

**ADDISABABA UNIVERSITY
ADDIS ABABA INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL AND BIO ENGINEERING**



**STUDY ON THE PREPARATION OF MAGNETIC
SORBENT FROM BAGASSE FOR CHROMIUM ION
REMOVAL**

By: Habtamu Belachew

**June, 2015
Addis Ababa, Ethiopia**

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**A Thesis Submitted to Addis Ababa Institute of Technology, School of Chemical And Bio
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Science in Chemical Engineering Under Process Engineering Stream.**

Advisor: Dr. S. Anuradha Jabasingh

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Declaration

I declare that the thesis for the M.Sc. degree at the University of Addis Ababa, hereby submitted by me, is my original work and has not previously been submitted for degree at this or any other university, and that all resources of materials used for this thesis have been duly acknowledged.

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Acronyms

AC	Activated carbon
ATP	Adenosine triphosphate
BOD	Biological oxygen demand
CAS	Chemical Abstracts Service
CCD	Central composite design
CNTs	Carbon nanotubes
CNS	Central nervous system
COD	Chemical oxygen demand
DE	Desorption efficiency
DPC	Diphenylcarbazide
EPA	Environmental protection agency
LC	Ligocellulosic
MCL	Maximum contaminant leve
MCLG	Maximum Contaminant Level Goal
MNPs	Magnetic nanoparticles
MWCNTs	Multi walled CNTs
PMT	Potentiometric mass titration
PNS	Peripheral nervous system
SWCNTs	Single walled CNTs
WHO	World health organization

Abstract

Heavy metals in the environment are hazardous to human health and require better methods for detection and remediation. Industrial effluent often contains the significant amount of hexavalent chromium. The discharge of wastewater without proper treatment into water streams consequently enters the soil and disturbs the aquatic and terrestrial life. A range of wastewater treatment technologies have been proposed which can efficiently reduce Cr(VI) to less toxic form such, as biodegradation, sorption, bioaccumulation, and nanotechnology.

In this study, bagasse coated iron oxide magnetic sorbent were prepared using iron salts in presence of NH_3 by co- precipitation process and then the magnetic sorbent is used as an adsorbent for chromium removal. All the adsorption experiments were carried out in batch mode to optimize process parameters using response surface methodology. Based on central composite design, quadratic model was developed to correlate the variables to the response.

The effect of different parameters on optimum function of this process has been analysed. The results showed that maximum chromium adsorption of 91.95% occurs at pH levels of about 4. Optimum dosage of sorbent, chromium concentration and contact time are 1.1g, 20mg/l and 90min, respectively. Adsorption isotherms and kinetics were investigated. The experimental data were analyzed by the Langmuir, Freundlich and Temkin models of adsorption. The adsorption isotherm data were fitted well to Langmuir isotherm. Results show that the kinetic model of pseudo-first order provided a good description of the experimental data. Thus, the chromium adsorption by magnetic sorbent can be considered as a potential treatment process for chromium removal in which the adsorbents and the adsorbed pollutant can be quickly recycled by the application of magnet.

1. Introduction

As human needs increase and civilization changes, more and more finished products of different types are required. Large number of industries are born and grown in every country and industry plays an important role in economic development of the world. It improves the economic welfare of citizens and supplies the material goods they consume. The way in which society will develop in the future is largely dependent on how the growth which industry generates is distributed. Industry is also a major consumer of natural resources and a major contributor to the overall pollution load. Process waste streams from the mining operations, metal-plating facilities, power generation facilities, electronic device manufacturing units, and tanneries may contain heavy metals at concentrations exceeding the local discharge limits.

Heavy metal pollution of water is a major environmental problem facing the modern world. The global heavy metal concentration in various environments is increasing in the environment due to an increase in number of industries. Most of the industrial wastewaters contain heavy metals like Cadmium, Lead, Zinc, Arsenic, Cobalt and Chromium. Among the heavy metals, Chromium is the major pollutant from the leather tanning industry and is toxic to plants and animals around the environment. Generally, humans are exposed to these metals by ingestion (drinking or eating) or inhalation (breathing). Working in or living near an industrial site, which utilizes these metals and their compounds increases ones risk of exposure, as does living near a site where these metals have been improperly disposed.

Environmental contamination induced by chromium arises mainly via various sources like chrome pigments, leather tanneries, chrome plating, metal finishing industries and some textile plants are considered to contaminate the environment with chromium. The application of chromium, a heavy metal in various industries, especially in leather tanning has gained a negative impact in the society with respect to its pollution potential. The damage to the environment by the hazardous tannery effluent is becoming an acute problem in several countries. The chrome tanning process results in toxic metals, especially Chromium III passing to waste water and are not easily eliminated by ordinary treatment process. Tannery waste waters are mainly characterized by high salinity, high organic loading and specific pollutants such as Chromium. The industrial effluent released directly or indirectly into natural water resources, mostly without proper treatment, poses a major threat to the environment (Smrithi and Ushak, 2012).

Among the different forms of Chromium, the hexavalent Chromium, Cr^{6+} is the most toxic and carcinogenic due to its high solubility in water, rapid permeability through biological membranes and subsequent interaction with intracellular proteins and nucleic acids. The heavy metals in general cannot be biologically transformed to more or less toxic products and hence persist in the environment indefinitely. They are significantly toxic even in small amounts and can cause diseases in humans and animals as they cause irreversible changes in the body, especially in the central nervous system. Soil contamination by heavy metals is often irreversible and may repress or even kill parts of the microbial community and it is generally assumed that the exposure to metals leads to the establishment of a resistant microbial population (Smrithi and Ushak, 2012).

It is thus a necessary to remove metal ions from wastewater before it can be discharged. In this respect, many physicochemical methods have been developed for the removal of metal ions from aqueous solutions including precipitation, evaporation, electro deposition, ion exchange, membrane separation, coagulation etc. However these methods have disadvantages such as secondary pollution, high cost, high energy input, and large quantities of chemical reagents or poor treatment efficiency at low metal concentration. It can be said that the conventional methods for metal ions removal from wastewater are limited by technical and economic barriers, especially when concentration of metals in the wastewater is low (<100 ppm) (Nour et al., 2014).

Therefore the search and development of an efficient and low-cost metal removal processes is of paramount importance. Adsorption is now reorganized as an effective and economical process for a wide variety of applications, especially for the removal of heavy metals from waste waters. The most widely used adsorbent is activated carbon, but it is quite expensive and, possibly, non-cost-effective in the treatment of large waste water volumes. That is why, an alternative low-cost adsorbents has been paid the considerable attention.

During the past few decades, scientists have been developing cheap and environmentally friendly technologies for the treatment of wastewater generated at the household and up to the industrial scale. In this regard, methods like ion-exchange, membrane filtration, catalysts including photo catalysts, microbe-assisted phyto-bioremediation and adsorption over low-cost biosorbents and nanomaterials have been developed and demonstrated to be successful. Because of the demand for water to feed the growing population and the needs for industrial processing, the separation and purification of generated wastewater by adsorption phenomena is gaining major relevance.

Adsorption over biomass derived biosorbents has provided the capability to treat wastewater on a large scale. Several low-cost biosorbents have been synthesized and successfully applied to remove toxic metals and metalloids from wastewater. Nanomaterials and their analogues, such as magnetic nanosorbents and layered double hydroxides, have been the focus for the development of novel materials with high surface area and low cost synthesis to develop new generation super-adsorbents (Ravindra et al., 2014). Nano-adsorbents because of their extremely small size and high surface area to volume ratio, which provide better kinetics for adsorption of metal ions from aqueous solutions, have drawn particular attention recently.

Magnetic nano-particles have found many exciting applications in various areas of biosciences, medicine, biotechnology and environmental technology. Different types of responses of such materials to an external magnetic field enable various applications, namely selective separation, targeting and localization of magnetically responsive nano-particles and other relevant materials using an external magnetic field (Ivo et al., 2012).

Recently the most common method which has been used for heavy metal removal is biosorption. The word “biosorption” consists of using biomass as polymeric matrix. The biomasses, because of their significant advantages such as: cheapness, availability, recyclability and etc. are the most common materials used in adsorption processes. Biosorption is effective for both organic and inorganic pollutants (heavy metals) as investigated by many researches. Sugarcane bagasse is one of the low cost biomasses which can be found with high quality. Preparation of biosorbent and its use as a polymeric matrix for magnetic nanoparticles embedding is a method with high level of efficiency to remove heavy metal. This study show the preparation of magnetic sorbent from bagasse and the adsorption capacities of the magnetic sorbent to remove chromium ion. The experiments was conducted by varying process parameters like adsorbent dosage, initial metal ion concentration, pH, and contact time under batch studies to determine optimal values of the parameters.

1.1. Statement of the problem

There has been growing concern over the diverse effects of heavy metals on humans and aquatic ecosystems. Wastewater from textile, tannery, electroplating, galvanizing, pigment and dyes, metallurgical and paint industries and other metal processing and refining operations at small and large scale sector contain significant amounts of toxic metal ions. The toxic metals and their ions are not only potential human health hazards but also to other life forms. Toxic metal ions cause physical discomfort and sometimes life threatening illness including irreversible damage to crucial body system. Metal ions are reported as priority pollutants, due to their mobility in natural water ecosystems and due to their toxicity. The problem associated with metal ions pollution is that they are not biodegradable and are highly persistent in the environment. Thus, they can be accumulated in living tissues, causing various diseases and disorders. Heavy metals toxicity can result in damage or reduced mental and central nervous function, lower energy levels and damage to blood composition, lungs, kidneys, liver and other vital organs.

