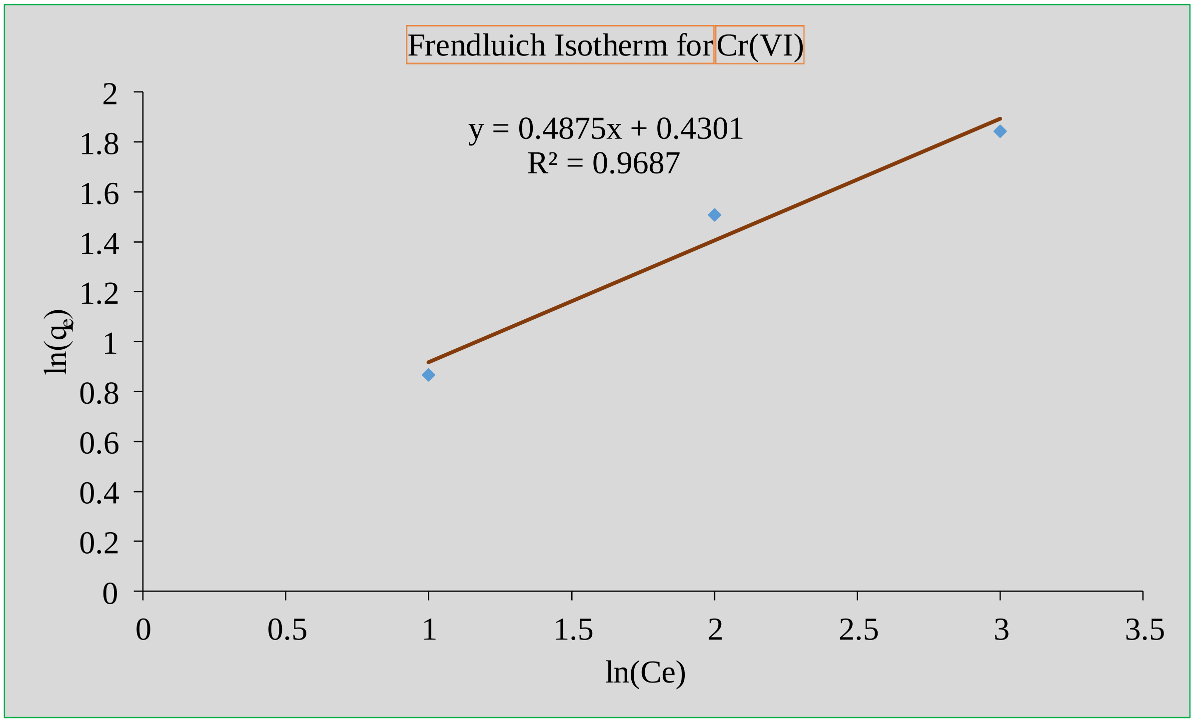


Figure 4.12 Freundlich Isotherm for Cr (VI) adsorption by BSG

Generally, from Langmuir Isotherm model the value of maximum sorption capacity, $q_m$ of BSG for adsorption of Pb (II) were 26.3mg/g which is greater than for adsorption of Cr(VI), 10.75 mg/g. The constant parameter $K_L$ in Langmuir equation is related to the energy of adsorption (Mehrasbi et al., 2009) and $K_L$ values for adsorption of Pb (II) was greater than Cr(VI).

Table 4.3 Langmuir and Freundlich Isotherm Correlation coefficient and constants of the Sorption of Cd $Pb^{2+}$ and Cr(VI) brewery spent grain.

| Heavy metal ions | Langmuir Isotherm | | | Freundlich Isotherm | | |
|---|---|---|---|---|---|---|
| | $R^2$ | $Q_m$(mg/gm) | $K_L$(l/mg) | $K_f$ (mg/g) | n | $R^2$ |
| Pb (II) | 0.9801 | 26.3 | 0.127 | 2.88 | 1.27 | 0.9918 |
| Cr(VI) | 0.9822 | 10.75 | 0.0376 | 1.53 | 1.98 | 0.9687 |

## 4.7. Adsorption kinetics

Pseudo first and second order kinetic models have been tested to fit the data obtained from different sorption experiments of chromium (VI) and Pb(II) ions onto brewery spent grain. The pseudo first order plots of $\ln(q_e/q_t)$ versus t for both metal sorption did not give approximate lines in figure 4.13 and the rate constants ($k_f$) can be calculated from the slope. The experimental and calculated qe values, pseudo-first order rate constants and regration coefficient of determination ($R^2$) values are given in Table 4.4. Since the plots shown non linearity and the $R^2$ values were found to be 0.7655 and 0.5639 for chromium and lead respectively, the calculated qe values ($q_{cal}$) was not in agreement with the experimental qe values ($q_{exp}$).

A pseudo second order kinetic model was applied to fit the experimental data. It was plotted t/q against t and constant parameters of $k_s$ and h values were determined from the slopes and intercepts. The linear pseudo-second order equation showed good agreement of experimental data with correlation coefficients 0.9998 and 0.9999 for lead and chromium respectively as shown in Table 4.4 and Figure 4.14.

The experimental and calculated qe values, pseudo second order rate constants are in good agreement with those obtained experimentally. The applicability of this model suggested that biosorption of lead and chromium(VI), on brewery spent grain was based on chemical reaction, between metals and active sites of the biosorbent.

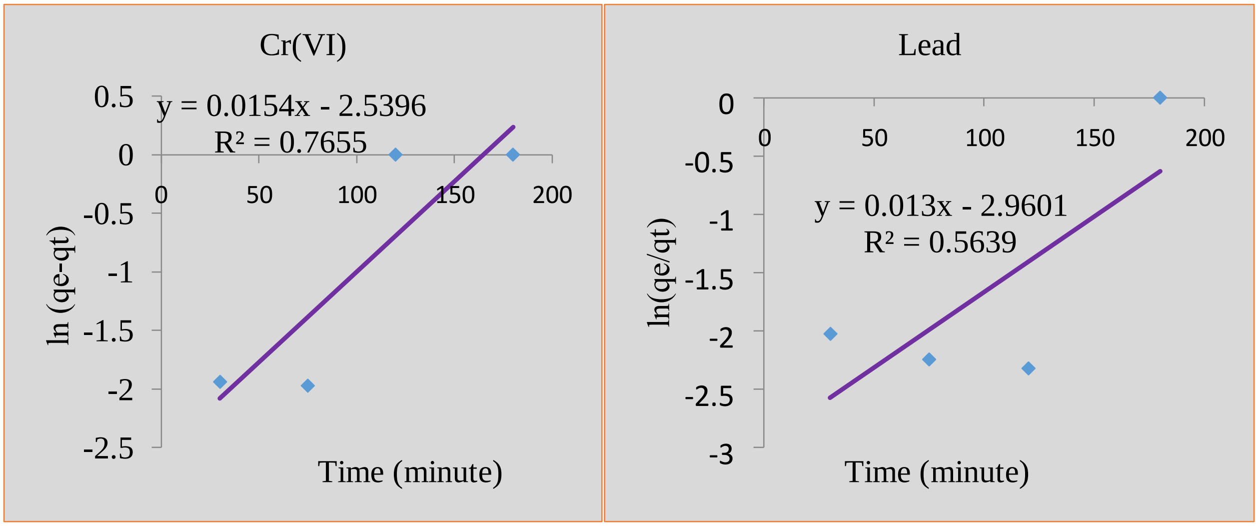


Figure 4.13 Pseudo first order for sorption of Cr(VI) and lead

The initial adsorption rate, h was high for both metals. This is attributed to the fact that the initial rapid uptake could be ascribed to the concentration gradient, created at the start of the adsorption process, between solute concentration in solution and that at the BSG surface (Itodo et al., 2014).

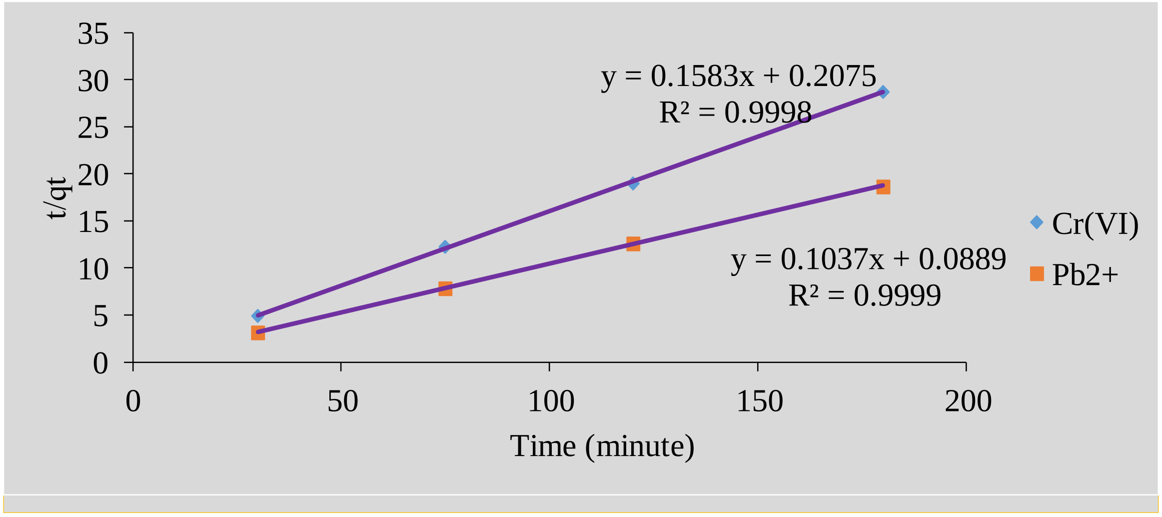


Fig 4.14 Pseudo second order for sorption of Cr(VI) and lead onto BSG

Table 4.4 Kinetic parameters for the adsorption of Pb(II) and Cr(VI) onto BSG at temp. of 298K.

| Metal ions | Pseudo first order | | | Pseudo second order | | | |
|---|---|---|---|---|---|---|---|
| | $q_{cal}$(mg/gm) | $R^2$ | $K_f$($min^{-1}$) | h(g/mg/min) | $q_{cal}$(mg/gm) | Ks (g/mg/min) | $R^2$ |
| Pb(II) | 0.078 | 0.5639 | 0.0154 | 11.11 | 11.24 | 0.12 | 0.9999 |
| Cr(VI) | 0.05 | 0.7655 | 0.013 | 4.78 | 4.8 | 0.122 | 0.998 |

## 4.8. Data analysis using Design expert 7.0.0 software

Three basic factors were selected for design expert to determine the total experiment runs. After finding their optimum values the fixed dose of 2gm BSG was varied over the range of 0.5gm to 2gm. Additional time level was selected for determining sorption equilibrium and kinetics up to 180minutes. Initially three factors and three levels were selected to give a total experimental runs of 27 with a factorial design of $3^3$ for each metals. The results were replicated two times to improve reliability of the data and that resulted to perform 108 experiments.

A planning matrix was set up to take account of the factors that could influence with responses, such as measurement of initial metal ions concentration, contact time, and pH of the solution of metals at different levels. Table 4.5 shows the factors and levels chosen for the planning matrix. The experiments were performed in batches at 25°C under constant stirring (200 rpm).

Table 4.5 Factors and levels for the biosorption experiments evaluated for each metal

| Factors | Level | Level value | Representation |
|---|---|---|---|
| PH | 1 | 2 | 0 |
| | 2 | 4 | 1 |
| | 3 | 6 | 2 |
| Concentration | 1 | 30 mg/l | 0 |
| | 2 | 65 mg/l | 1 |
| | 3 | 100 mg/l | 2 |
| Time | 1 | 30 min | 0 |
| | 2 | 75 min | 1 |
| | 3 | 120 min | 2 |

The aim of applying a factorial design analysis was to identify the most significant factors affecting the metals removal percentages after the sorption process of batch experiments.