From the eco-toxicological point of view, the most dangerous metals are Mercury, Lead, Cadmium and Chromium (VI). Metal ions in the environment bio-accumulate and are biomagnified along the food chain. Therefore, their toxic effect is more pronounced in animals at higher trophic levels. The analysis of wastewater for trace and heavy metal contamination is an important step in ensuring human and environmental health. Wastewater is regulated in different ways in different countries, but the goal is to minimize the pollution introduced into natural streams. [Omran Abdia and Mosstafa Kazemi, 2015]

Chromium occurs in a number of oxidation states, but Cr(III) (trivalent Chromium) and Cr(VI) (Hexavalent Chromium) are of main biological relevance. There is a great difference between Cr(III) and Cr(VI) with respect to toxicological and environmental properties, and they must always be considered separately. Cr³⁺ is considerably less toxic than Cr⁶⁺. Hexavalent chromium has been demonstrated to have a number of adverse effects ranging from causing irritation to cancer. Almost all the Cr(VI) in the environment is a result of human activities.

It is thus a necessary to remove metal ions from wastewater before it can be discharged. In this respect, various physicochemical remediation technologies have been developed for the removal of metal ions from aqueous solutions.

Recently new and cost-effective nanomaterials for environmental remediation, pollution detection and other applications have attracted considerable attention. Magnetic nanoparticles (MNPs) are of great interest in a wide range of disciplines due to their distinctive physical and chemical properties such as size effects, surface-to-volume ratio, interaction, magnetic adsorption separation, specificity and surface chemistry. MNPs are a new class of nano-adsorbents which not only possess quite good performance owing to high efficient specific surface area and absence of internal diffusion resistance compared to the traditional adsorbents, furthermore can be recovered rapidly by an external magnetic field (Nejat et al., 2014).

The basic aim of the study was to prepare magnetic sorbent from waste biomass (sugarcane bagasse) for chromium ion removal from waste water. The magnetic sorbents of large surface area and high magnetization was synthesized. The Fe_3O_4 -LC (Ligocellulosic) sorbent was synthesized by a modified in situ chemical co-precipitation method, where the biosorbent uses as a polymeric matrix for magnetic nanoparticles embedding.

1.2. Objectives of the study

1.2.1. General objectives

The fundamental goal of this study was to synthesize low cost and effective adsorbent for chromium ion removal by modifying sugarcane bagasse with iron salts which have magnetic property.

1.2.2. Specific objectives

- To synthesize the adsorbent using bagasse and Fe_3O_4
- To characterize the modified magnetic sorbent
- To examine the sorption/desorption behavior of metal ion with the magnetic sorbent
- To examine and optimize the effect of pH, initial metal concentration, contact time and adsorbent dosage
- To investigate and describe the batch kinetics of adsorption and sorption isotherm with different models

1.3. Significant of the study

Growing concern for the presence and contamination of heavy metals in our water supplies has steadily increased over the last few years. Elements such as mercury, arsenic, chromium, lead and

cadmium exhibit human toxicity at extremely low concentrations. These heavy metals which are transferred to the environment are highly toxic and can bio-accumulate in the human body, aquatic life and natural water bodies and also possibly get trapped in the soil.

Various methods of treating effluents containing heavy metals have been developed over years. These methods have significant disadvantages, including high energy requirements, inefficient metal removal, generation of toxic sludge, and expensive equipment. Therefore, there is a need to develop an efficient, rapid, cost-effectively and environment friendly method for the removal of heavy metals from effluents. Among these techniques, as a simple, efficient, cost-effective, and ecofriendly approach for removing extremely toxic metal ions in drinking water and in hydrometallurgical streams, adsorption offers good flexibility in design and operation and will generate high quality treated effluents for safe and healthy use.

The removal of heavy metals by using low cost adsorbent is found to be more promising in long terms as there are many materials available locally and abundantly. Hence, the conversion of these materials as low cost adsorbents is recognized as a potential and economic application for wastewater treatment. The adsorption of heavy metal by a number of materials such as agroindustry waste residues, forestry waste, fruit peelings and leaves, fungi, dead bacterial, and diatom biomass has been reported in literatures.

In this work, using iron salts as an iron source and using sugarcane bagasse as template, magnetic nano iron oxide bagasse matrix was prepared as adsorbent for chromium from aqueous solution.

2. Literature review

Environment is defined as the totality of circumstances surrounding an organism or group of organisms especially, the combination of external physical conditions that affect and influence the growth, development and survival of organisms. It consists of the flora, fauna and the abiotic, and includes the aquatic, terrestrial and atmospheric habitats. The environment is considered in terms of the most tangible aspects like air, water and food, and the less tangible, though no less important, the communities we live in. A pollutant is any substance in the environment, which causes objectionable effects, impairing the welfare of the environment, reducing the quality of life and may eventually cause death. Hence, environmental pollution is the presence of a pollutant in the environment; air, water and soil, which may be poisonous or toxic and will cause harm to living things in the polluted environment.

Humanity's ability to mine and use metals has played a major role in development of modern human society. Many metals have a wide range of uses, but these have come at a significant environmental price: some (generally called heavy metals) have serious negative environmental consequences, yet our dependence on them continues to result in large inputs into our environment. Heavy metals are an important category of pollutants and as such have major detrimental impacts on both human health and the health of terrestrial and aquatic communities and ecosystems. A number of metals have been included in the term "heavy metal" (Robert, 2010).

The term "heavy metals" refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration. "Heavy metals" is a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4 g/cm^3 , or 5 times or more, greater than water. However, being a heavy metal has little to do with density but concerns chemical properties. Heavy metals include lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag) chromium (Cr), copper (Cu) iron (Fe), and the platinum group elements.

2.1. Source of heavy metal

Heavy metals differ widely in their chemical properties, and are used extensively in electronics, machines and the artifacts of everyday life, as well as in high-tech applications. As a result they are able to enter into the aquatic and food chains of humans and animals from a variety of anthropogenic sources as well as from the natural geochemical weathering of soil and rocks. The

main sources of contamination include mining wastes, land fill leaches, municipal wastewater, urban runoff and industrial wastewaters, particularly from the electroplating, electronic and metal finishing industries. With increasing generation of metals from technologies activities, the problem of waste disposal has become one of paramount importance. Many aquatic environments face metal concentrations that exceed water quality criteria designed to protect the environment, animals and humans. The problems are exacerbated because metals have a tendency to be transported with sediments, are persistent in the environment and can bio accumulate in the food chain (Ravindra et al., 2014).

2.2. Toxicological Aspects of Heavy metals

Due to their mobility in aquatic ecosystems and their toxicity to higher life forms, heavy metals in surface and groundwater supplies have been prioritized as major inorganic contaminants in the environment. Even if they are present in dilute, undetectable quantities, their recalcitrance and consequent persistence in water bodies imply that through natural processes such as biomagnification, concentrations may become elevated to such an extent that they begin exhibiting toxic characteristics. These metals can either be detected in their elemental state, which implies that they are not subject to further biodegradative processes or bound in various salt complexes. In either instance, metal ions cannot be mineralized. Apart from environmental issues, technological aspects of metal recovery from industrial waters must also be considered (Ramachandra et al., 2013).

Heavy metals disrupt metabolic functions in two ways:

1. They accumulate and thereby disrupt function in vital organs and glands such as the heart, brain, kidneys, bone, liver, etc.
2. They displace the vital nutritional minerals from their original place, thereby, hindering their biological function. It is, however, impossible to live in an environment free of heavy metals. There are many ways by which these toxins can be introduced into the body such as consumption of foods, beverages, skin exposure, and the inhaled air.

Chromium: Humans are exposed to chromium through breathing, eating or drinking and through skin contact with chromium or chromium compounds. The level of chromium in air and water is generally low. In drinking water the level of chromium is usually low as well, but contaminated well water may contain the dangerous chromium (VI); hexavalent chromium. For most people

eating food that contains chromium (III), it is the main route of chromium uptake, as chromium (III) occurs naturally in many vegetables, fruits, meats, yeasts and grains. Various ways of food preparation and storage may alter the chromium contents of food, as in the case of food stored in steel tanks or cans leading to enhanced chromium concentrations. Chromium (VI) is a danger to human health, mainly for people who work in the steel and textile industry. Chromium (VI) is known to cause various health effects. When it is a compound in leather products, it can cause allergic reactions, such as skin rash. Inhaling chromium (VI) can cause nose irritations and nosebleeds. Other health problems that are caused by chromium (VI) are skin rashes, respiratory problems, weakened immune systems, kidney and liver damage, alteration of genetic material, lung cancer and death. The health hazards associated with exposure to chromium are dependent on its oxidation state. The metal form (chromium as it exists in this product) is of low toxicity. The hexavalent form is toxic. Adverse effects of the hexavalent form on the skin may include ulcerations, dermatitis, and allergic skin reactions. Inhalation of hexavalent chromium compounds can result in ulceration and perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis, bronchospasms and edema. Respiratory symptoms may include coughing and wheezing, shortness of breath, and nasal itch.

2.3. Heavy Metal Emission and Chemistry

Heavy metals can be emitted into the environment by both natural and anthropogenic causes. The major causes of emission are the anthropogenic sources specifically mining operations. In some cases, even long after mining activities have ceased, the emitted metals continue to persist in the environment. Hard rock mines operate from 5-15 years until the minerals are depleted, but metal contamination that occurs as a consequence of hard rock mining persist for hundreds of years after the cessation of mining operations. Apart from mining operations, mercury is introduced into the environment through cosmetic products as well as manufacturing processes like making of sodium hydroxide. Heavy metals are emitted both in elemental and compound (organic and inorganic) forms. Anthropogenic sources of emission are the various industrial point sources including former and present mining sites, foundries and smelters, combustion by-products and traffics (Duruibe et al., 2007).