Table 4.6 Analysis of variance (ANOVA) - Influence of the factors studied in metal biosorption. (a) Pb (R= 0.9863); (b) Cr (VI) ($R^2$ = 0.9592)

a)

| Source | Sum of Squares | Degree of Freedom | Mean Square | F Value | Prob > F |
|---|---|---|---|---|---|
| Model | 33178.94 | 9 | 3686.55 | 350.88 | < 0.0001 |
| A | 21918.32 | 1 | 21918.32 | 2086.15 | < 0.0001 |
| B | 37.05 | 1 | 37.05 | 3.53 | 0.0670 |
| C | 319.54 | 1 | 319.54 | 30.41 | < 0.0001 |
| AB | 16.88 | 1 | 16.88 | 1.61 | 0.2117 |
| AC | 91.37 | 1 | 91.37 | 8.70 | 0.0051 |
| BC | 2.410E-003 | 1 | 2.410E-003 | 2.294E004 | 0.9880 |
| $A^2$ | 10627.30 | 1 | 10627.30 | 1011.49 | < 0.0001 |
| $B^2$ | 14.89 | 1 | 14.89 | 1.42 | 0.2403 |
| $C^2$ | 153.59 | 1 | 153.59 | 14.62 | 0.0004 |
| Residual | 462.29 | 44 | 10.51 | | |
| Lack of Fit | 420.69 | 17 | 24.75 | 16.06 | < 0.0001 |
| Error | 41.60 | 27 | 1.54 | | |
| Total | 33641.23 | 53 | | | |

b)

| Source | Sum of Squares | Degree of Freedom | Mean Square | F Value | Prob > F |
|---|---|---|---|---|---|
| Model | 7057.82 | 10 | 705.78 | 101.16 | < 0.0001 |
| A | 5001.35 | 1 | 5001.35 | 716.84 | < 0.0001 |
| B | 147.58 | 1 | 147.58 | 21.15 | < 0.0001 |
| C | 16.09 | 1 | 16.09 | 2.31 | 0.1362 |
| AB | 7.83 | 1 | 7.83 | 1.12 | 0.2954 |
| AC | 1361.08 | 1 | 1361.08 | 195.08 | < 0.0001 |
| BC | 26.42 | 1 | 26.42 | 3.79 | 0.0582 |
| $A^2$ | 459.72 | 1 | 459.72 | 65.89 | < 0.0001 |
| $B^2$ | 0.35 | 1 | 0.35 | 0.050 | 0.8248 |
| $C^2$ | 28.87 | 1 | 28.87 | 4.14 | 0.0481 |
| Residual | 308.55 | 44 | 7.01 | | |
| Lack of Fit | 146.40 | 17 | 8.61 | 1.43 | 0.1959 |
| Error | 162.15 | 27 | 6.01 | | |
| Total | 7357.83 | 53 | | | |

A= pH, B= Time, C= Initial Concentration

The Model generated for both metals adsorption was significant that ANOVA analysis shown in table 4.6 proves the results discussed above at a confidence level of 95%. As shown from table 4.6 values of P less than 0.05 indicate model terms are significant. Results showed that the effect of pH (factor A) and C(initial concentration) are of major importance for sorption of lead while A (PH), B(contact time) are significant parameters for chromium ion removal. Combination of A*C (pH and concentration), were significant model terms for both chromium and lead removal.

As shown from the ANOVA results, pH was the dominant factor that affects lead and chromium biosorption. This result confirmed from many litratures that pH is the main factor influences the sorption pattern of metal ions. For lead and chromium ions adsorption contact time and initial metal ion concentration respectively, including their combination showed insignificant; meaning their contribution was very low.

However, the interactions of pH with initial concentration AC (pH and initial concentration) significantly affect sorption of Chromium and lead ions next to pH. On the other hand the combination of contact (B) main factor with metal initail ions concentration (C) did not influences their adsorption pattern. Modeling equations show the removal efficiency of BSG in relation to different metals according to the factor levels. Note that the highest coefficients are related to the factors that most influence the efficiency of adsorption (Seolatto et al., 2012).

Final Equation in Terms of Coded Factors and actual factors of chromium (VI) respectively:

**lead (II) Removal** =+98.81+24.67* A+1.01* B+2.98* C-0.84* A * B-1.95*A*C-0.010 * B * C-29.76* A2-1.11* B2-3.58* C2

**Lead (II) Removal=** -102.30772+74.36636* pH+0.14274 * Time +0.57675* Initial con. -9.31766E-003* pH * Time -0.027874* pH * Initial con. -6.36243E-006* Time * Initial con. -7.43979* pH$^2$-5.50065E-004* Time $^2$-2.92045E-003* Initial con.$^2$

Final Equation in Terms of Coded Factors and actual factors of chromium (VI) respectively:

**Cr(II) Removal** = +50.17 -11.79* A+2.02 * B-0.67* C+0.57* A * B+7.53* A * C-1.05 * B *C+6.19* A$^2$-0.17* B$^2$+1.55* C$^2$

**Cr(II) Removal**=+127.87036-25.74112*PH+0.075485*Time-0.5640*Concentration + 6.34637E-003*PH*Time+0.10758*PH*Concentration-6.66143E 004*Time*Concentration+1.5473*PH$^2$-8.38516E-005*Time$^2$+1.26618E-003*Concentration$^2$

### 4.8.1. Model adequacy check

The adequacy of model was tested by analysis of variance (ANOVA). The regression model was found to be significant with the correlation coefficients of determination of R-Squared, adjusted R-Squared and predicted R-Squared having a value of 0.986258, 0.983447 and 0.978474 for lead (II) ions and 0.958065, 0.949487 and 0.934633 for chromium respectively. The value of Rsquared for the developed correlation is 0.986258 and 0.95065 for lead and chromium(II) respectively. It implies that experimental variables studied attributed for the removal were 98.62% and 95.065% for lead and chromium adsorption respectively.

The results in Figure 4.15 and 4.16 shows that the regression model equations provided a description of the experimental data, in which all the points are close to the line of perfect fit. This result indicates that the agreement between the experimental and the predicted values was good. In other ways it indicates that there is a linearity relationship between the removal efficiency and the three factors considered. The figures 4.15 and 4.16 show how the data generated from developed model equation is close to the actual data obtained.

Table 4.7 The R-squared values for lead(II) and chromium adsorption

| Lead (II) | | | | Chromium(VI) | | | |
|---|---|---|---|---|---|---|---|
| Std. Dev. | 3.241386 | R-Squared | 0.986258 | Std. Dev. | 2.64812 | R-Squared | 0.958065 |
| Mean | 75.84181 | Adj R-Squared | 0.983447 | Mean | 55.21364 | Adj R-Squared | 0.949487 |
| C.V. % | 4.273877 | Pred R-Squared | 0.978474 | C.V. % | 4.796133 | Pred R-Squared | 0.934633 |
| PRESS | 724.1529 | Adeq Precision | 47.25811 | PRESS | 480.9608 | Adeq Precision | 39.29781 |

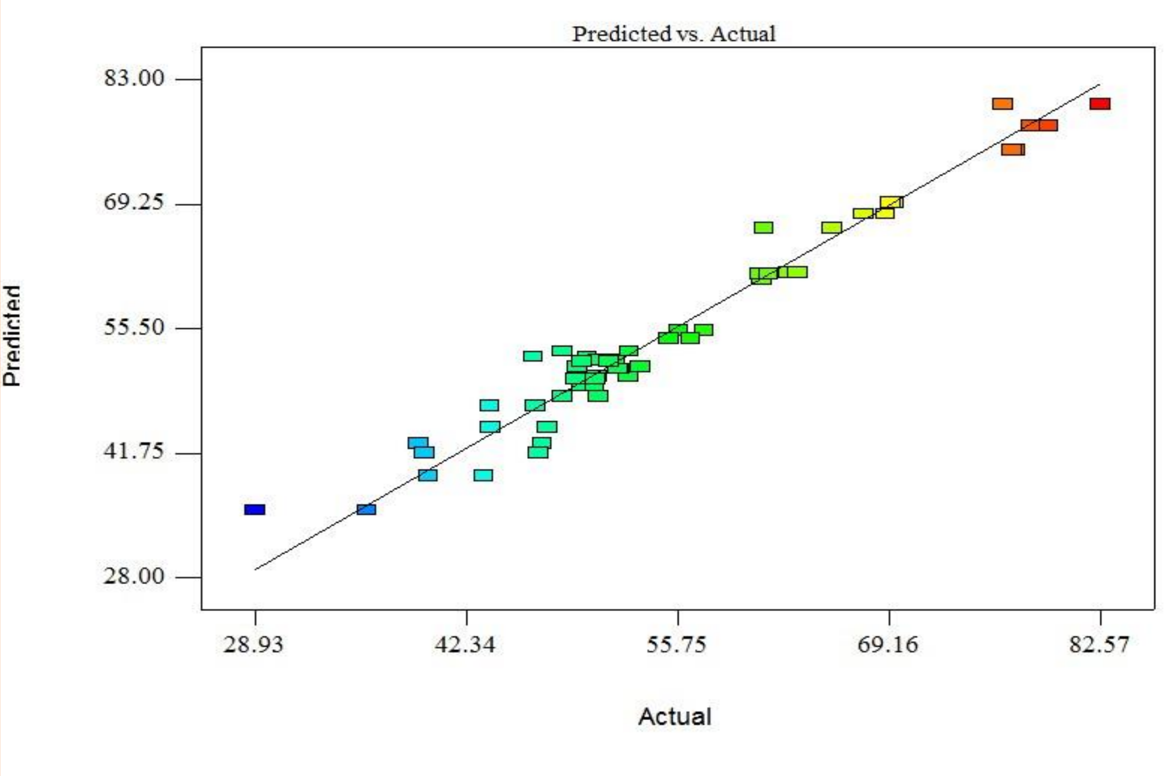


Figure 4.15 predicted Vs actual experimental value for adsorption removal of Chromium (VI)

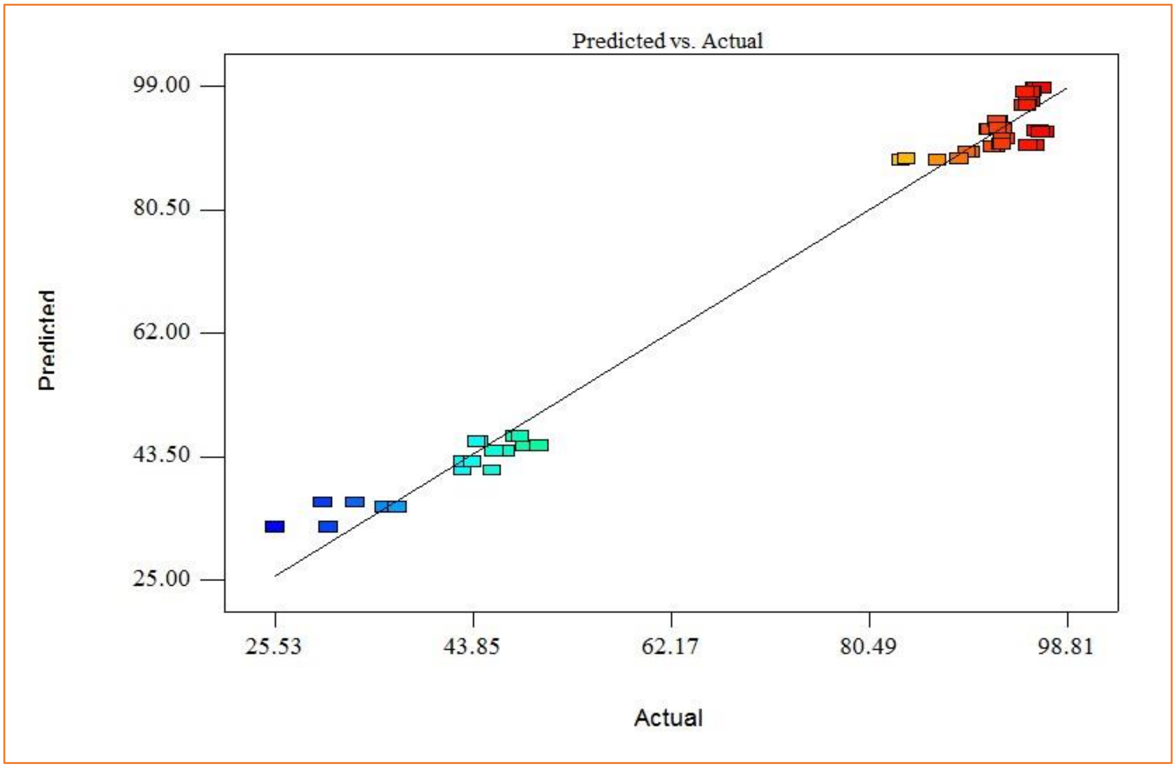


Figure 4.16 Predicted Vs actual experimental value for adsorption removal of Chromium (VI)

### 4.8.2. Interaction Effects

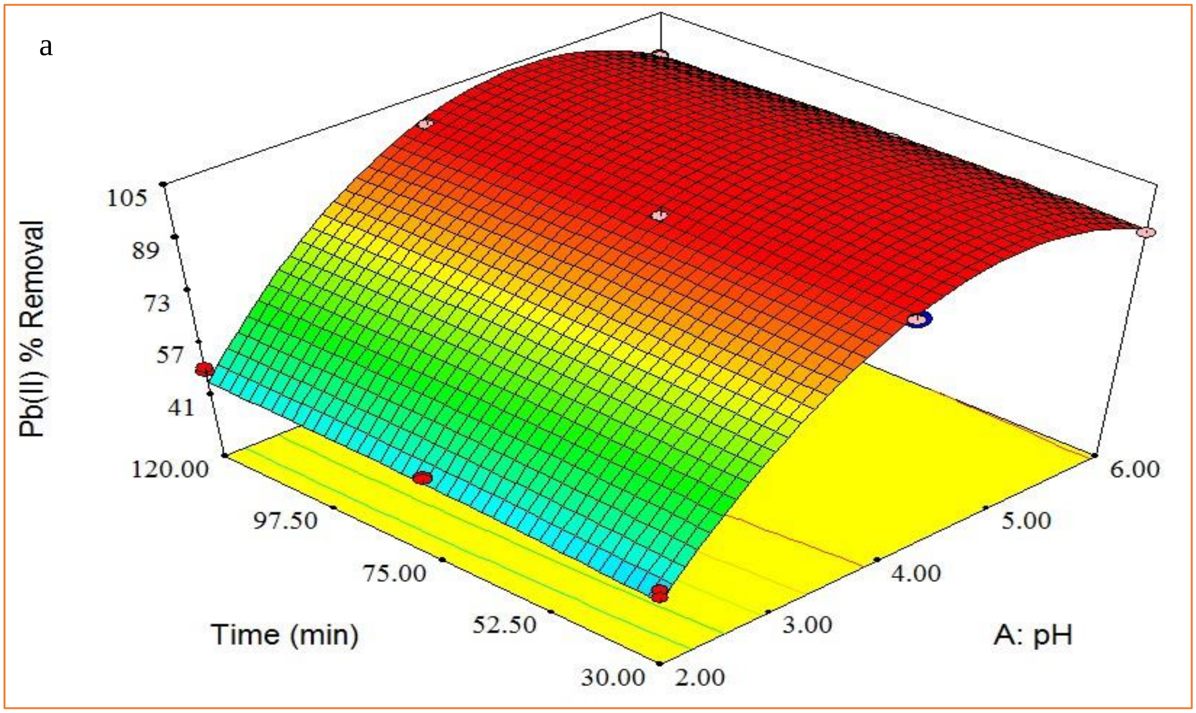
The removal efficiency of both metal ions were plotted as a function of the interactions of two of the factors by holding the other one variable at average value. There are three interaction factors analyzed by the model equation. These are:

1. AB (pH and contact time)
2. AC (pH and initial metal ion concentration)
3. BC (contact time and initial metal ion concentration)

The three-dimensional response surfaces, plot are shown in figures 4.17, 4.18, and 4.19 as a function of the interactions of two of the factors.