Heavy metals are an important class of pollutants with both lethal and sub-lethal effects on organisms. The latter are receiving increased attention, as these may have harmful ecological

outcomes. To assess properly the possible short-and long-term problems associated with the release of heavy metals to the environment, it is necessary to understand the biogeochemical cycling in such systems. The behavior of heavy metals in aquatic and terrestrial systems is very largely governed by the speciation. Speciation will influence heavy metal bioavailability and toxicity to biota, its transportation and mobilization, and its interaction with the sediments and soils (Barry, 1987).

2.3.1. Chemical and Physical Information Relevant to Assessments

Chromium (Cr) is a metallic element belonging to the first transitional series of the periodic table. Elemental chromium has a CAS Registry Number of 7440-47-3. The three most stable forms in which chromium occurs in the environment are the 0 (metal and alloys), +3 (trivalent chromium), and +6 (hexavalent chromium) valence states. In the +3 valence state, the chemistry of chromium is dominated by the formation of stable complexes with both organic and inorganic ligands. In the +6 valence state, chromium exists as oxo species such as CrO_3 and CrO_4^{2-} that are strongly oxidizing. Chromium in the ambient air occurs from natural sources, industrial and product uses, and burning of fossil fuels and wood. The most important industrial sources of chromium in the atmosphere originate from ferrochrome production. Ore refining, chemical and refractory processing, cement-producing plants, automobile brake lining and catalytic converters for automobiles, leather tanneries, and chrome pigments also contribute to the atmospheric burden of chromium. Under normal conditions, Cr (III) and Cr (0) in the air do not undergo any reaction. Cr (VI) in the air eventually reacts with dust particles or other pollutants to form Cr (III); however, the exact nature of such atmospheric reactions has not been studied extensively. Chromium is removed from air by atmospheric fallout and precipitation. The atmospheric half-life for the physical removal mechanism depends on the particle size and particle density of atmospheric chromium. Chromium particles of small aerodynamic diameter ($< 10 \mu\text{m}$) may remain airborne for long periods and may be transported great distances by wind currents and diffusion forces. Surface runoff, deposition from air, and release of municipal and industrial waste waters are the sources of chromium in surface waters. The most significant removal mechanism for Cr (III) from the aquatic environment is precipitation as $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$ followed by sedimentation. Cr(VI), however, can exist in aquatic media as a water-soluble complex anion and may persist in water for long periods. Cr(VI) is a moderately strong oxidizing agent and will react with organic matter or other reducing agents to form Cr(III). Therefore, in surface water rich in organic content, Cr(VI) will exhibit a much

shorter lifetime. Chromium probably occurs as insoluble $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$ in soil, given that organic matter in soil converts soluble chromate to insoluble Cr_2O_3 . There is no known chemical process that can cause chromium to be lost from soil. The primary processes by which chromium is lost from soil are physical. For example, chromium in soil can be transported to the atmosphere by way of dust or aerosol formation. Chromium is also transported from soil through runoff. Runoff can remove both chromium ions and bulk precipitates of chromium. In addition, flooding of soils and the subsequent anaerobic decomposition of plant matter may increase dissolution of Cr_2O_3 in soil through complexation (US EPA, 1998).

2.4. Regulatory limits

Technological advancement, increase in incomes and betterment of standards of living have resulted in the increased demand for almost everything. With more income people use more resources and have more wants and needs. Such a situation has led to an increase in the number of uses of heavy metals. Every year, more and more amounts of heavy metals are being used and incorporated into products. These heavy metals are toxic to human health and the environment at trace level concentrations, which is a major cause of concern. Wastewater regulations were established to minimize human and environmental exposure to hazardous chemicals. This includes limits on the types and concentration of heavy metals that may be present in the discharged water.

Table 2.1. Guideline of heavy metals discharge limitations

Heavy metal	WHO drinking water guideline (mg/L)	US EPA MCLG (mg/L)	US EPA MCL (mg/L)
As	0.01	0	0.01
Cd	0.003	0.005	0.005
Cr	0.05	0.1	0.1
Cu	2	1.3	1.3
Pb	0.01	0	0.015
Mn	0.4	-	-
Hg	0.001	0.002	0.002

Source US EPA toxicological review, 1998

2.5. Treatment techniques for removal of heavy metals from industrial wastewaters

Growing concern for the presence and contamination of heavy metals in our water supplies has steadily increased over the last few years. Elements such as mercury and cadmium exhibit human toxicity at extremely low concentrations. The elements silver, chromium, lead, copper, and zinc also exhibit toxic properties to humans although the concentrations are orders of magnitude higher than that required for Cd or Hg toxicity.

Removals or reductions of total heavy metal concentrations usually desirable prior to any wastewater treatment operation since many heavy metals, adversely affect biological oxidation processes, such as trickling filters, activated sludge, and anaerobic digestion. A number of specialized processes have been developed for the removal of metals from waste discharges. These unit operations include: chemical precipitation, coagulation/flocculation, ionexchange/solvent extraction, cementation, complexation, electrochemical operations, biological operations, adsorption, evaporation, filtration and membrane processes.

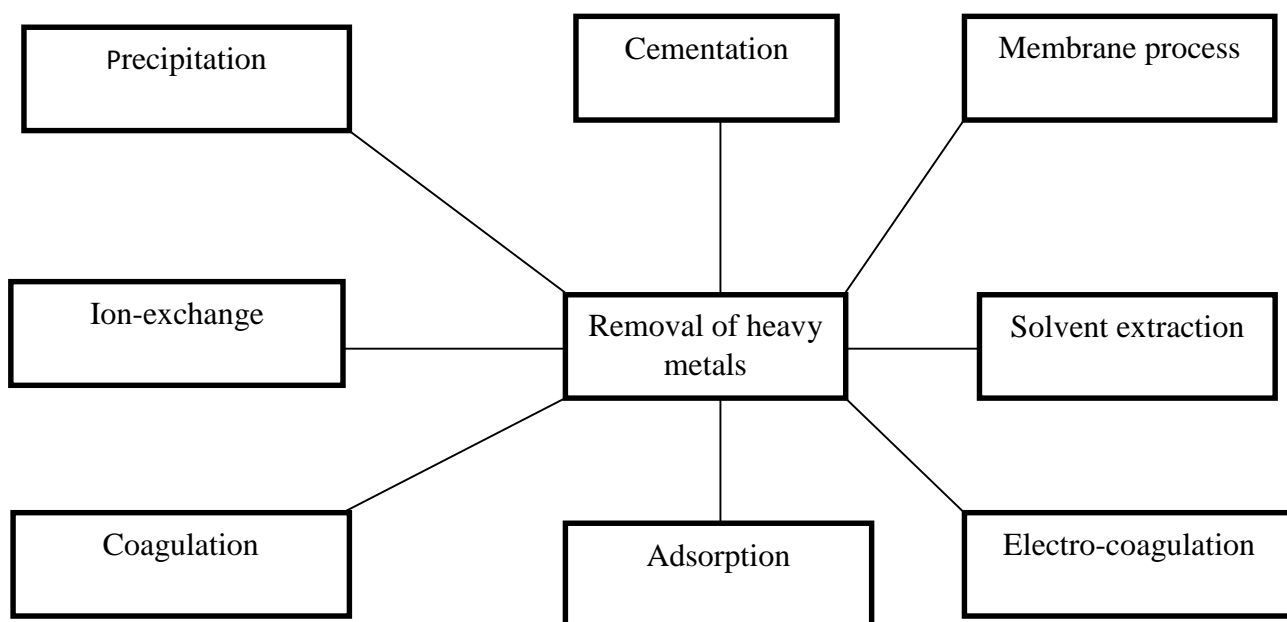


Figure 2.1: Some conventional methods for the removal of heavy metals.

2.5.1. Chemical precipitation

Chemical precipitation is effective and by far the most widely used process in industry because it is relatively simple and inexpensive to operate. In precipitation processes, chemicals react with heavy metal ions to form insoluble precipitates. The forming precipitates can be separated from the

water by sedimentation or filtration. And the treated water is then decanted and appropriately discharged or reused. The conventional chemical precipitation processes include hydroxide precipitation and sulfide precipitation.

Hydroxide precipitation

The most widely used chemical precipitation technique is hydroxide precipitation due to its relative simplicity, low cost and ease of pH control. The solubility's of the various metal hydroxides are minimized in the pH range of 8.0 - 11.0. The metal hydroxides can be removed by flocculation and sedimentation. A variety of hydroxides has been used to precipitate metals from wastewater, based on the low cost and ease of handling, lime is the preferred choice of base used in hydroxide precipitation at industrial settings. In hydroxide precipitation process, the addition of coagulants such as alum, iron salts, and organic polymers can enhance the removal of heavy metals from wastewater.

Although widely used, hydroxide precipitation also has some limitations. Firstly, hydroxide precipitation generates large volumes of relatively low density sludge, which can present dewatering and disposal problems. Secondly, some metal hydroxides are amphoteric, and the mixed metals create a problem using hydroxide precipitation since the ideal pH for one metal may put another metal back into solution. Thirdly, when complexing agents are in the wastewater, they will inhibit metal hydroxide precipitation.

Sulfide precipitation

Sulfide precipitation is also an effective process for the treatment of toxic heavy metals ions. One of the primary advantages of using sulfides is that the solubility's of the metal sulfide precipitates are dramatically lower than hydroxide precipitates and sulfide precipitates are not amphoteric. And hence, the sulfide precipitation process can achieve a high degree of metal removal over a broad pH range compared with hydroxide precipitation. Metal sulfide sludge also exhibit better thickening and dewatering characteristics than the corresponding metal hydroxide sludge.