**i. Time and pH**

The effect of pH of metal solutions and contact time on removal efficiency is shown form 3D plot of Figure 4.17. As it can be observed from the lead (II) removal plot, as both pH and time increased the removal also increased and it started to decline after reaching its maximum. The maximum yield was found at the moderate values of both factors. On the other hand, the heights removal of chromium observed at lower pH value and higher contact times. This confirmed to the fact that maximum removal occurred at pH=4 and pH=2.



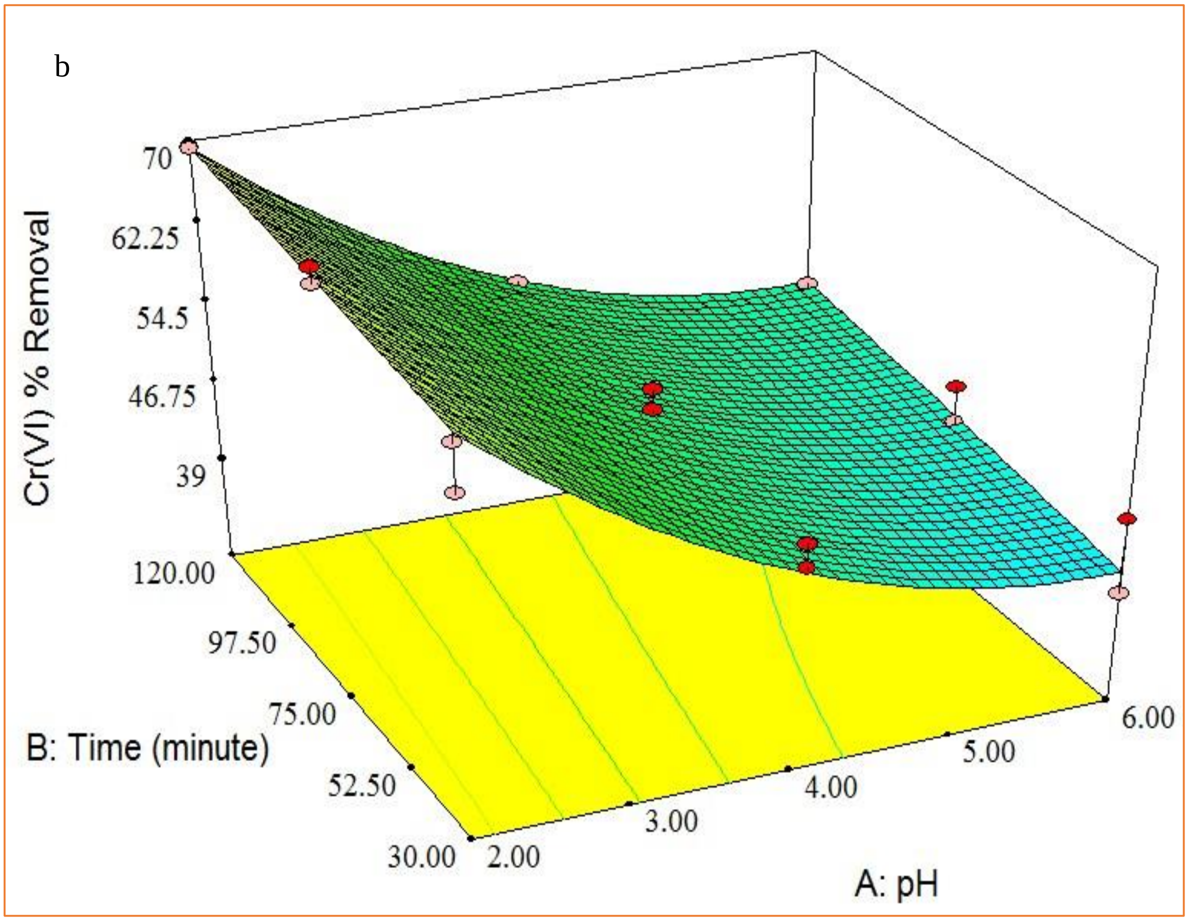


Figure 4.17: 3D plot (a) lead (II) removal (b) chromium (VI) showing the interaction effect of pH and contact time

### ii. pH and metal ion initial concentration

From figure 4.18a, shows that both pH and initial metal ion concentration have strong effect on lead (II) removal at their mid-level values. At lower level values of both factors and further increment beyond mid values showed a decrease in removal efficiency of lead (II) ion. The plot indicates that maximum lead removal occurred at pH=4 and initial concentration of 65mg/l with fixed adsorbent dose of 2g/l.

The effect of pH and initial metal ion concentrations on removal efficiency of chromium (VI) is shown form 3D plot of Figure 4.18b. As it can be observed from the chromium (II) removal plot, when the pH of metal ion solution and initial metal ions concentration low removal efficiency was found to be high. This attributed to the fact that at pH=2 and minimum initial concentration of chromium(VI) ions, the fixed adsorbent dosage of brewery spent grain sorbed it because of the availability of unoccupied free surfaces.

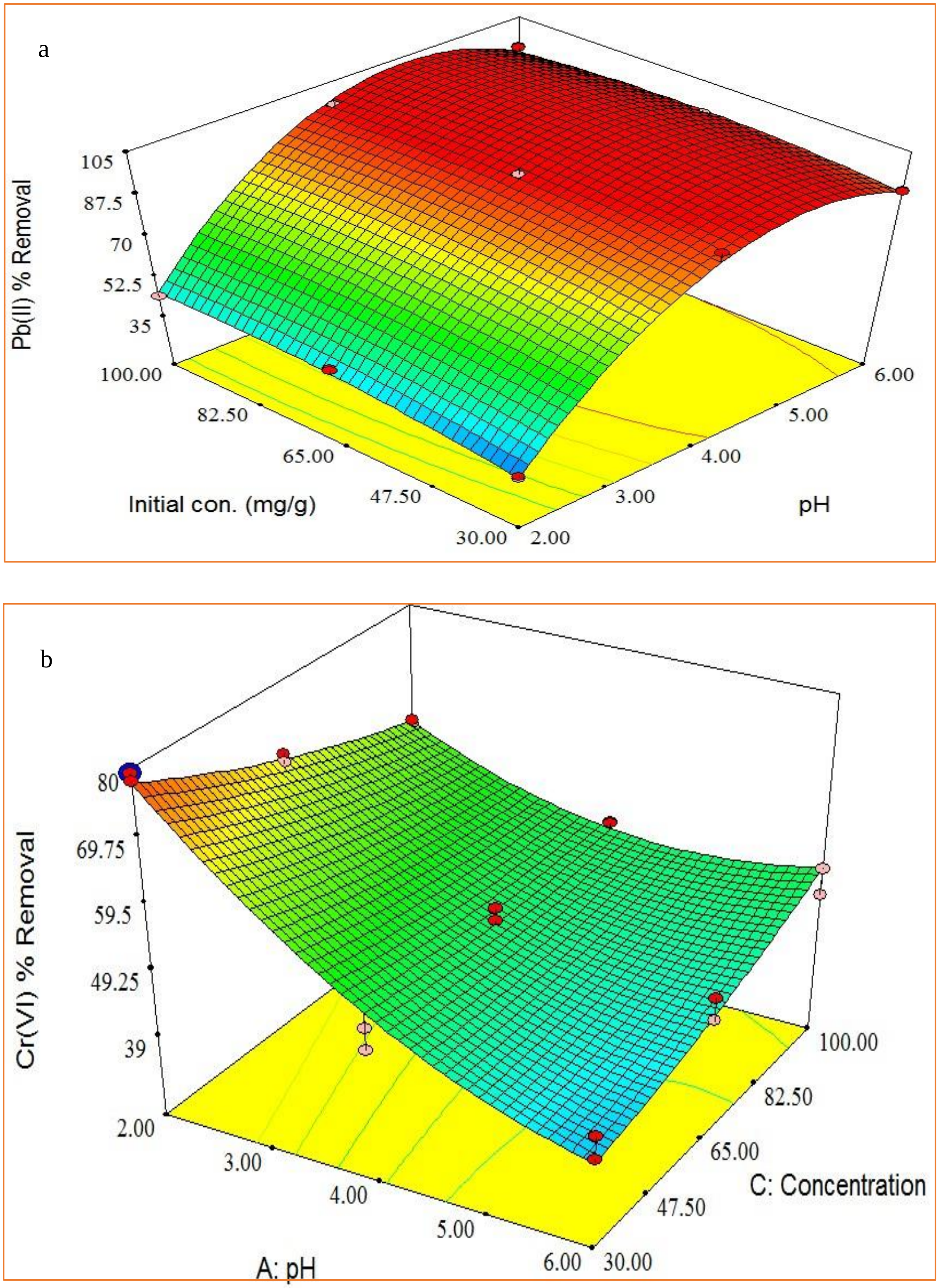


Figure 4.18: 3D plot (a) lead (II) removal (b) chromium (VI) showing the interaction effect of pH and initial metal concentration

### iii. Time and initial concentration

In the case of lead (II) and chromium (II) sorptive as shown from figure 4.19a and 4.19b respectively removal was high at mid value of its initial concentration with correspond to high its contact time.

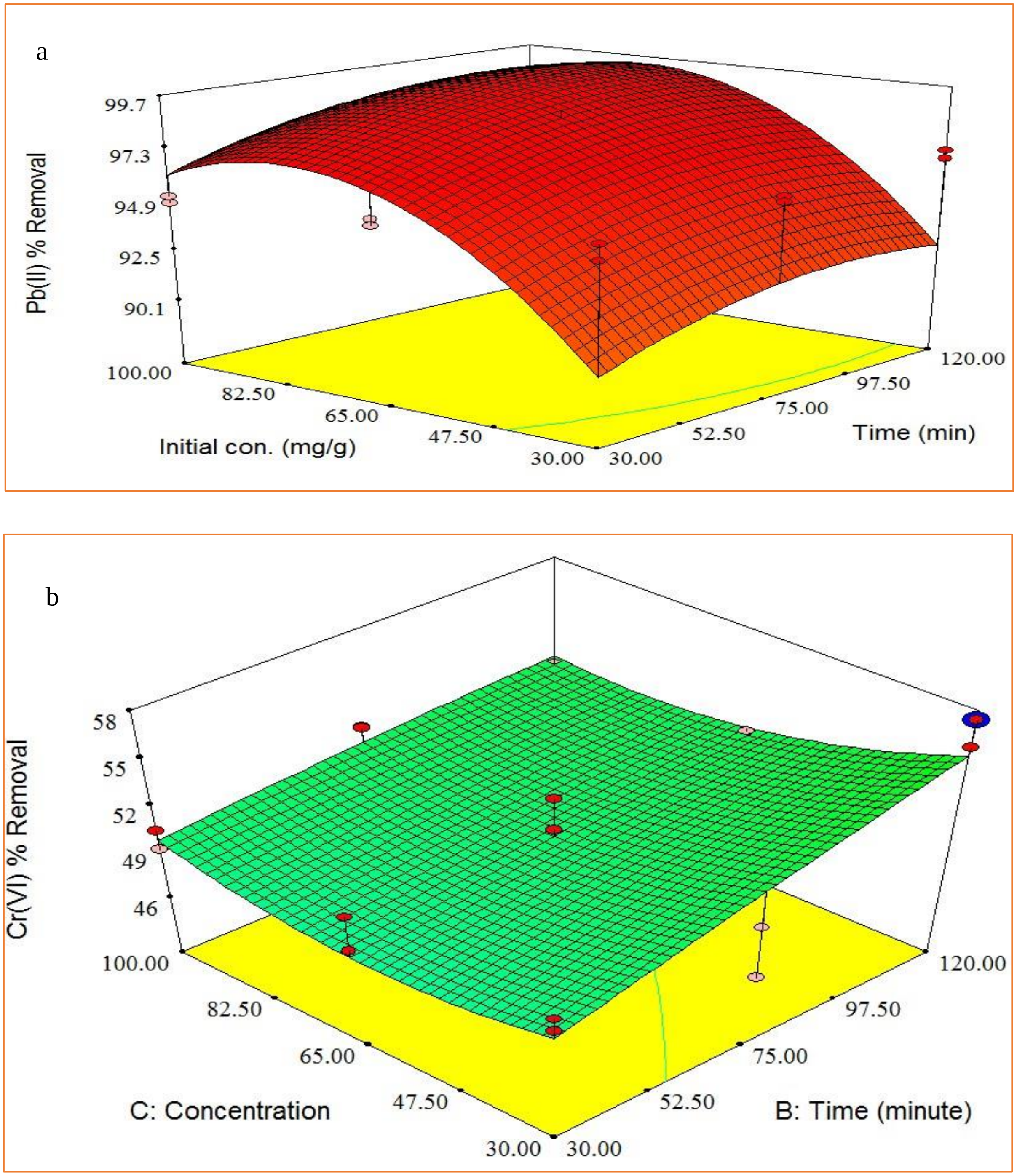


Figure 4.19: 3D plot (a) lead (II) removal (b) chromium (VI) showing the interaction effect of initial metal ions concentration and contact time

## 4.9. Removal efficiency of BSG for real waste water

Attempts were made to apply laboratory experimental results to real wastewater samples in order to move from the experiment to the application in real world. Waste water samples containing chromium (VI) and lead were obtained from metal and engineering corporation (METEC) electro plating section which is located in Addis Ababa. currently the waste is accumulated and finally discharged to the river without proper treatment and the effluent is not complying to the standard limits as it was measured for each metals ion.

Batch sorption test was conducted for both metals at their optimum points obtained from prior synthetic waste water batch sorption experiment. The feasibility and efficiency of a biosorption process depends not only on the properties of the biosorbents, but also on the composition of the waste water (Kratochvil & Volesky, 1998). Taking this statement into consideration both metal wastewaters were taken from mixing point as they are discharging to investigate other metals ions interference for sorbent sites. The samples were taken from four different sites within the factory and analyzed the major metal constituents as shown in table 4.9 below.

Table 4.9 Metal ions concentration from electroplating waste

| | Places | | | | |
|---|---|---|---|---|---|
| Metals (mg/L | 1 | 2 | 3 | 4 | Average |
| Zinc | 777.9 | 3.0 | 0.6 | 187.2 | 242.175 |
| Lead | 82 | 2.6 | 0.13 | 2.8 | 21.8825 |
| Chromium | 2342.3 | 2.5 | 1.1 | 156.9 | 625.7 |
| Nickel | 4238 | 210.8 | 4.6 | 1090.6 | 1386 |

In order to conduct batch sorption for real wastewater each bath should contain one high level toxic metal and other heavy metals at low levels such as $Al^{2+}$ and $Cu^{2+}$ that may not be considered toxic (Kratochvil & Volesky, 1998) and usually affinity and concentration of this metal will determine the efficiency of the biosorption process. Otherwise column experiment will be needed to determine competitive ion exchange to the sorbent bed and presence of other metals will affect acceptable limits of columns effluent.

For sorption of wastewater containing chromium, optimum parameters from batch synthetic wastewater adsorption were selected as; pH=2, contact time =120 mins, and BSG dosage of 2g. The initial measured concentration of chromium ions of the wastewater was 156.9 mg/l. While optimum parameters for lead batch sorption were; pH=4, contact time =120 mins, and BSG dosage of 2gm and its initial concentration in wastewater was 82mg/l

Table 4.10 Optimum points chosen for batch chromium and lead sorption onto BSG

| Metal ions | Optimum parameters | | | Real waste water parameters | |
|---|---|---|---|---|---|
| | pH | Contact time (min) | BSG dose (gm) | pH | Initial con. (mg/L) |
| $Pb^{2+}$ | 4 | 120 | 2gm | 4 (after adjusting) | 156.9 |
| Cr(VI) | 2 | 120 | 2gm | 2 (after adjusting) | 82 |

After adsorption of waste water containing each metal ions onto brewery spent grain, it was found that lead reduction was observed by 53.21% while chromium removal was 43.45%. The results were much lower than the removal efficiency of synthetic waste water containing individual metal ions. This can be justified to the fact that the presence other metal ions in the solution affect the removal efficiency by competing one another to the adsorbent site.

Taking into consideration of this result, almost half of the targeted metal ions were removed by brewery spent grains from electro plating wastewater. The better way would be effective if effluents are discharged separately and treated before mixing all waste streams together. This adsorption technique eliminates the interference of other metal ions for the adsorbent sites. The optimum conditions may be important and more effective for other waste water sources since they will contain small amount of metal ions concentrations.

# 5. CONCLUSION AND RECOMMENDATION

## 5.1. Conclusion

The adsorption of lead(II), and chromium(VII) from aqueous solution by brewery spent grain was investigated. The effect of contact time, initial metal ion concentration, solution pH and adsorbent dose on metal ions removal has been studied. pH was found to be dominant factor as per analysis of ANOVA and optimal pH for lead (II) and chromium (VI) was 4 and 2, respectively. Isothermal data of metal ions sorption by brewery spent grain indicated that, the biosorption process followed both the Langmuir and Freundlich models. Data analyzed from the models, showed the adsorption capacity of brewery spent grain for lead found to be higher than chromium. From this, it can be concluded that the affinity of brewery spent grain for Pb(II) is greater than that of Cr(VI). The kinetics of biosorption was well represented by pseudo second order kinetic model.

These experimental studies on BSG were conducted in removing of chromium and lead from electroplating waste using BSG as adsorbent. The results showed that the removal efficiencies for lead and chromium from electroplating were 53.4 and 43.6% respectively. This reduction in removal efficiency may be attributed to the presence of competitive metal ions. The affinity to the sorbent would be the governing mechanism for sorption of metals. The study revealed that brewery spent grain is potentially useful material for the removal of lead and chromium from aqueous solutions.

## 5.2. Recommendation

Based on the results gained from the study, the following suggestions have been made for future work.

- The sorption effect of multi component heavy metal ions such as Pb(II) and Cr(VI), Pb(II) and Cu(II), Nickel and Zink and so on or the combination of three metals study can be made using the same adsorbent, BSG.
- Batch adsorption can be carried out by considering other excluded parameters such as various particle size, temperature and stirring rpm.
- Adsorption experiments can be carried out by treating raw brewery spent grains with different chemicals such as inorganic acids (hydrochloric acid, nitric acid sulfuric acid, tartaric acid, citric acid, thioglycollic acid), base (sodium hydroxide, calcium hydroxide, sodium carbonate), organic compounds (ethylenediamine, formaldehyde, epi-chlorohydrin, methanol) and oxidizing agent (hydrogen peroxide),
- Regeneration of brewery spent grain can be done which involves the fate of the metal loaded biomass after the biosorption process. Regenerated brewery spent grain can be used for another cycle of adsorption until it become exhausted. The final cycle of metal ions loaded with brewery spent grain disposal should be to the landfill or incineration.
- Column adsorption can be developed to move laboratory batch adsorption results into practical real wastewater treatment containing heavy metal ions. The development of the biosorption processes by BSG requires further investigation in the direction of modeling, of regeneration of biosorbent material and of testing immobilized raw biomasses with industrial effluents.

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# 7. APPENDIXES

## Appendix A: Experimental Results

Table A1: Lead adsorption results at different levels of pH, contact time and metal initial concentration with constant BSG dose of 2g, temperature of 298K and stirring of 200rpm

| Run | pH | $C_o$ | T | $C_{e1}$ | $C_{e2}$ | $C_e$ avg. | %$R_1$ | %$R_2$ | %R avg. | $q_{e1}$ | $q_{e2}$ | qe avge |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 30 | 30 | 20.87 | 22.34 | 21.60 | 30.45 | 25.53 | 27.99 | 0.914 | 0.77 | 0.840 |
| 2 | 2 | 30 | 75 | 19.29 | 18.94 | 19.12 | 35.70 | 36.87 | 36.28 | 1.071 | 1.11 | 1.089 |
| 3 | 2 | 30 | 120 | 20.12 | 21.02 | 20.57 | 32.93 | 29.93 | 31.43 | 0.988 | 0.90 | 0.943 |
| 4 | 2 | 65 | 30 | 35.36 | 37.12 | 36.24 | 45.61 | 42.89 | 44.25 | 2.965 | 2.79 | 2.876 |
| 5 | 2 | 65 | 75 | 34.56 | 35.21 | 34.89 | 46.83 | 45.83 | 46.33 | 3.044 | 2.98 | 3.011 |
| 6 | 2 | 65 | 120 | 33.35 | 32.54 | 32.95 | 48.69 | 49.94 | 49.32 | 3.165 | 3.25 | 3.206 |
| 7 | 2 | 100 | 30 | 57.03 | 56.21 | 56.62 | 42.97 | 43.79 | 43.38 | 4.297 | 4.38 | 4.338 |
| 8 | 2 | 100 | 75 | 55.64 | 55.81 | 55.72 | 44.37 | 44.19 | 44.28 | 4.437 | 4.42 | 4.428 |
| 9 | 2 | 100 | 120 | 52.26 | 51.81 | 52.04 | 47.74 | 48.19 | 47.97 | 4.774 | 4.82 | 4.797 |
| 10 | 4 | 30 | 30 | 1.23 | 1.44 | 1.34 | 95.90 | 95.20 | 95.55 | 2.877 | 2.86 | 2.867 |
| 11 | 4 | 30 | 75 | 1.14 | 1.21 | 1.18 | 96.20 | 95.97 | 96.08 | 2.886 | 2.88 | 2.883 |
| 12 | 4 | 30 | 120 | 0.98 | 1.10 | 1.04 | 96.73 | 96.33 | 96.53 | 2.902 | 2.89 | 2.896 |
| 13 | 4 | 65 | 30 | 2.94 | 3.13 | 3.04 | 95.48 | 95.18 | 95.33 | 6.206 | 6.19 | 6.197 |
| 14 | 4 | 65 | 75 | 2.73 | 2.41 | 2.57 | 95.80 | 96.29 | 96.05 | 6.227 | 6.26 | 6.243 |
| 15 | 4 | 65 | 120 | 2.64 | 2.29 | 2.47 | 95.94 | 96.48 | 96.21 | 6.236 | 6.27 | 6.254 |
| 16 | 4 | 100 | 30 | 5.23 | 4.91 | 5.07 | 94.77 | 95.09 | 94.93 | 9.477 | 9.51 | 9.493 |
| 17 | 4 | 100 | 75 | 5.11 | 4.51 | 4.81 | 94.89 | 95.49 | 95.19 | 9.489 | 9.55 | 9.519 |
| 18 | 4 | 100 | 120 | 4.50 | 4.95 | 4.73 | 95.50 | 95.05 | 95.28 | 9.550 | 9.51 | 9.528 |
| 19 | 6 | 30 | 30 | 4.97 | 3.97 | 4.47 | 83.43 | 86.77 | 85.10 | 2.503 | 2.60 | 2.553 |
| 20 | 6 | 30 | 75 | 3.03 | 3.15 | 3.09 | 89.89 | 89.50 | 89.70 | 2.697 | 2.69 | 2.691 |
| 21 | 6 | 30 | 120 | 4.82 | 3.36 | 4.09 | 83.92 | 88.80 | 86.36 | 2.518 | 2.66 | 2.591 |
| 22 | 6 | 65 | 30 | 5.52 | 5.45 | 5.49 | 91.51 | 91.62 | 91.56 | 5.948 | 5.96 | 5.952 |
| 23 | 6 | 65 | 75 | 4.91 | 5.01 | 4.96 | 92.45 | 92.29 | 92.37 | 6.009 | 6.00 | 6.004 |
| 24 | 6 | 65 | 120 | 4.61 | 4.97 | 4.79 | 92.91 | 92.35 | 92.63 | 6.039 | 6.00 | 6.021 |
| 25 | 6 | 100 | 30 | 7.86 | 8.12 | 7.99 | 92.14 | 91.88 | 92.01 | 9.214 | 9.19 | 9.201 |
| 26 | 6 | 100 | 75 | 6.92 | 7.21 | 7.07 | 93.08 | 92.79 | 92.94 | 9.308 | 9.28 | 9.294 |
| 27 | 6 | 100 | 120 | 7.36 | 7.22 | 7.29 | 92.64 | 92.78 | 92.71 | 9.264 | 9.28 | 9.271 |