However, there are potential dangers in the use of sulfide precipitation process. As we know, heavy metal ions often in acid conditions and sulfide precipitants in acidic conditions can result in the evolution of toxic H₂S fumes. It is essential that this precipitation process be performed in a neutral or basic medium. Moreover, metal sulfide precipitation tends to form colloidal precipitates that cause some separation problems in either settling or filtration processes (Fenglian, 2011).

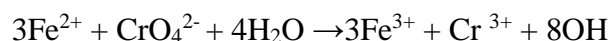
Iron manganese, copper, zinc, nickel, and cobalt result in almost complete removal by hydroxide precipitation with almost no special modification required. However, precipitation of mercury, cadmium, and lead may be slow and incomplete. When chromium is present, reduction of the solution with sodium metabisulfite, ferrous sulfate, or metallic iron prior to lime treatment is necessary.

Reduce hexavalent chromium trivalent form, chrome bearing streams are generally segregated and treated separately. Chlorination is sometimes required to break down the complexed organic metallic compounds prior to chemical precipitation. Employing hydroxide precipitation at elevated pH provides conditions where the metal hydroxides have low solubility and precipitate out upon settling, typically over time periods of 2 to 4 hours. When two or more heavy metals are found in the same waste stream, the optimum pH for precipitation each cation may be different. The question then becomes whether it is possible and practical to precipitate one or more of the metals separately at the source at one pH and treat the remaining stream(s) at another pH.

Chemical precipitation of heavy metals may be accomplished by either batch or continuous systems. For small flow rates simpler and less expensive batch systems are more feasible. Another application of the batch system is where the waste characteristics may be variable and require modification of treatment from time to time. A continuous treatment system is applicable when wastewater characteristics are uniform or when flow rates are large.

2.5.2. Chemical reduction

Reduction of hexavalent chromium can also be accomplished with electro-chemical units. The electrochemical chromium reduction process uses consumable iron electrodes and an electric current to generate ferrous ions that react with hexavalent chromium to give trivalent chromium as follows



2.5.3. Solvent extraction

Liquid-liquid extraction (also frequently referred as solvent extraction) of metals from solutions on a large scale has experienced a phenomenal growth in recent years due to the introduction of selective complexing agents. In addition to hydrometallurgical applications, solvent extraction has gained widespread usage for waste reprocessing and effluent treatment.

Solvent extraction involves an organic and an aqueous phase. The aqueous solution containing the metal or metals of interest is mixed with the appropriate organic solvent and the metal passes into the organic phase. In order to recover the extracted metal, the organic solvent is contacted with an aqueous solution whose composition is such that the metal is stripped from the organic phase and is reextracted into the stripping solution. The concentration of the metal in the strip liquor may be increased, often 10 to 100 times over that of the original feed solution. Once the metal of interest has been removed, the organic solvent is recycled either directly or after a fraction of it has been treated to remove the impurities.

2.5.4. Ion exchange

Ion-exchange processes have been widely used to remove heavy metals from wastewater due to their many advantages, such as high treatment capacity, high removal efficiency and fast kinetics. Ion-exchange resin, either synthetic or natural solid resin, has the specific ability to exchange its cations with the metals in the wastewater. Among the materials used in ion-exchange processes, synthetic resins are commonly preferred as they are effective to nearly remove the heavy metals from the solution.

The most common cation exchangers are strongly acidic resins with sulfonic acid groups ($-\text{SO}_3\text{H}$) and weakly acid resins with carboxylic acid groups ($-\text{COOH}$). Hydrogen ions in the sulfonic group or carboxylic group of the resin can serve as exchangeable ions with metal cations. As the solution containing heavy metal passes through the cations column, metal ions are exchanged for the hydrogen ions on the resin.

The uptake of heavy metal ions by ion-exchange resins is rather affected by certain variables such as pH, temperature, initial metal concentration and contact time. Ionic charge also plays an important role in ion-exchange process.

Besides synthetic resins, natural zeolites, naturally occurring silicate minerals, have been widely used to remove heavy metal from aqueous solutions due to their low cost and high abundance. Though there are many reports on the use of zeolites and montmorillonites as ion-exchange resin to remove heavy metal, they are limited at present compared with the synthetic resins.

The advantages of ion exchange processes are the very low running costs. Very little energy is required, the regenerant chemicals are cheap and if well maintained resin beds can last for many years before replacement is needed. There are, however, a number of limitations which must be

taken into account very carefully during the design stages. When these limitations itemised appear to represent a formidable list and the impression can be given that ion exchange methods might have too many short comings to be useful in practice. Certain disadvantages associated with ion exchange, such as calcium sulfate fouling, iron fouling, adsorption of organic matter, organic contamination from the resin, bacterial contamination and chlorine contamination (Fenglian, 2011).

2.5.5. Membrane process

Membranes are complex structures that contain active elements on the nanometer scale. Modern day reverse osmosis membranes are typically homogeneous polymer thin films supported by a porous support structure. Partitioning water and dissolved salts between the membrane and the bulk solution, and transport of water and salts across the membrane, depend on the chemical properties of the membrane as well as the physical structures on nano - to micro scales. The nanometer length scale is defined as between the scale of macroscopic particles suspended in water and dissolved atomic and molecular species. From a filtration perspective, this intermediate range contains, for example, colloidal solids, large organic and biological molecules, polymers and viruses. It also corresponds to the dimensions at which that were cognize distinct modes of material transport across a membrane. For a larger dimension of porous membranes, transport is described in terms of convective flow through pores. On the other hand, transport in a dense reverse osmosis membrane is typically described in terms of diffusive flow through a homogeneous material (Fenglian, 2011).

Important examples of membrane process applicable to inorganic wastewater treatment include reverse osmosis and electro dialysis. These processes involve ionic concentration by the use of selective membrane with a specific driving force. For reverse osmosis, pressure difference is employed to initiate the transport of solvent across a semipermeable membrane and electro dialysis relies on ion migration through selective permeable membranes in response to a current applied to electrodes. The application of the membrane process described is limited due to pretreatment requirements, primarily, for the removal of suspended solids. The methods are expensive and sophisticated, requiring a higher level of technical expertise to operate (Ravindra et al., 2014).

2.5.6. Electrocoagulation

Electrocoagulation consists of electrodes that act as the anode and cathode, where oxidation and reduction takes place. Many physicochemical processes such as oxidation, reduction, coagulation

and adsorption govern the electrocoagulation. Similarly to other treatment techniques, the electrocoagulation of heavy metals offers a cost-effective and easy-handling technique on an industrial scale. This technique has been used for the treatment of dyes, heavy metals, nitrates, fluorides and phenolic compounds from wastewater. Recently, various researchers have investigated electrocoagulation for the removal of heavy metals from wastewater (Ravindra et al., 2014).

2.5.7. Evaporators

In the electroplating industry, evaporators are used chiefly to concentrate and recover valuable plating chemicals. Recovery is accomplished by boiling sufficient water from the collected rinse stream to allow the concentrate to be returned to the plating bath. Many of the evaporators in use also permit the recovery of the condensed steam for recycle as rinse water. Four types of evaporators are used throughout the electroplating industry

- (I) Rising film evaporators;
- (II) Flash evaporators using waste heat;
- (III) submerged tube evaporators;
- (IV) Atmospheric evaporators.

Both capital and operational costs for evaporative recovery systems are high. Chemical and water reuse values must offset these costs for evaporative recovery to become economically feasible.

2.5.8. Adsorption

Adsorption is now recognized as an effective and economic method for heavy metal wastewater treatment. The adsorption process offers flexibility in design and operation and in many cases will produce high-quality treated effluent. In addition, because adsorption is sometimes reversible, adsorbents can be regenerated by suitable desorption process.

Activated carbon adsorbents

Activated carbon (AC) adsorbents are widely used in the removal of heavy metal contaminants. Its usefulness derives mainly from its large micropore and mesopore volumes and the resulting high surface area.

Carbon nanotubes adsorbents

Due to a large surface area, small, hollow, and layered structures, carbon nanotubes (CNTs) have already been investigated as promising adsorbents for various organic pollutants and metal ions and can be easily modified by chemical treatment to increase their adsorption capacity. CNTs have been used for the treatment of heavy metals contaminated aqueous solutions. Unlike many adsorbents, CNTs possess different features that contribute to the superior removal capacities; such as fibrous shape with high aspect ratio, large accessible external surface area, and well developed mesopores. The pores have been reported to be mostly mesopores due to a high van der Waals interaction forces along the length axis. [V.K. Gupta et al., 2011]

CNTs are divided into two types: (1) single-walled CNTs (SWCNTs) and (2) multi-walled CNTs (MWCNTs). The mechanisms by which the metal ions are sorbed onto CNTs are very complicated and appear attributable to electrostatic attraction, sorption-precipitation and chemical interaction between the metal ions and the surface functional groups of CNTs.

Low-cost adsorbents

AC has been the most used adsorbent, nevertheless it is relatively expensive. Searching for low-cost and easily available adsorbents to remove heavy metal ions have become a main research focus. To date, numerous studies on the use of low-cost adsorbents have been published. Agricultural wastes, industrial byproducts and wastes and natural substances have been studied as adsorbents for the heavy metal wastewater treatment.

Bioadsorbents

Biosorption of heavy metals from aqueous solutions is a relatively new process that has been confirmed a very promising process in the removal of heavy metal contaminants. The major advantages of biosorption are its high effectiveness in reducing the heavy metal ions and the use of inexpensive biosorbents. Biosorption processes are particularly suitable to treat dilute heavy metal wastewater. Typical biosorbents can be derived from three sources as: (1) Non-living biomass such as bark, lignin, shrimp, krill, squid, crab shell, etc.; (2) algal biomass; (3) microbial biomass, e.g. bacteria, fungi and yeast (Fenglian, 2011).

Agricultural wastes represent a potential source for producing biosorbents as they have no prominent utilization. Biosorbent production may be added value to the agrowastes and eventually reduced the agro-wastes management problems over the world. Agro-materials usually are

composed of lignin and cellulose as major constituents and may also include other polar functional groups of lignin, which includes alcohols, aldehydes, ketones, carboxylic, phenolic and ether groups. These groups have the ability to some extent to bind heavy metals by donation of an electron pair from these groups to form complexes with the metal ions in solution. [Nour T. et al., 2014]

The term ‘algae’ refers to a large and diverse assemblage of organisms that contain chlorophyll and carry out oxygenic photosynthesis. Among biosorbent materials, algae have proved to be both economic and eco-friendly, as they are abundantly available, have regeneration and metal recovery potentiality, lesser volume of chemical and/or biological sludge to be disposed off, high efficiency in dilute effluents and high surface area to volume ratio. They provide a cost effective solution for industrial wastewater management. Generally speaking about the biosorption mechanism it can be said that the presence of biosorbents’ cell wall as well as its chemistry are of greater importance. In this respect, the biosorption in algae has mainly been attributed to the cell wall properties where both electrostatic attraction and complexation can play a role. Algal biomasses contain high content of carboxyl groups from mannuronic and guluronic acids on the cell wall polysaccharides. . [Nour T. et al., 2014]

Table 2.2: Conventional treatment for heavy metal removal

Conventional treatment	Advantages	Disadvantages
Ion exchange	Metal selective High regeneration of metals	High initial capital maintenance cost
Chemical precipitation	Simple operation Non-metal selective Inexpensive cost	Large production of sludge High cost of sludge disposal
Membrane process	Less production of solid waste Low chemical consumption	High initial capital and maintenance cost Low flow rate
Electrochemical treatment	Metal selective Potential treat effluent > 2000 mg dm ⁻³	High initial capital cost

2.6. Adsorption Process

Despite conventional methods being very costly, they contribute to most of the disposal problems and are even practicable for the treatment of water contaminated with heavy metals. The problems emerge during the conventional treatments, this include high consumption of reagent and energy, low selectivity, high operational cost and generation of secondary pollutants. Apart from this, it is crucial to look for an alternative treatment to replace the conventional methods of removing heavy metal from polluted water sources.

Recently, the adsorption process has gained interest as a more promising method for the long term as it is seen to be a more effective and economic approach for heavy metal removal. Adsorption is a fundamental process today due to its flexibility in design and simple operation instead of having to perform adsorptions that are perceived as impractical by most conventional techniques. The term “adsorption” refers as a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid and becomes bound by physical and/or chemical interactions. The advantages of the adsorption process in removing or minimizing the heavy metals even at low concentration enhance the application of adsorption as one practical treatment.

The effectiveness of the adsorption process is mainly influenced by the nature of solution in which the contaminants are dispersed, the molecular size and the polarity of the contaminant and also the type of adsorbent used. Adsorption also exists due to the attractive interactions between a surface and the species being adsorbed at certain molecular level. Adsorption can be categorized into two; physical adsorption and chemisorption. Physical adsorption is a reversible phenomenon resulting from intermolecular forces of attraction between molecules of the adsorbent and the adsorbate. Meanwhile, chemisorption is a result of the chemical interaction between the solid and the adsorbed substance. It is an irreversible phenomenon and is also called activated adsorption. In terms of the temperature, high physical adsorption occurs at a temperature as close to the critical temperature of a given gas while chemical adsorption occurs at temperatures much higher than the critical temperature. Under certain conditions, both processes can occur simultaneously or alternately (Siti et al., 2013).

Some parameters should be considered during the adsorption process between adsorbent and adsorbate including the physical and chemical characteristics of adsorbent and adsorbate, the concentration of adsorbate in liquid solution, temperature, pH and also contact time. pH is the most

important factors than others, as pH controls the distribution of charge on the adsorbent surface between the adsorbate ion. However, in most sorption studies point of zero charge (pzc) should be considered to be compared with pH as it determines the limitations of the adsorbent's pH. Point of zero charge is the charge at the solid surface of adsorbent determined by the protonation and deprotonation of adsorbate ions. The surface charge density of surface depends on the specific metal ions which react directly with the adsorbent surface. For instance, when the pH value of solution is higher than pzc, the surface charge of the adsorbent will be negatively charged and vice versa. Otherwise, the increase of pH within a certain limit can increase the adsorption rate but further increase in pH can decrease the adsorption rate as certain adsorbate ions in a particular range tends to be unaffected by pH (Siti et al., 2013).

Instead of pH, the adsorbent dose is another factor which influences the adsorption process. Based on assumption, when the adsorbent doses increase, the adsorption rate also increases. However, the adsorption rate can decrease if the adsorbent dose further increases, due to the presence of more occupied active sites when the concentration gradient of the adsorbate is kept constant. Higher adsorption rate can be obtained once the temperature increases due to the increase of the surface area and the pore volume of adsorbent. Initial metal concentration can be the driving force to overcome the mass transfer between the surface of adsorbent and the solution. The initial metal concentration influences the adsorption rate based on the availability of the specific surface functional groups and the ability of the surface functional groups to bind metal ions (especially at high concentrations). Thus, any parameters influencing the adsorptive capacity of adsorbent should be considered during the adsorption process (Siti et al., 2013).

2.6.1. Adsorption Mechanism

Adsorption mechanisms are complicated as no simple theory adequately explains the adsorption of metal ions on the adsorbent surface. Previous studies have reported on the various models that describe the mechanism between the adsorbate and the adsorbent. The Langmuir model and Freundlich models are commonly used to describe the sorption isotherms while in terms of kinetics, the pseudo first order and pseudo second order kinetic models can be used to describe the sorption kinetics.

2.7. Magnetic Nanoparticles

Magnetic nanoparticles are of great interest for a broad range of applications, including catalysis, biotechnology, biomedicine, data storage, magnetic resonance imaging and environmental remediation. The use of nanoparticles offers several advantages due to their unique size and physical properties.

Magnetic nanomaterials are one of the recently highlighted branches of materials science and technology that have been utilized in the removal of pollutants from aqueous solutions. Magnetic nanoparticles (MNPs) are a new class of nano-adsorbents which not only possess quite good performance owing to high efficient specific surface area and absence of internal diffusion resistance compared to the traditional adsorbents, furthermore can be recovered rapidly by an external magnetic field. Nanoparticles possessing magnetic properties offer great advantages in that they can provide selective attachment to a functional molecule, confer magnetic properties to the target, and allow manipulation and transportation to a desired location through the control of a magnetic field produced by an electromagnet or permanent magnet.

2.7.1. Iron oxide nanoparticles

In nature, iron oxides exist in various forms, the most common being magnetite (Fe_3O_4), maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$). Fe_3O_4 exhibits the strongest magnetism of all three mentioned iron oxides because it is in a more stable form. It is also known as black oxide and contains both divalent and trivalent Fe ions. On the other hand, $\gamma\text{-Fe}_2\text{O}_3$ consists of magnetite and hematite which reflect the similarity between the magnetite and maghemite structures. Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) is reddish brown in color and it occurs in soil as a weathering product of magnetite. Hematite ($\alpha\text{-Fe}_2\text{O}_3$) is the oldest known of the iron oxides and is sometimes referred to as ferric oxide. At ambient condition, these iron oxides are extremely stable and often may occur as the end products of transformation of other iron oxides (Chuka, 2012).

Table 2.3: Physical and magnetic properties of iron oxide nanoparticles

Property	Magnetite	Maghemite	Hematite
Molecular formula	Fe ₃ O ₄	γ-Fe ₂ O ₃	α-Fe ₂ O ₃
Lattice parameter (nm)	a = 0.8396	a = 0.8347	a = 0.5034
Crystallographic system	Cubic	Cubic or tetrahedral	Hexagonal
Structural type	Inverse spinel	Defect spinel	Corundum
Type of magnetism	Ferromagnetic or superparamagnetic	Ferromagnetic or superparamagnetic	Weakly ferromagnetic

2.7.2. Magnetic behavior

Magnetic materials are usually classified based on their magnetic susceptibility (χ), which is defined as the ratio between the induced magnetization (M) and the applied magnetic field (H). The iron atom has a very strong magnetic moment as a result of four unpaired electrons in its $3d$ orbital; conversely, when crystals are formed from iron atoms, several magnetic states can arise. Magnetic iron oxide nanoparticles may be broadly divided into three main classes: paramagnetic, ferromagnetic and superparamagnetic. A material is said to be in paramagnetic state when the magnetic dipoles are oriented in random directions at normal temperature due to unpaired electrons. Some of these single-electron dipoles align to the direction of applied magnetic field, which causes them to display a low positive susceptibility (weak attraction) in a magnetic field; however, when the magnetic field is removed, they do not remain magnetized, because the ambient thermal energy is sufficient to spin the dipoles in random directions. Ferromagnetic materials, on the other hand, contain unpaired electrons, but unlike the unpaired electrons in paramagnetic materials, these are arranged into domains consisting of many ions and atoms, whilst each domain is a single magnetic dipole with dimensions less than 100 nm. The magnetic dipoles of ferromagnets are equally organized in random directions; however, when a magnetic field is applied, they spin in the direction of the applied field, and remain aligned even in the absence of field because the ambient thermal energy is insufficient to flip them back. Since the ferromagnetic materials depend on their domain structure to remain magnetized even in the absence of an applied field, their size decreases to less than the domain size (of the order of tens of nanometers) when their properties undergo a significant change. Magnetic nanoparticles of this size are said to be superparamagnetic because,

even though their dipoles align parallel to an applied magnetic field, the ambient thermal energy is sufficient to spontaneously disorganize the direction of their magnetization in the absence of applied magnetic field (Chuka, 2012).