Co= metal ions initial concentration (mg/l)

T= reaction/contact time (min)

$C_{e1}$, $C_{e2}$, $C_{e\ avg.}$= equilibrium concentration (mg/L) for replicate 1, 2 and average respectively $q_{e1}$, $q_{e2}$, $q_{eavg}$= sorption capacities (mg/g) for replicate 1, 2and average respectively

$R_1$, $R_2$, $R_{avge}$= % removal for replicate 1, 2 and average respectively

Table A2: Chromium (VI) adsorption results at different levels of pH, contact time and metal initial concentration with constant BSG dose of 2g, temperature of 298K and stirring of 200rpm

| Run | pH | $C_o$ | T | $C_{e1}$ | $C_{e2}$ | $C_e$ avg. | %$R_1$ | %$R_2$ | %R avg. | $q_{e1}$ | $q_{e2}$ | qe avge |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 30 | 30 | 6.84 | 6.91 | 6.88 | 77.19 | 76.97 | 77.08 | 2.32 | 2.309 | 2.312 |
| 2 | 2 | 30 | 75 | 6.21 | 6.56 | 6.39 | 79.30 | 78.13 | 78.72 | 2.38 | 2.344 | 2.362 |
| 3 | 2 | 30 | 120 | 7.09 | 5.23 | 6.16 | 76.37 | 82.57 | 79.47 | 2.29 | 2.477 | 2.384 |
| 4 | 2 | 65 | 30 | 25.20 | 22.40 | 23.80 | 61.23 | 65.54 | 63.38 | 3.98 | 4.26 | 4.120 |
| 5 | 2 | 65 | 75 | 20.20 | 21.11 | 20.66 | 68.92 | 67.52 | 68.22 | 4.48 | 4.389 | 4.435 |
| 6 | 2 | 65 | 120 | 19.85 | 19.97 | 19.91 | 69.46 | 69.28 | 69.37 | 4.52 | 4.503 | 4.509 |
| 7 | 2 | 100 | 30 | 38.98 | 38.90 | 38.94 | 61.02 | 61.10 | 61.06 | 6.10 | 6.11 | 6.106 |
| 8 | 2 | 100 | 75 | 39.08 | 38.50 | 38.79 | 60.92 | 61.50 | 61.21 | 6.09 | 6.15 | 6.121 |
| 9 | 2 | 100 | 120 | 37.23 | 36.65 | 36.94 | 62.77 | 63.35 | 63.06 | 6.28 | 6.335 | 6.306 |
| 10 | 4 | 30 | 30 | 15.11 | 14.86 | 14.99 | 49.62 | 50.47 | 50.05 | 1.49 | 1.514 | 1.501 |
| 11 | 4 | 30 | 75 | 15.00 | 16.03 | 15.51 | 50.02 | 46.57 | 48.29 | 1.50 | 1.397 | 1.449 |
| 12 | 4 | 30 | 120 | 12.77 | 13.26 | 13.02 | 57.43 | 55.80 | 56.61 | 1.72 | 1.674 | 1.698 |
| 13 | 4 | 65 | 30 | 32.04 | 33.52 | 32.78 | 50.71 | 48.43 | 49.57 | 3.30 | 3.148 | 3.222 |
| 14 | 4 | 65 | 75 | 30.81 | 32.10 | 31.45 | 52.61 | 50.62 | 51.61 | 3.42 | 3.29 | 3.355 |
| 15 | 4 | 65 | 120 | 32.04 | 31.34 | 31.69 | 50.71 | 51.78 | 51.25 | 3.30 | 3.366 | 3.331 |
| 16 | 4 | 100 | 30 | 49.46 | 50.72 | 50.09 | 50.54 | 49.28 | 49.91 | 5.05 | 4.928 | 4.991 |
| 17 | 4 | 100 | 75 | 47.97 | 48.06 | 48.02 | 52.03 | 51.94 | 51.98 | 5.20 | 5.194 | 5.198 |
| 18 | 4 | 100 | 120 | 50.32 | 48.65 | 49.49 | 49.68 | 51.35 | 50.51 | 4.97 | 5.135 | 5.051 |
| 19 | 6 | 30 | 30 | 19.19 | 21.32 | 20.26 | 36.02 | 28.93 | 32.48 | 1.08 | 0.868 | 0.974 |
| 20 | 6 | 30 | 75 | 16.97 | 18.02 | 17.50 | 43.43 | 39.93 | 41.68 | 1.30 | 1.198 | 1.250 |
| 21 | 6 | 30 | 120 | 18.21 | 15.86 | 17.03 | 39.31 | 47.13 | 43.22 | 1.18 | 1.414 | 1.297 |
| 22 | 6 | 65 | 30 | 34.51 | 39.21 | 36.86 | 46.91 | 39.68 | 43.29 | 3.05 | 2.579 | 2.814 |
| 23 | 6 | 65 | 75 | 36.49 | 34.15 | 35.32 | 43.87 | 47.46 | 45.66 | 2.85 | 3.085 | 2.968 |
| 24 | 6 | 65 | 120 | 34.63 | 36.53 | 35.58 | 46.72 | 43.80 | 45.26 | 3.04 | 2.847 | 2.942 |
| 25 | 6 | 100 | 30 | 46.62 | 50.64 | 48.63 | 53.38 | 49.36 | 51.37 | 5.34 | 4.936 | 5.137 |
| 26 | 6 | 100 | 75 | 51.56 | 47.32 | 49.44 | 48.44 | 52.68 | 50.56 | 4.84 | 5.268 | 5.056 |
| 27 | 6 | 100 | 120 | 44.79 | 43.44 | 44.12 | 55.21 | 56.56 | 55.88 | 5.52 | 5.656 | 5.588 |

Co= metal ions initial concentration (mg/l)

T= reaction/contact time (min)

$C_{e1}$, $C_{e2}$, $C_{e\ avg.}$= equilibrium concentration (mg/L) for replicate 1, 2 and average respectively

$q_{e1}$, $q_{e2}$, $q_{eavg}$ = sorption capacities (mg/g) for replicate 1, 2 and average respectively

$R_1$, $R_2$, $R_{avge}$ = % removal for replicate 1, 2 and average respectively

Table A3: Effect of pH, contact time, metal ions concentration and adsorbent dose on % removal and sorption capacity of BSG

| Metals | pH | % Removal | $q_e$(mg/gm) | Remark |
|---|---|---|---|---|
| $Pb^{2+}$ | 2 | 47.97 | 2.9 | |
| | 4 | 96.53 | 6.25 | |
| | 6 | 92.94 | 9.52 | |
| Cr(VI) | 2 | 79.47 | 2.38 | |
| | 4 | 56.61 | 4.51 | |
| | 6 | 55.88 | 6.31 | |
| Metals | BSGDose (g) | % Removal | $q_e$(mg/gm) | Remark |
| $Pb^{2+}$ | 0.5 | 87.2 | 10.46 | |
| | 1 | 95.4 | 5.724 | |
| | 1.5 | 96.2 | 3.848 | |
| | 2 | 96.53 | 2.9 | |
| Cr(VI) | 0.5 | 41 | 4.92 | |
| | 1 | 74.62 | 4.47 | |
| | 1.5 | 76.82 | 3.07 | |
| | 2 | 79.47 | 2.38 | |
| Metals | Time(min) | % Removal | $q_e$(mg/gm) | Remark |
| $Pb^{2+}$ | 0 | 0 | 0 | |
| | 30 | 95.55 | 2.87 | |
| | 75 | 96.08 | 2.88 | |
| | 120 | 96.53 | 2.902 | |
| | 180 | 96.56 | 2.90 | |
| Cr(VI) | 0 | 0 | 0 | |
| | 30 | 77.08 | 2.31 | |
| | 75 | 78.71 | 2.36 | |
| | 120 | 79.47 | 2.38 | |
| | 180 | 79.51 | 2.3 | |
| Metals | Initial con. | % Removal | $q_e$(mg/gm) | Remark |
| $Pb^{2+}$ | 30 | 96.53 | 2.9 | |
| | 65 | 96.21 | 6.25 | |
| | 100 | 95.24 | 9.52 | |
| Cr(VI) | 30 | 79.47 | 2.38 | |
| | 65 | 69.37 | 4.51 | |
| | 100 | 63.06 | 6.31 | |

## Appendix B: Adsorption Isotherms

- The linear form of the Langmuir equation:

$$C_e/q_e = 1/Kq_m + C_e/q_m$$

where $C_e$ is the concentration of the sorbate at equilibrium (mg/L), $q_e$ is the amount of sorbate sorbed at equilibrium per unit mass (mg/g), $q_m$is the monolayer sorption capacity at equilibrium (mg/g) and k is the Langmuir equilibrium constant (l/mg).

- The linearized form of Freundlich equation is:

$$Ln(q_e) = (1/n)\ \ln(C_e) + \ln(K_f)$$

where $K_f$ and n are Freundlich adsorption constants, related to adsorption capacity and sorption intensity respectively.

Table B1: Freundlich and Langmuir models for sorption of Cr(VI) and Pb(II) onto BSG and their respective constant values

| Langmuir Isotherm for Cr(VI) | | | Freundlich Isotherm for Cr(VI) | |
|---|---|---|---|---|
| Ce | qe | Ce/qe | ln(qe) | ln(Ce) |
| 6.16 | 2.38 | 2.588235 | 0.8671 | 1.818077 |
| 19.91 | 4.51 | 4.414634 | 1.506297 | 2.991222 |
| 36.65 | 6.31 | 5.808241 | 1.842136 | 3.601413 |
| **Langmuir Isotherm for Cr(VI)** | | | **Freundlich Isotherm for Cr(VI)** | |
| Ce | qe | Ce/qe | Ln(qe) | Ln(qc) |
| 1.04 | 2.9 | 0.358621 | 1.064711 | 0.039221 |
| 2.47 | 6.25 | 0.3952 | 1.832581 | 0.904218 |
| 4.79 | 9.52 | 0.503151 | 2.253395 | 1.56653 |

| Heavy metal ions | Langmuir Isotherm | | | Freundlich Isotherm | | |
|---|---|---|---|---|---|---|
| | $R^2$ | $Q_m$(mg/gm) | $K_L$(l/mg) | $K_f$ (mg/g) | n | $R^2$ |
| $Pb^{2+}$ | 0.999 | 26.3 | 0.127 | 2.88 | 1.27 | 0.997 |
| Cr(VI) | 0.998 | 10.75 | 0.0376 | 1.53 | 1.98 | 0.961 |

## Appendix C: Adsorption Kinetics

- Pseudo first order kinetics equation

$$\log (q_e - q_t) = \log(q_e) - (K_f/2.303) * t$$

$q_t$ is the amount of adsorbate adsorbed at time t (mg/g), qe is the adsorption capacity at equilibrium (mg/g), $K_f$ is the seudo first order rate constant ($min^{-1}$), and t is the contact time (min).

- Pseudo first order kinetics equation

$$\frac{t}{q_t} = \frac{1}{K_s {q_e}^2} + \frac{1}{q_e} t,$$

where ks, seudo second order rate constant (g/mg/min)

The initial adsorption rate, *h* (mg/g min) is defined as: $h = k_s {q_e}^2$

Table C1: Pseudo first and second order kinetics and constant values

| Pseudo second order kinetics | | | | |
|---|---|---|---|---|
| Time(min) | $q_t$ (Cr(VI)(mg/g) | $t/q_t$ | $q_t$Pb (mg/g) | $t/q_t$ |
| 0 | 0 | | | |
| 30 | 6.116 | 4.904978 | 9.493 | 3.160223 |
| 75 | 6.121 | 12.253 | 9.519 | 7.878979 |
| 120 | 6.306 | 19.02923 | 9.527 | 12.59578 |
| 180 | 6.26 | 28.75399 | 9.625 | 18.7013 |
| **Pseudo first order kinetics** | | | | |
| Time(min) | $q_t$ (Cr(VI)(mg/g) | ln ($q_e$-$q_t$) | $q_t$Pb (mg/g) | ln ($q_e$-$q_t$) |
| 0 | 0 | | | |
| 30 | 6.116 | -1.93958 | 9.493 | -2.02495 |
| 75 | 6.121 | -1.97291 | 9.519 | -2.24432 |
| 120 | 6.306 | - | 9.527 | -2.32279 |
| 180 | 6.26 | 0 | 9.625 | 0 |

| Metal ions | Pseudo first order | | | Pseudo second order | | | |
|---|---|---|---|---|---|---|---|
| | $q_{cal}$(mg/gm) | $R^2$ | $k_f$($min^{-1}$) | h(gm/mg/min) | $q_{cal}$(mg/gm) | ks (g/mg/min) | $R^2$ |
| $Pb^{2+}$ | 0.078 | 0.5639 | 0.0154 | 11.11 | 11.24 | 0.12 | 0.9999 |
| Cr(VI) | 0.05 | 0.7655 | 0.013 | 4.78 | 4.8 | 0.122 | 0.998 |