2.7.3. Synthesis of magnetic nanoparticles

Solution Methods

Uniform nanoparticles are usually prepared via the homogeneous precipitation reaction, a process that involves separation between nucleation and the growth of nuclei. In homogeneous precipitation, a short single burst of nucleation occurs when the concentration of the constituent species reaches critical supersaturation. The nuclei so obtained are allowed to grow uniformly by diffusion of solutes from solution to surface until the final size is attained. To achieve monodispersity, these two stages must be separated, and nucleation should be avoided during the growth of nuclei.

For different applications, several chemical methods can be used to synthesize magnetic nanoparticles: co-precipitation, reverse micelles and micro-emulsion technology, sol-gel syntheses, sonochemical reactions, hydrothermal reactions, hydrolysis and thermolysis of precursors, flow injection syntheses, and electrospray synthesis. The synthesis of super paramagnetic nanoparticles is a complex process because of their colloidal nature. For metal removal applications, an adequate surface modification of the nanoparticles is a critical aspect regarding both selectivity and aqueous stability of these materials (Luciano et al., 2013).

A brief description of the methods most widely used for preparing materials with applications for metal removal is given below:

Co-precipitation: This method is probably the simplest and most efficient chemical pathway to obtain magnetic particles. Magnetite is usually prepared by an ageing stoichiometric mixture of ferrous and ferric salts in aqueous medium. The precipitation of Fe_3O_4 is expected at a pH between 8 and 14. The size and shape of the nanoparticles can be controlled by adjusting pH, ionic strength, temperature and nature of the salts. Particles with sizes ranging from 5 to 100 nm have been obtained using this method.

Some advantages of co-precipitation method are:

1. Simple and rapid preparation.
2. Easy control of particle size and composition and
3. Various possibilities to modify the particle surface state and overall homogeneity.

Reverse micelles and micro-emulsion technology: This method includes amphoteric surfactants to create water-swollen reversed micellar structures in nonpolar solvents. Surfactant molecules may spontaneously form nano droplets of different sizes, micelles (1-10 nm) or water-in-oil emulsions (10-100 nm). In these nano droplets, aqueous iron salt solutions are encapsulated by a surfactant coating that separates them from a surrounding organic solution. Thus, this system act as nano reactor for synthesizing nanoparticles as provides a confinement that limits particle nucleation and growth. The main advantage of the reverse micelle or emulsion technology is the diversity of nanoparticles that can be obtained by varying the nature and amount of surfactant and cosurfactant, the oil phase, or the reacting conditions. In addition, the size of the magnetite particle can be controlled by the temperature and the surfactant concentration.

Thermolysis of precursors: Organic solution-phase decomposition of the iron precursor at high temperatures (higher than 200⁰C) has been widely used in iron oxide nanoparticle synthesis. This method has improved significantly the control of the mean size, the size distribution and the crystallinity of magnetic iron nanoparticles. In this process, the reaction conditions, such as solvent, temperature, and time, usually have important effects on the products.

Hydrothermal reactions: Hydrothermal synthesis of Fe₃O₄ nanoparticles have been reported in the literature during the last decade. These reactions are performed in aqueous media in reactors or autoclaves where the pressure can be higher than 2000 psi and the temperature can be above 200⁰C. There are two main routes for the formation of magnetite via hydrothermal conditions: hydrolysis and oxidation or neutralization of mixed metal hydroxides. These two reactions are very similar, except that only ferrous salts are used in the first method. In this process, the reaction conditions, such as solvent, temperature, and time, usually have important effects on the products. In the hydrothermal process, the particle size is controlled mainly through the rate processes of nucleation and grain growth (Luciano et al., 2013).

Aerosol and Vapor Methods

Spray and laser pyrolysis have been shown to be excellent techniques for direct and continuous production of well-defined magnetic nanoparticles with exhaustive control on experimental conditions. Their high production rate can hold a promising future for magnetic nanoparticles useful for in vivo and in vitro applications. The main difference between spray and laser pyrolysis is in the final state of the ultrafine particles. In spray pyrolysis, the ultrafine particles are usually aggregated into larger particles, while in laser pyrolysis; the ultrafine particles are less aggregated due to the shorter reaction time.

Spray pyrolysis: Spray pyrolysis is a process in which a solid is obtained by spraying a solution into a series of reactors where the aerosol droplets undergo evaporation of solvent and solute condenses within the droplet, followed by drying and thermolysis of the precipitated particles at higher temperature. This procedure gives rise to microporous solids, which finally sinter to form dense particles.

This method represents a convenient procedure for obtaining finely dispersed particles of predictable shape, size, and variable composition. The resulting powders generally consist of spherical particles, the final diameter of which can be predetermined from that of the original droplets. The method offers certain advantages over other more commonly used techniques (such as precipitation from homogeneous solution) as it is simple, rapid, and continuous. Recently, this method has been used for the production of mesoporous microspheres and phosphorescent nanoparticles.

Most of the pyrolysis-based processes employed to produce maghemite nanoparticles start with Fe^{3+} salt and some organic compound that acts as a reducing agent. It was shown that in this procedure, Fe^{3+} is partially reduced to a mixture of Fe^{2+} and Fe^{3+} in the presence of organic compounds with the formation of magnetite, which is finally oxidized to maghemite. In absence of a reducing agent, hematite is formed instead of maghemite.

Laser pyrolysis: The method involves heating a flowing mixture of gases with a continuous wave carbon dioxide laser, which initiates and sustains a chemical reaction. Above certain pressure and laser power, a critical concentration of nuclei is reached in the reaction zone, which leads to the homogeneous nucleation of particles that are further transported to a filter by an inert gas.

2.8. Comparison of various magnetic sorbents

Currently, there is a fast growing interest in using iron oxide nanomaterials for heavy metal removal. Several studies have been conducted for aqueous hexavalent chromium removal and other heavy metals using iron oxide magnetic particles.

Table 2.4 Comparison of various sorbent for chromium removal capacity

Sorbent used	Heavy metal removed	Adsorption capacity(mg/g)	Reference
Iron oxide NPs embedded in orange peel pith	Cr(VI)	5.37	(López et al., 2011)
Maghemite NPs	Cr(VI)	17	(Hu, et al., 2006)
Magnetic iron oxide (Fe ₃ O ₄) nanoparticles from tea waste	As(V)	153.8	(Sneha et al., 2014)
Iron oxide coated sand	As(V)	0.043	(Thirunavukkarasu et al., 2003)
Iron hydroxide coated alumina	As(V)	36.34	(J. Hlavay and K. Polyak, 2005)
magnetic Fe ₃ O ₄ nanoparticles	As(III)	46.06	(L. Feng et al., 2012)

3. Material and methods

3.1. Materials

3.1.1. Chemicals

All chemicals were analytical grade and collected from chemical shops in Addis Ababa. Iron (III) chloride, ammonia solution iron sulphate distilled water are used for preparation of magnetic sorbent. For batch adsorption experiments, stock solutions Cr(VI) were prepared by dissolving analytical grade of $K_2Cr_2O_7$ in distilled water. NaOH, HCl, KOH and HNO_3 are used for desorption experiment, titration and to adjust the pH of the solutions used for optimization experiments. The sugarcane bagasse used in this study was obtained from Wonji sugar factory.

3.1.2. Equipment

Uv spectrophotometer was used for the concentration measurement. Hot plat, pH meter, digital balance, heating bath, oven and furnace were major equipments in AAiT laboratory used in the preparation sorbent.

3.2. Methods

3.2.1. Magnetic Sorbent Preparation

The sugarcane bagasse used in this study was obtained from Wonji sugar factory. The sugarcane bagasse was cut and sieved and washed with distilled water to purify from its impurities and was dried in oven for 24 hours at $50^\circ C$. The sieve used for this process was 500 micron. Magnetic sorbent was synthesized by using co- precipitation process.

Using $FeCl_3 \cdot 6H_2O$ and iron sulphate ($FeSO_4 \cdot 7H_2O$) in presence of ammonia

Five gram of bagasse powder was added to a solution of 2.78g $FeSO_4 \cdot 7H_2O$ and 5.4g $FeCl_3 \cdot 6H_2O$ in 100ml of distilled water. To this 50 ml of ammonia solution was added drop wise and the reaction held for 2 hours at $70^\circ C$. Then the process was stopped and the solution was placed on a magnet. At this stage, the solution was separated into two phases, 1st is the clear water on top, and 2nd is the precipitate at bottom, under the effect of magnetic field. Therefore, the black precipitate was washed several times by distilled water to remove the ammonia added and dry for 24 hours at $60^\circ C$. Finally, the brown powder from the oven calined for 2 hours at $400^\circ C$. Mass of magnetic sorbent finally found was 2.7g. The powder material produced in these two methods was called magnetic biosorbent powder.

3.2.2. Characterization

Surface area

Microspore volume and surface area are two important properties of adsorbents. Value of surface area is one of the factors that govern the intensity of physical forces acting between adsorbate and adsorbent. The intensity of these forces, in turn, affects the amount of adsorbate to be adsorbed to the adsorption sites.

Point zero charge determination

The knowledge of pzc allows one to hypothesize on the ionization of functional groups and their interaction with metal species in solution; at solution pHs higher than pzc, sorbent surface is negatively charged and could interact with metal positive species while at pHs lower than pzc, solid surface is positively charged and could interact with negative species.

Different methods have been used for point of zero charge determination like potentiometric mass titration, mass titration and immersion technique.

Potentiometric mass titration (PMT)

Three different masses of sorbent material (15g/L, 25g/L and 35g/L) were added in to 20ml of 0.03 M HNO₃ solution. The mixture was agitated for 6 h at 250 rpm until the pH was kept constant. Vigorous agitation was needed to ensure homogenization of the suspension.

A small volume of 1 M KOH solution was added to the suspensions before titrations to deprotonate surface sites, and then, suspensions were titrated by adding 0.05 mL of HNO₃ (0.1 M) under continuous agitation. After each addition, the pH value was recorded as a function of the added volume of titration solution. The same treatment and procedure was used for blank solution (0.03 M KNO₃).

Equilibrium pH values were plotted as a function of acid volume added to obtain the potentiometric curves. Point of zero charge was identified as the intersection point of the potentiometric curves with the blank.

3.2.3. Preparation of Cr (VI) Solutions

The stock solutions of Cr(VI) of concentration 1 g/L was prepared by dissolving 2.8 g of analytical grade of K₂Cr₂O₇ in 1 L of distilled water. The stock solution was further diluted with distilled

water to desired concentration for obtaining the standard solutions for absorbance measurement. The initial pH of the test solutions was adjusted to the desired value by using dilute solutions of HCl and NaOH. The required lower concentrations were prepared by dilution of the stock solution. All precautions were taken to minimize the loss due to evaporation during the preparation of solutions and subsequent measurements. The stock solutions were prepared fresh for each experiment as the concentration of the stock solution may change on long standing.

Preparation of Diphenylcarbazide (DPC) Solution

Diphenylcarbazide (DPC) solution was prepared by dissolving 250mg of DPC in 50ml of acetone in a 100ml volumetric flask.

Analysis of chromium

0.2mL of sulfuric acid was added to 4mL of standard sample containing known concentration of chromium, pH was adjusted using 0.1M hydrochloric acid and sodium hydroxide. The solution was mixed well and then diluted in a volumetric flask using distilled water. Further 0.2 mL of DPC solution was added and mixed well. After full colour development for 10min, 4mL of this solution was used in an absorption cell and the concentrations were measured spectrometrically at 540nm in UV spectrophotometer (Lambda 950 UV/Vis spectrometer). The calibration curve is prepared by measuring the absorbance of different known concentrations of chromium solutions and plotting a graph between concentrations versus absorbance.

3.2.4. Batch Biosorption Experiments

All batch experiments were carried out on a constant temperature $25 \pm 2^{\circ}\text{C}$. The designed solution pH was adjusted using 0.1 M NaOH or HCl. A known amount of adsorbent was added to samples and was agitated by a shaker at 1500 rpm agitation speed, allowing sufficient time for adsorption equilibrium. The extent of heavy metal removal was investigated separately by changing adsorption dose, contact time, initial chromium concentration and changing pH of the solution. After adsorption, the magnetic biosorbent were separated from the solutions using a permanent magnet, and the initial and final metal concentrations were determined. The equilibrium adsorption capacity (q_e) was calculated according to the following equation,

$$q_e = \frac{(C_o - C_e)}{M}V \quad (3.1)$$

Where q_e is the equilibrium adsorption capacity (mg/g), C_0 and C_e are the initial and equilibrium liquid phase solute concentration (mg/L), respectively; V is the liquid phase volume (L) and M is the amount of adsorbent (g).

The removal percentage was determined by

$$\text{Sorption percentage} = \frac{C_0 - C}{C_0} \times 100 \quad (3.2)$$

Where, C_0 and C represent the initial concentration and final concentration (mg/l) respectively.

The chromium mass adsorbed per gram of magnetic biosorbent was calculated by difference between the Cr^{6+} concentration of the solution before equilibrium and in the equilibrium, multiplied.

3.2.5. Desorption experiments

Desorption studies are important since they contribute to elucidate the nature of adsorption process. Additionally, it is necessary to examine the possibility to recover metal ions and to regenerate and recycle the adsorbent. The experiments for desorption efficiency were carried out with dilute HNO_3 solutions. The desorption efficiency (DE) was determined using the following Eq. (3.4):

$$DE = \frac{C \times V}{q \times m} \times 100 \quad (3.4)$$

Where, C (mg/L) is the concentration of chromium ions in the desorption solution, V (L) is the volume of the desorption solution, q (mg/g) is the amount of chromium ions adsorbed on the adsorbents before desorption experiment, and m (g) is the amount of the adsorbent used in the desorption experiments.

3.3. Design of Experiments using Central Composite Design (CCD)

Four variables were chosen for the five levels four factor composite design to determine optimal values of these factors. The parameters initial metal ion concentration, pH, contact time and sorbent dosage were chosen as independent variables and the sorption percentage were output response. Each independent variable had 5 levels which were -2, -1, 0, +1 and +2. A 2^4 factorial central composite design was designed with eight star points, and six replicates at the center points which gives 30 runs. The variables were coded according to the following equation,

$$X_i = \frac{x_i - x_o}{\Delta x}, i = 1, 2, 3, \dots, k \quad (3.5)$$

Where X_i is the dimensionless value of an independent variable, x_i is the real value of an independent variable, x_o is the value of X_i at the centre point and Δx is the step change.

Therefore, a total of 30 different combinations were chosen in random order according to a CCD configuration for four factors. Table 3.1 shows the levels of chosen variables used in the experiment for the removal of chromium.

The analysis focused on how the removal efficiency is influenced by independent variables, metal concentration (mg/l) (x_1), pH (x_2), contact time (min) (x_3) and sorbent dosage (mg) (x_4). The dependent output variables are maximum removal efficiency (Y).

3.3.1. Response surface methodology

Response surface methodology is an empirical statistical technique employed for multiple regression analysis by using quantitative data obtained from properly designed experiments to solve multivariate equations simultaneously.

There are two main types of response surface designs:

Central Composite designs: Central Composite designs can fit a full quadratic model. They are often used when the design plan calls for sequential experimentation because these designs can include information from a correctly planned factorial experiment.

Box-Behnken designs: Box-Behnken designs usually have fewer design points than central composite designs, thus, they are less expensive to run with the same number of factors. They can efficiently estimate the first- and second-order coefficients; however, they can't include runs from a factorial experiment. Box-Behnken designs always have 3 levels per factor, unlike central composite designs which can have up to 5. Also, unlike central composite designs, Box-Behnken designs never include runs where all factors are at their extreme setting, such as all of the low settings.

The experiments with different pH, metal ion concentration, contact time and adsorbent dosage were employed simultaneously covering the spectrum of variables for the removal of chromium in CCD.

Table 3.1: Central composite design for sorption of chromium

Independent variable	Range and Level				
	-2	-1	0	+1	+2
x_1 (mg/l)	10	20	30	40	50
x_2	3	4	5	6	7
x_3 (min)	60	90	120	150	180
x_4 (mg)	200	500	800	1100	1400

The regression analysis was performed to estimate the response functions as a second order polynomial as shown in equation (3.6)

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{44} X_4^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 + \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 + \beta_{34} X_3 X_4 \quad (3.6)$$

X_1, X_2, X_3, X_4 are linear effects, $X_1^2, X_2^2, X_3^2, X_4^2$ are squared effects, $X_1 X_2, X_1 X_3, X_1 X_4, X_2 X_3, X_2 X_4, X_3 X_4$ are interaction effects and Y is the predicted response. β_0 is constant coefficient, $\beta_1, \beta_2, \beta_3, \beta_4$ are linear coefficients, $\beta_{11}, \beta_{22}, \beta_{33}, \beta_{44}$ are squared coefficients, and $\beta_{12}, \beta_{13}, \beta_{14}, \beta_{23}, \beta_{24}, \beta_{34}$ are interactive coefficients, respectively.

Design expert 9, was used for regression analysis of the data obtained and to estimate the coefficient of the regression equation. The equations were validated by the statistical test called ANOVA. The significance of each term in the equation is to estimate the goodness of fit in each case. Response surface were drawn to determine the individual, square and interactive effects of test variable on percentage removal of chromium.

3.3.2. Optimization of the sorption conditions

The parameters initial chromium ion concentration, pH, contact time and sorbent dosage were chosen as independent variables and the removal efficiency of chromium is output response. The analysis focused on how the removal efficiency is influenced by independent variables, metal concentration (X_1), pH (X_2), time of contact (X_3) and sorbent dosage (X_4). The dependent output variable is maximum removal efficiency (Y). The second degree polynomial equation is solved and the optimum values for the variables are obtained using design expert 9.

3.4. Sorption kinetic

Kinetic studies are significant for any kind of sorption processes. Adsorption kinetics not only describes the adsorption mechanism of metals on adsorbents but also describe the metal adsorption rate which controls the contact time of metals at the solid-liquid interface. The adsorption mechanism depends on the physical and chemical characteristics of adsorbent and adsorbate, pH of medium, temperature, contact time and aids and mass transport process.