## Appendix D: Data analysis by design expert 7.0.0 software

Table D1: Analysis of variance (ANOVA) for lead adsorption; 1) Normal probability vs. studentized residuals to check for normality of residuals 2) Studentized residuals versus predicted values to check for constant error 3) Outlier t versus run order to look for influential values

| Standard Order | Actual Value | Predicted Value | Residual | Leverage | student Residual | Influence on Fitted Value | cook's Distance | Run Order |
|---|---|---|---|---|---|---|---|---|
| 1 | 30.45 | 32.89 | -2.44 | 0.255 | -0.872 | -0.508 | 0.026 | 28 |
| 2 | 25.53 | 32.89 | -7.36 | 0.255 | -2.629 | -1.654 | 0.236 | 34 |
| 3 | 95.90 | 90.11 | 5.79 | 0.171 | 1.961 | 0.923 | 0.079 | 14 |
| 4 | 95.20 | 90.11 | 5.09 | 0.171 | 1.724 | 0.802 | 0.061 | 37 |
| 5 | 83.43 | 87.82 | -4.39 | 0.255 | -1.567 | -0.932 | 0.084 | 46 |
| 6 | 86.77 | 87.82 | -1.05 | 0.255 | -0.376 | -0.218 | 0.005 | 11 |
| 7 | 35.70 | 35.87 | -0.17 | 0.171 | -0.057 | -0.025 | 0.000 | 21 |
| 8 | 36.87 | 35.87 | 1.00 | 0.171 | 0.339 | 0.152 | 0.002 | 35 |
| 9 | 96.20 | 92.25 | 3.95 | 0.130 | 1.306 | 0.508 | 0.025 | 10 |
| 10 | 95.97 | 92.25 | 3.71 | 0.130 | 1.228 | 0.477 | 0.022 | 23 |
| 11 | 89.89 | 89.12 | 0.77 | 0.171 | 0.261 | 0.118 | 0.001 | 48 |
| 12 | 89.50 | 89.12 | 0.38 | 0.171 | 0.129 | 0.058 | 0.000 | 33 |
| 13 | 32.93 | 36.62 | -3.68 | 0.255 | -1.316 | -0.776 | 0.059 | 16 |
| 14 | 29.93 | 36.62 | -6.68 | 0.255 | -2.388 | -1.479 | 0.195 | 38 |
| 15 | 96.73 | 92.16 | 4.57 | 0.171 | 1.549 | 0.716 | 0.050 | 40 |
| 16 | 96.33 | 92.16 | 4.17 | 0.171 | 1.413 | 0.650 | 0.041 | 18 |
| 17 | 83.92 | 88.19 | -4.27 | 0.255 | -1.526 | -0.906 | 0.080 | 22 |
| 18 | 88.80 | 88.19 | 0.61 | 0.255 | 0.218 | 0.126 | 0.002 | 54 |
| 19 | 45.61 | 41.41 | 4.20 | 0.171 | 1.423 | 0.655 | 0.042 | 29 |
| 20 | 42.89 | 41.41 | 1.48 | 0.171 | 0.503 | 0.227 | 0.005 | 52 |
| 21 | 95.48 | 96.68 | -1.20 | 0.130 | -0.398 | -0.152 | 0.002 | 44 |
| 22 | 95.18 | 96.68 | -1.50 | 0.130 | -0.495 | -0.189 | 0.004 | 13 |
| 23 | 91.51 | 92.43 | -0.93 | 0.171 | -0.314 | -0.141 | 0.002 | 53 |
| 24 | 91.62 | 92.43 | -0.82 | 0.171 | -0.278 | -0.125 | 0.002 | 45 |
| 25 | 46.83 | 44.37 | 2.45 | 0.130 | 0.812 | 0.312 | 0.010 | 4 |
| 26 | 45.83 | 44.37 | 1.46 | 0.130 | 0.481 | 0.184 | 0.003 | 51 |
| 27 | 95.80 | 98.81 | -3.01 | 0.130 | -0.995 | -0.384 | 0.015 | 3 |
| 28 | 96.29 | 98.81 | -2.52 | 0.130 | -0.832 | -0.320 | 0.010 | 43 |
| 29 | 92.45 | 93.72 | -1.28 | 0.130 | -0.423 | -0.162 | 0.003 | 32 |
| 30 | 92.29 | 93.72 | -1.43 | 0.130 | -0.474 | -0.181 | 0.003 | 20 |
| 31 | 48.69 | 45.11 | 3.58 | 0.171 | 1.213 | 0.554 | 0.030 | 15 |
| 32 | 49.94 | 45.11 | 4.82 | 0.171 | 1.635 | 0.758 | 0.055 | 17 |
| 33 | 95.94 | 98.71 | -2.77 | 0.130 | -0.916 | -0.353 | 0.013 | 7 |

Table D1 Continued

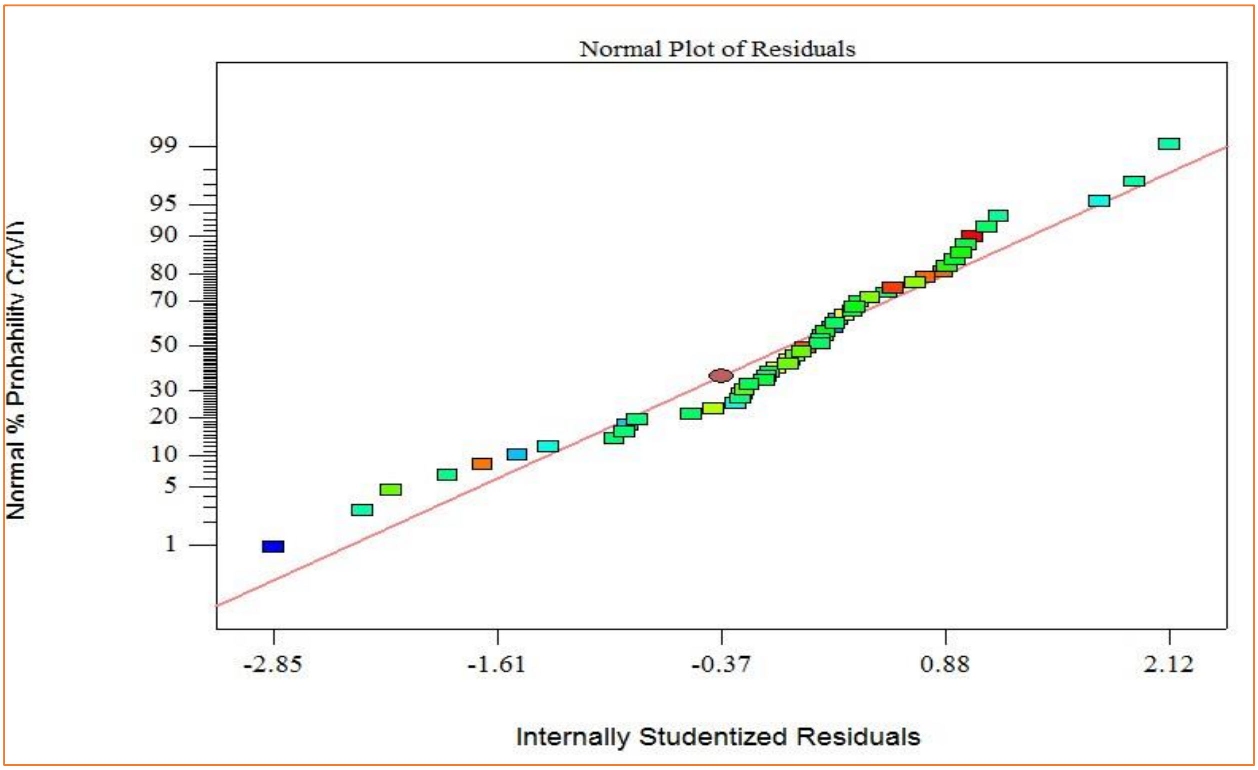
| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 34 | 96.48 | 98.71 | -2.23 | 0.130 | -0.738 | -0.283 | 0.008 | 5 |
| 35 | 92.91 | 92.79 | 0.12 | 0.171 | 0.041 | 0.018 | 0.000 | 9 |
| 36 | 92.35 | 92.79 | -0.43 | 0.171 | -0.147 | -0.066 | 0.000 | 41 |
| 37 | 42.97 | 42.77 | 0.20 | 0.255 | 0.071 | 0.041 | 0.000 | 24 |
| 38 | 43.79 | 42.77 | 1.02 | 0.255 | 0.364 | 0.211 | 0.005 | 1 |
| 39 | 94.77 | 96.09 | -1.32 | 0.171 | -0.448 | -0.202 | 0.004 | 26 |
| 40 | 95.09 | 96.09 | -1.00 | 0.171 | -0.340 | -0.153 | 0.002 | 19 |
| 41 | 92.14 | 89.90 | 2.24 | 0.255 | 0.802 | 0.467 | 0.022 | 36 |
| 42 | 91.88 | 89.90 | 1.98 | 0.255 | 0.709 | 0.412 | 0.017 | 8 |
| 43 | 44.37 | 45.73 | -1.36 | 0.171 | -0.462 | -0.208 | 0.004 | 31 |
| 44 | 44.19 | 45.73 | -1.54 | 0.171 | -0.521 | -0.235 | 0.006 | 30 |
| 45 | 94.89 | 98.21 | -3.32 | 0.130 | -1.098 | -0.425 | 0.018 | 25 |
| 46 | 95.59 | 98.21 | -2.62 | 0.130 | -0.867 | -0.333 | 0.011 | 42 |
| 47 | 93.08 | 91.17 | 1.91 | 0.171 | 0.646 | 0.292 | 0.009 | 50 |
| 48 | 92.79 | 91.17 | 1.62 | 0.171 | 0.547 | 0.247 | 0.006 | 49 |
| 49 | 47.74 | 46.46 | 1.28 | 0.255 | 0.458 | 0.266 | 0.007 | 12 |
| 50 | 48.19 | 46.46 | 1.73 | 0.255 | 0.619 | 0.359 | 0.013 | 6 |
| 51 | 95.50 | 98.10 | -2.60 | 0.171 | -0.882 | -0.400 | 0.016 | 47 |
| 52 | 94.92 | 98.10 | -3.18 | 0.171 | -1.078 | -0.491 | 0.024 | 2 |
| 53 | 92.64 | 90.23 | 2.41 | 0.255 | 0.862 | 0.502 | 0.025 | 27 |
| 54 | 92.78 | 90.23 | 2.55 | 0.255 | 0.912 | 0.532 | 0.028 | 39 |

Table D2: Analysis of variance (ANOVA) for Cr(VI) adsorption; 1) Normal probability vs. studentized residuals to check for normality of residuals 2) Studentized residuals versus predicted values to check for constant error 3) Outlier t versus run order to look for influential values

| Standard Order | Actual Value | Predicted Value | Residual | Leverage | Student Residual | Influence on Fitted Value | Cook's Distance | Run Order |
|---|---|---|---|---|---|---|---|---|
| 1 | 77.19 | 75.22 | 1.97 | 0.255 | 0.862 | 0.502 | 0.025 | 35 |
| 2 | 76.97 | 75.22 | 1.75 | 0.255 | 0.764 | 0.444 | 0.020 | 54 |
| 3 | 49.62 | 49.14 | 0.48 | 0.171 | 0.200 | 0.090 | 0.001 | 20 |
| 4 | 50.47 | 49.14 | 1.32 | 0.171 | 0.549 | 0.248 | 0.006 | 34 |
| 5 | 36.02 | 35.44 | 0.57 | 0.255 | 0.251 | 0.145 | 0.002 | 42 |
| 6 | 28.93 | 35.44 | -6.51 | 0.255 | -2.847 | -1.822 | 0.277 | 3 |
| 7 | 79.30 | 77.89 | 1.41 | 0.171 | 0.584 | 0.263 | 0.007 | 51 |
| 8 | 78.13 | 77.89 | 0.24 | 0.171 | 0.100 | 0.045 | 0.000 | 12 |
| 9 | 50.02 | 52.39 | -2.37 | 0.130 | -0.959 | -0.370 | 0.014 | 21 |
| 10 | 46.57 | 52.39 | -5.82 | 0.130 | -2.355 | -0.961 | 0.083 | 36 |
| 11 | 43.43 | 39.26 | 4.17 | 0.171 | 1.730 | 0.805 | 0.062 | 14 |
| 12 | 39.93 | 39.26 | 0.68 | 0.171 | 0.280 | 0.126 | 0.002 | 8 |
| 13 | 76.37 | 80.23 | -3.86 | 0.255 | -1.688 | -1.008 | 0.097 | 5 |
| 14 | 82.57 | 80.23 | 2.34 | 0.255 | 1.024 | 0.599 | 0.036 | 49 |

Table D2 Continued

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 15 | 57.43 | 55.29 | 2.14 | 0.171 | 0.887 | 0.402 | 0.016 | 2 |
| 16 | 55.80 | 55.29 | 0.51 | 0.171 | 0.212 | 0.095 | 0.001 | 33 |
| 17 | 39.31 | 42.73 | -3.42 | 0.255 | -1.497 | -0.888 | 0.077 | 11 |
| 18 | 47.13 | 42.73 | 4.40 | 0.255 | 1.925 | 1.162 | 0.127 | 25 |
| 19 | 61.23 | 66.52 | -5.29 | 0.171 | -2.194 | -1.045 | 0.099 | 7 |
| 20 | 65.54 | 66.52 | -0.98 | 0.171 | -0.407 | -0.183 | 0.003 | 37 |
| 21 | 50.71 | 47.97 | 2.73 | 0.130 | 1.107 | 0.428 | 0.018 | 27 |
| 22 | 48.43 | 47.97 | 0.46 | 0.130 | 0.186 | 0.071 | 0.001 | 6 |
| 23 | 46.91 | 41.80 | 5.10 | 0.171 | 2.117 | 1.004 | 0.093 | 31 |
| 24 | 39.68 | 41.80 | -2.13 | 0.171 | -0.882 | -0.400 | 0.016 | 44 |
| 25 | 68.92 | 68.14 | 0.78 | 0.130 | 0.316 | 0.121 | 0.001 | 48 |
| 26 | 67.52 | 68.14 | -0.62 | 0.130 | -0.251 | -0.096 | 0.001 | 45 |
| 27 | 52.61 | 50.17 | 2.44 | 0.130 | 0.988 | 0.381 | 0.015 | 39 |
| 28 | 50.62 | 50.17 | 0.45 | 0.130 | 0.182 | 0.069 | 0.000 | 52 |
| 29 | 43.87 | 44.57 | -0.70 | 0.130 | -0.285 | -0.109 | 0.001 | 4 |
| 30 | 47.46 | 44.57 | 2.89 | 0.130 | 1.171 | 0.454 | 0.020 | 46 |
| 31 | 69.46 | 69.43 | 0.035 | 0.171 | 0.015 | 0.007 | 0.000 | 23 |
| 32 | 69.28 | 69.43 | -0.15 | 0.171 | -0.062 | -0.028 | 0.000 | 38 |
| 33 | 50.71 | 52.02 | -1.31 | 0.130 | -0.532 | -0.204 | 0.004 | 13 |
| 34 | 51.78 | 52.02 | -0.24 | 0.130 | -0.096 | -0.037 | 0.000 | 18 |
| 35 | 46.72 | 47.00 | -0.28 | 0.171 | -0.116 | -0.052 | 0.000 | 1 |
| 36 | 43.80 | 47.00 | -3.20 | 0.171 | -1.325 | -0.608 | 0.036 | 43 |
| 37 | 61.02 | 60.92 | 0.10 | 0.255 | 0.046 | 0.026 | 0.000 | 29 |
| 38 | 61.10 | 60.92 | 0.18 | 0.255 | 0.079 | 0.045 | 0.000 | 47 |
| 39 | 50.54 | 49.90 | 0.64 | 0.171 | 0.265 | 0.119 | 0.001 | 9 |
| 40 | 49.28 | 49.90 | -0.62 | 0.171 | -0.259 | -0.116 | 0.001 | 40 |
| 41 | 53.38 | 51.27 | 2.12 | 0.255 | 0.927 | 0.541 | 0.029 | 19 |
| 42 | 49.36 | 51.27 | -1.91 | 0.255 | -0.834 | -0.486 | 0.024 | 17 |
| 43 | 60.92 | 61.49 | -0.58 | 0.171 | -0.239 | -0.107 | 0.001 | 32 |
| 44 | 61.50 | 61.49 | 5.411E-003 | 0.171 | 0.002 | 0.001 | 0.000 | 53 |
| 45 | 52.03 | 51.05 | 0.98 | 0.130 | 0.395 | 0.151 | 0.002 | 24 |
| 46 | 51.94 | 51.05 | 0.89 | 0.130 | 0.361 | 0.138 | 0.002 | 50 |
| 47 | 48.44 | 52.98 | -4.54 | 0.171 | -1.883 | -0.883 | 0.073 | 41 |
| 48 | 52.68 | 52.98 | -0.30 | 0.171 | -0.126 | -0.056 | 0.000 | 26 |
| 49 | 62.77 | 61.73 | 1.04 | 0.255 | 0.456 | 0.264 | 0.007 | 22 |
| 50 | 63.35 | 61.73 | 1.62 | 0.255 | 0.709 | 0.412 | 0.017 | 10 |
| 51 | 49.68 | 51.85 | -2.18 | 0.171 | -0.903 | -0.410 | 0.017 | 15 |
| 52 | 51.35 | 51.85 | -0.50 | 0.171 | -0.209 | -0.094 | 0.001 | 16 |
| 53 | 55.21 | 54.36 | 0.85 | 0.255 | 0.371 | 0.215 | 0.005 | 30 |
| 54 | 56.56 | 54.36 | 2.20 | 0.255 | 0.962 | 0.562 | 0.032 | 28 |



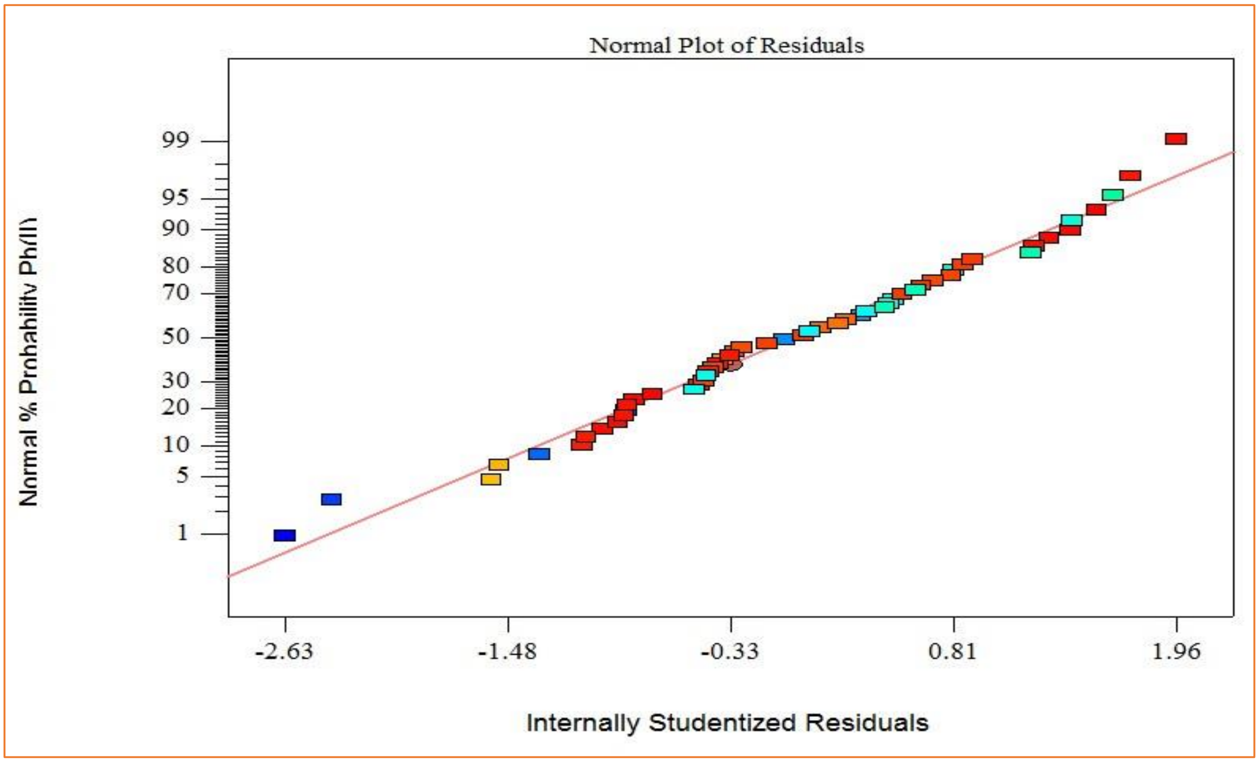


Figure D1 normal plots of residual versus residual for lead and chromium sorption onto BSG lead(II)

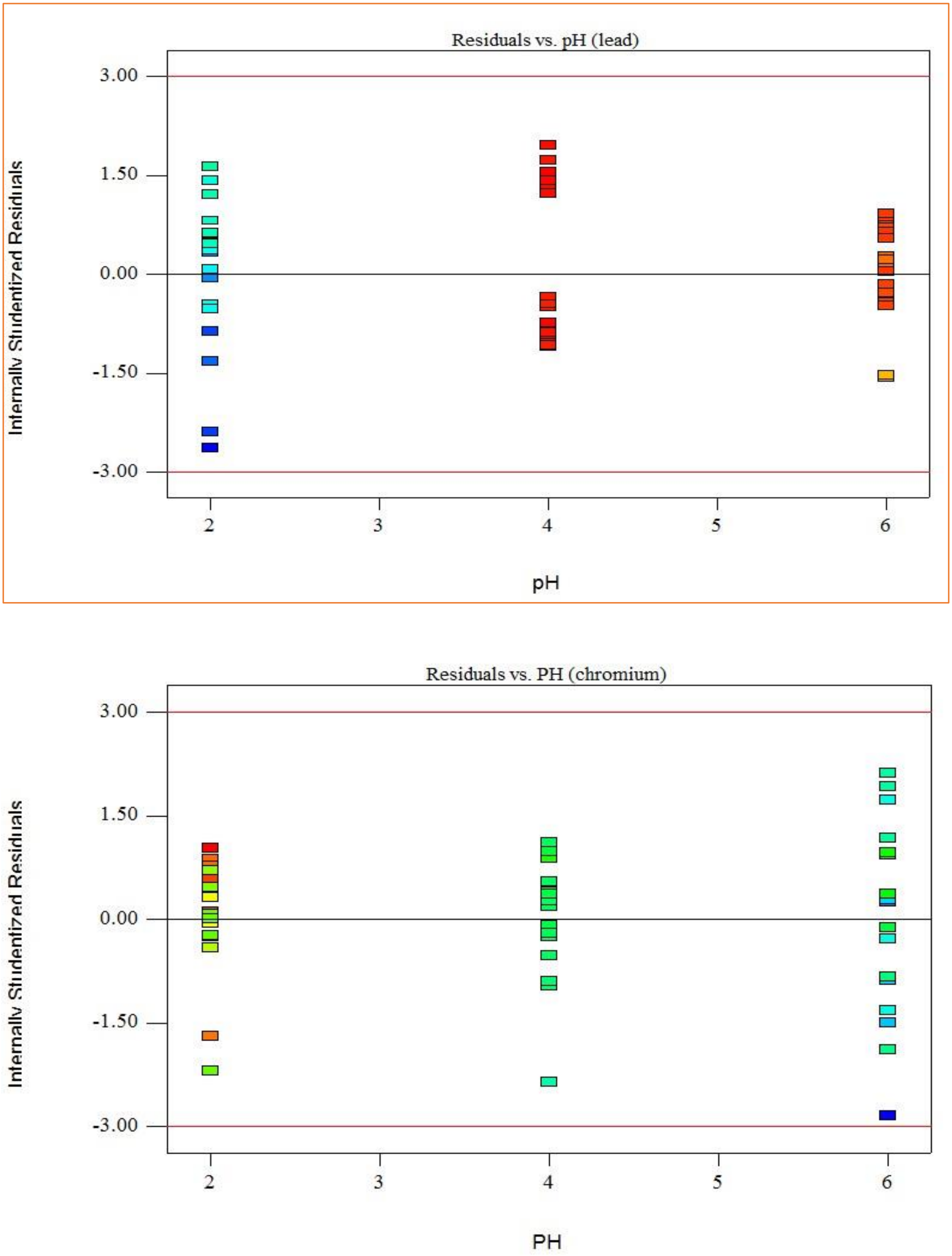
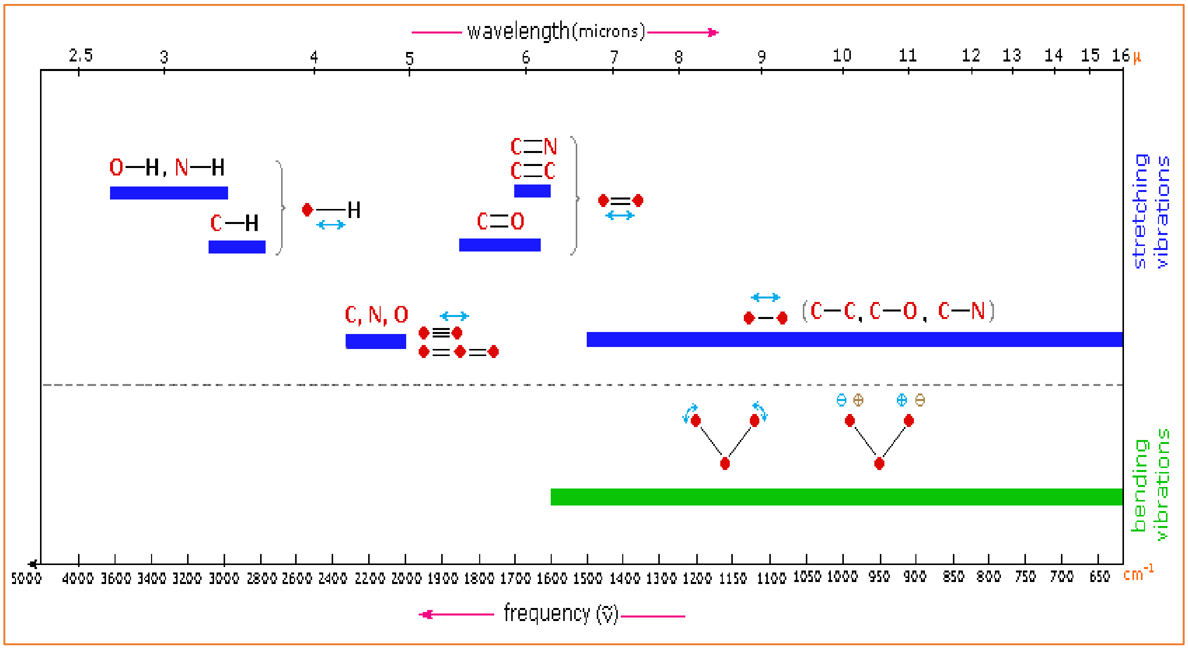


Figure D2: Residual versus factor for lead and chromium sorption onto BSG

## Appendix E: IR-Spectroscopy: Functional Group Identification

Infrared spectroscopy (IR spectroscopy or Vibrational Spectroscopy) is the spectroscopy that deals with the infrared region of the electromagnetic spectrum, that is light with a longer wavelength and lower frequency than visible light. It covers a range of techniques, mostly based on absorption spectroscopy (www.wikipedia.com).

The exact frequency at which a given vibration occurs is determined by the strengths of the bonds involved and the mass of the component atoms. For a more detailed discussion of these factors. In practice, infrared spectra do not normally display separate absorption signals for each of the 3n-6 fundamental vibrational modes of a molecule. The number of observed absorptions may be increased by additive and subtractive interactions leading to combination tones and overtones of the fundamental vibrations, in much the same way that sound vibrations from a musical instrument interact. Furthermore, the number of observed absorptions may be decreased by molecular symmetry, spectrometer limitations, and spectroscopic selection rules. One selection rule that influences the intensity of infrared absorptions, is that a change in dipole moment should occur for a vibration to absorb infrared energy. Absorption bands associated with C=O bond stretching are usually very strong because a large change in the dipole takes place in that mode.



**Some General Trends:**

iv. Stretching frequencies are higher than corresponding bending frequencies. (It is easier to bend a bond than to stretch or compress it.)

v. Bonds to hydrogen have higher stretching frequencies than those to heavier atoms.

vi. Triple bonds have higher stretching frequencies than corresponding double bonds, which in turn have higher frequencies than single bonds. (Except for bonds to hydrogen).

Table E1: Characteristic IR absorption frequencies of organic functional groups

| Functional Group Names | Absorption Ranges(cm$^{-1}$) | Type of Vibration causing IR absorption |
|---|---|---|
| Alkanes | 3000-2800 | H-C-H Asymmetric & Symmetric Stretch |
| | 1500-1440 | H-C-H Bend |
| Alkenes | 3100-3000 | C=C-H Asymmetric Stretch |
| | 1675-1600 | C-C=C Symmetric Stretch |
| Alkynes | 3300-3200 | ≡C H Stretch |
| | 2200-2100 | C‾C Stretch |
| Aromatic Rings | 3100-3000 | C=C-H Asymmetric Stretch |
| | 1600-1580 | C-C=C Symmetric Stretch |
| | 1500-1450 | C-C=C Asymmetric Stretch |
| Phenols & Alcohols | 3600-3100 | Hydrogen-bonded O-H Stretch |
| | 1730-1650 | C=O Stretch |
| Ketones | 1750-1625 | C=O Stretch |
| | 1750-1625 | C=O Stretch |
| Aldehydes | 2850-2800 | C-H Stretch off C=O |

Table E1 Continued

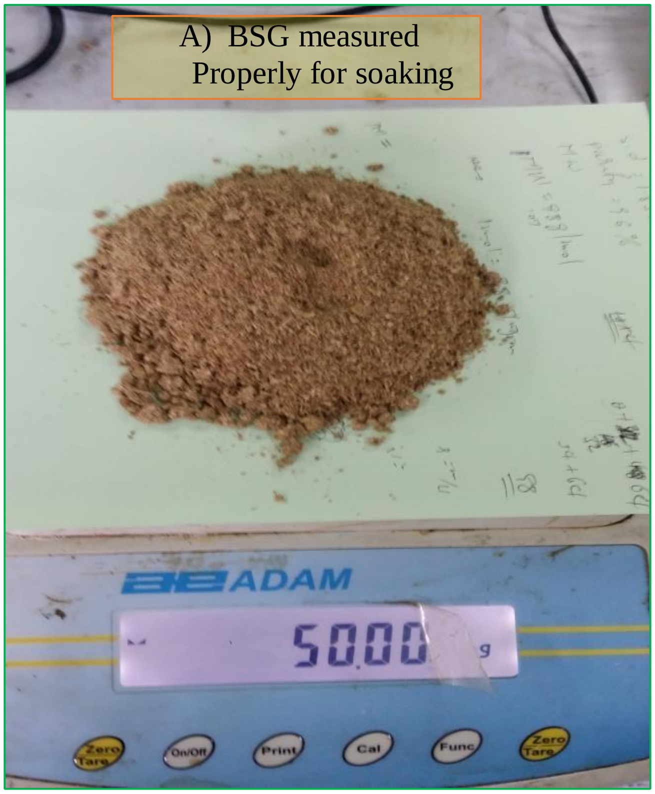
| | | |
|---|---|---|
| Esters | 1755-1650 | C=O Stretch |
| | (1300-1000) | (C-O Stretch) |
| Ethers | (1300-1000) | (C-O Stretch) |
| Amines—Primary | 3500-3100 (TWO PEAKS!) | N-H Stretch |
| | 1640-1560 | N-H Bend |
| Amines—Secondary | 3500-3100 (ONE PEAK!) | N-H Stretch |
| | 1550-1450 | N-H Bend |
| Nitriles | 2300-2200 | C N Stretch |
| Nitro Groups | 1600-1500 | N=O Stretch |
| | 1400-1300 | N=O Bend |
| Amides | 3500-3100 | N-H Stretch (similar to amines) |
| | 1670-1600 | C=O Stretch |
| | 1640-1550 | N-H Bend |
| Aldehydes | 2750-2700 | C-H Stretch off C=O |

## Appendix F: Laboratory pictures

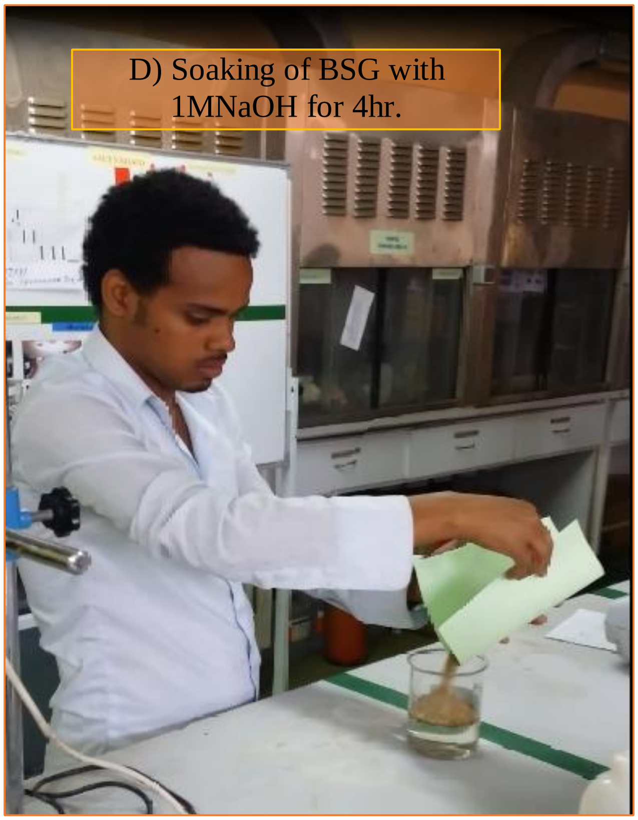
D) Succesive washing of Fresh BSG by distilled water to remove impurities

C) Drying of washed BSG

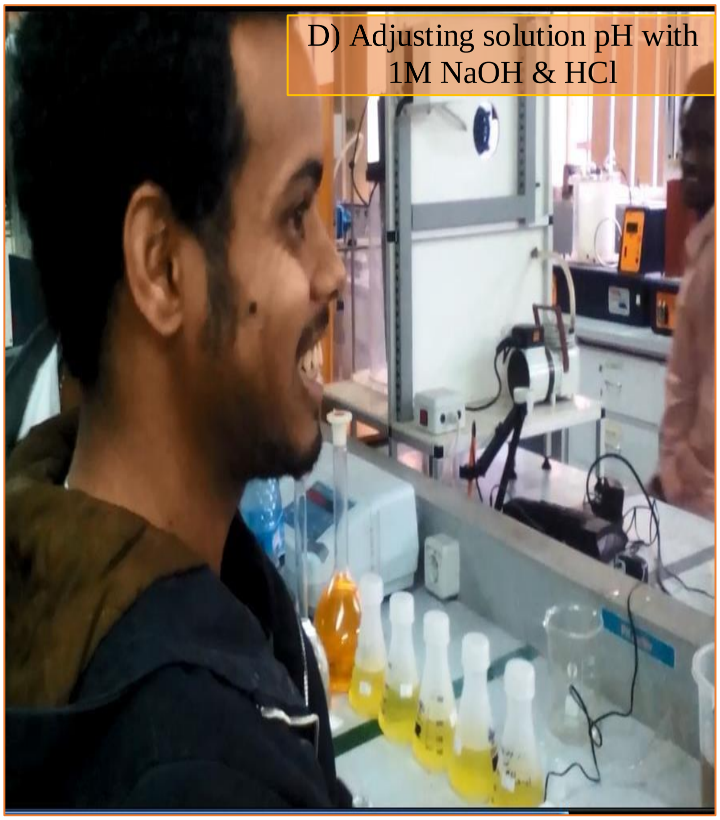
B) Grinding to have uniform particle size of 0.25mm



A) BSG measured Properly for soaking

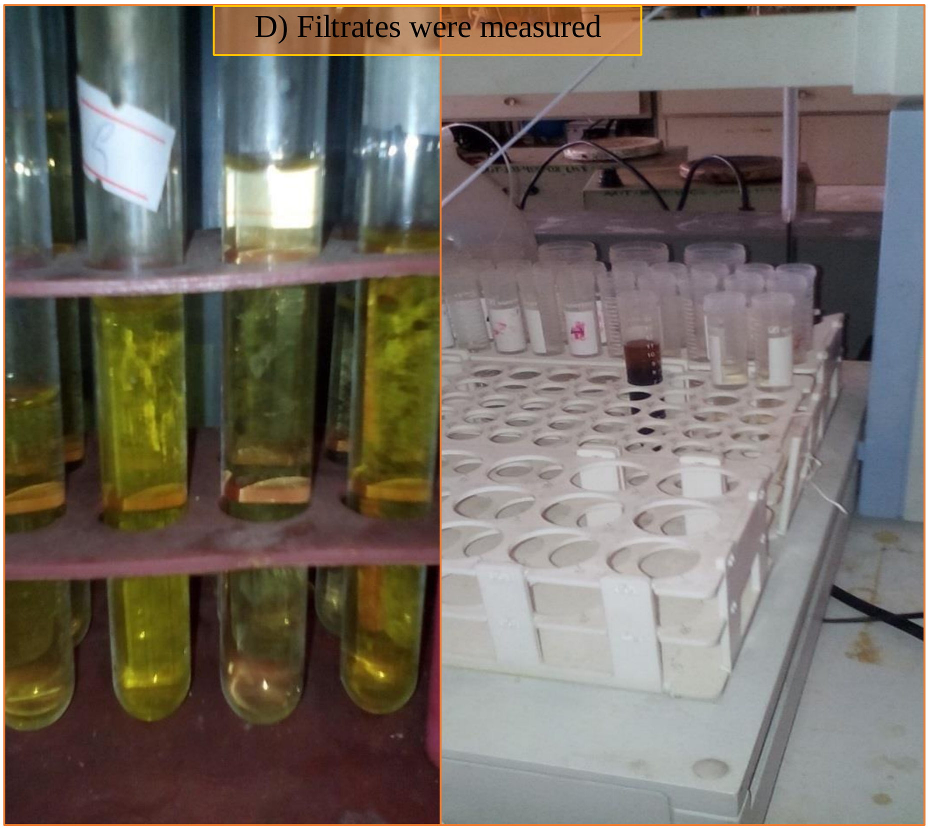


D) Soaking of BSG with 1MNaOH for 4hr.



D) Adjusting solution pH with 1M NaOH & HCl

D) shaking of adsorbet and adsornent



D) Filtrates were measured