Adsorption kinetics is performed to evaluate both the equilibrium time and the rate of Cr(VI) adsorption. The equilibrium time is one of the important parameters for subsequent adsorption isotherm studies. To evaluate the rate of Cr(VI) adsorption on adsorbents, the experimental data were analyzed using pseudo first and pseudo second order kinetic models. The pseudo second-order model has been commonly used to describe chemical adsorption process of pollutants from aqueous solutions in recent years. Linear regressions are frequently used to determine the best-fitting kinetic models, and the method of least squares is used for finding parameters of the kinetic model.

3.5. Sorption Isotherm Models

Sorption isotherm is an empirical relationship used to predict how much solute can be adsorbed by the adsorbent. Adsorption isotherm is defined as a graphical representation showing the relationship between the amount adsorbed by a unit weight of adsorbent and the amount of adsorbate remaining in a test medium at equilibrium, and it shows the distribution of adsorbable solute between the liquid and solid phases at various equilibriums.

The purpose of the adsorption isotherms is to relate the adsorbate concentration in the bulk and the adsorbed amount at the interface or to describe distribution of metal ions between the liquid phase and the solid phase. The isotherm results were analyzed using the Langmuir, Freundlich and Temkin isotherms.

Langmuir isotherm model

The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the sorbed molecules or that the uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The Langmuir adsorption

isotherm has been successfully used to explain the adsorption Cr(VI) from solutions. In the Langmuir model, adsorption increases with increasing solute concentration at low concentration values and approaches a constant value at high concentrations because there are a limited number of adsorption sites in the biosorbent. The expression of the Langmuir model is given by Eq. (3.7)

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad (3.7)$$

Where, q_e (mg/g) and C_e (mg/L) are the amount of adsorbed Chromium per unit mass of sorbent and unadsorbed chromium concentration in solution at equilibrium, respectively. Q_0 is the maximum amount of chromium per unit mass of sorbent to form a complete monolayer on the surface bound at high C_e , and b is a constant related to the affinity of the binding sites (L/mg).

Freundlich isotherm model

The model is based on the assumption that ions are accumulated infinitely on the sorbent surface. The Freundlich isotherm equation may also be given as:

$$q_e = K C_e^{1/n} \quad (3.8)$$

Where, $1/n$ (mg/L) is adsorption intensity and K constant related to the adsorption energy (mol^2/KJ^2). However, the Freundlich model assumes that the uptake of metal ions occurs on a heterogeneous surface by monolayer adsorption. In order to find the most appropriate model for the chromium adsorption, the data were fitted to each isotherm model.

4. Result and discussion

4.1. Characterization

4.1.1. Specific surface area

The specific surface area is increased as the particle size becomes small. The specific surface area is also increased if the particle has pores. The specific surface area is important for the industrial process and chemical reaction. Even with the same material that has the same weight and volume, the surface activity and adsorption volume are changed according to the specific surface area. So it is important to measure the specific surface area to evaluate the activity and adsorption capacity of materials. (e.g. catalysis and adsorbent)

Saer's method was used for the determination of the surface area.

$$S = 32V - 25 \quad (4.1)$$

Where V is the volume of 0.1M NaOH solution in mL required to achieve pH of 9 from pH 4 with 0.5g of sorbent and 10g of NaCl in 50mL of distilled water.

The amount of NaOH used for titration from pH 4 to 9 was 9.6ml which gives a specific surface area of 282.2 m²/g.

Table 4.1 Some physico-chemical parameters of the magnetic sorbent

Parameters	Characteristics
Color	Reddish brown
pH	6.8 -7.1
Surface area(m ² /g)	282.2

4.1.2. Point of zero charge determination

It is well known that pH has a great importance in cation sorption because it influences chemical speciation of the metal in solution and also on the ionization of chemically active sites on the sorbent. Thus, the net charge of sorbent surface might play a crucial role in sorption processes, and the characterization of protonation-deprotonation behavior of sorbent materials in aqueous media could be useful to explain sorption mechanism.

To obtain PZC using PMT method the sorbent was titrated as described earlier. The experimental curves corresponding to PMT technique were obtained for different mass of sorbent and are presented in Fig. 4.1.

The PZC values are estimated from the curve interceptions (from the plotted curves, the pzc is clearly identified as the pH where blank and titrations curves of different masses converge) and summarized in Table 4.2.

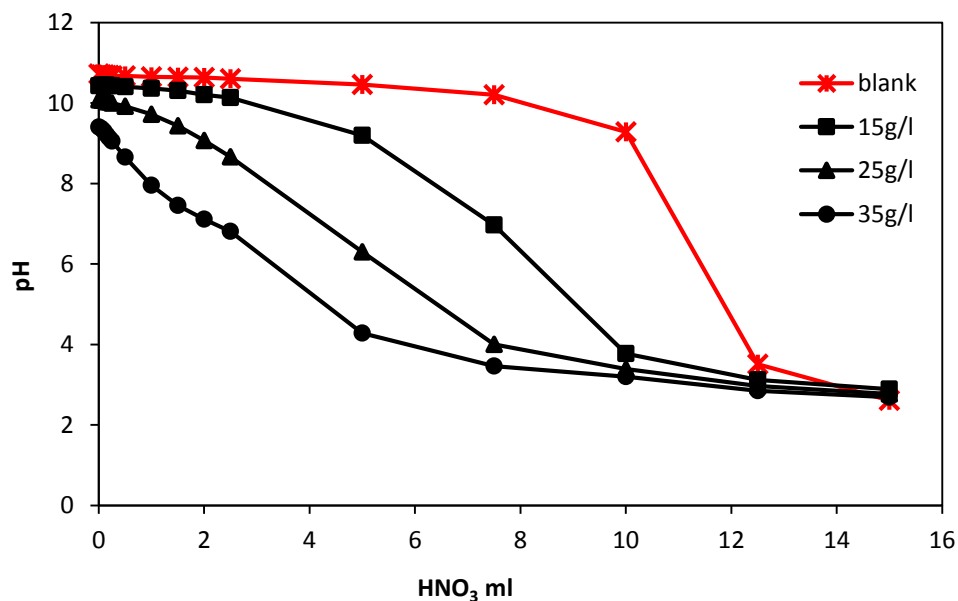


Figure 4.1 Potentiometric mass titration curve

Table 4.2 Experimental *pzc* values for triplicate experiments

Mass of sorbent(g/L)	PZC
15	3.00
25	2.80
35	2.70

The results shown in Table 4.2 are self-consistent. They give an overall average of 2.83 which is an acceptable standard deviation for such a varied range. This relatively low *pzc* value signals the predominance of positively-charged surface groups. With this, information users desiring positive

or negative surface charges to remove specific pollutants shall be able to adjust their pH values accordingly.

The point zero charge determines the surface charge of the sorbent at a given pH and its knowledge informs about the possible electrostatic interactions between sorbent and chemical species of metal. As previously mentioned at solution pHs higher than pzc, sorbent surface is negatively charged and could interact with metal positive species. From this we can observe that the prepared magnetic sorbent can interact with metal positive ions like Cr^{6+} .

4.2. Central Composite Design (CCD) Analysis

The results of experiments performed according to the CCD are given in Table 4.3. The results of CCD experiments with different combinations for initial chromium ion concentration, pH, contact time and sorbent dosage are tabulated along with experimental and predicted responses. We can see from the table maximum % removal (92.28%) occurred in Run No. 30.

4.2.1. Response surface methodology

Regression analysis was done to fit the response function as per the equation. The predicted responses, Y for the % removal, equation (4.2) was obtained as a function of pH, metal ion concentration, contact time and adsorbent dosage as follows:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{44} X_4^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 + \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 + \beta_{34} X_3 X_4 \quad (4.2)$$

And the results are reported as:

$$Y = 81.47 - 1.68X_1 + 0.53X_2 + 0.73X_3 + 3.35X_4 + 0.31X_1^2 + 0.30X_2^2 + 0.32X_3^2 + 0.59X_4^2 - 0.43X_1X_2 + 0.068X_2X_3 - 2.26X_2X_4 + 1.9X_1X_3 - 1.22X_1X_4 - 0.19X_3X_4 \quad (4.3)$$

Where Y is the response value (the adsorption percentage) and X_1 , X_2 , X_3 , X_4 are the coded levels of the independent input variables, i.e. the initial Cr^{6+} ion concentration, pH, contact time and magnetic sorbent dosage respectively. The above equation explain the effect of individual variables (linear and squared) and interactive effects on chromium adsorption onto the magnetic sorbent.

Multiple regression coefficient R^2 is calculated from the second degree polynomial equation is $R^2 = 0.996$ indicates that the predicted values are closer to experimental data as shown in Table 4.3. R^2 value always lie between 0 and 1. The closer the R^2 value to 1, the stronger the model and better it

predicts the response. And R^2 value of 0.996 indicates that more than 99.6% of experimental data was compatible with the model and only 0.4% of the total variance could not be explained by the model. The adjusted correlation coefficient (adjusted R^2) is a measure of goodness of a fit, but it corrects the R^2 for the sample size and the number of terms in the model by using the degrees of freedom on its computations. If there are many terms in the model and the sample size is not very large, the adjusted R^2 may be noticeably smaller than the R^2 value. Here, the adjusted R^2 values (0.9923) are also very high to advocate for a high significance of the models, which ensures a satisfactory adjustment to the polynomial model to the experimental data. As it is shown on the equation above the initial chromium ion concentration(X_1) and the amount of sorbent added to the solution(X_2) had strong effect on the yield (removal percentage).

Table 4.3 Central Composite Design Matrix of design specifications along with observed response for chromium removal.

Run	pH	Conc.(mg/l)	Time(min)	Dosage(mg)	Adsorption %	
	X_1	X_2	X_3	X_4	Actual	Predicted
1	6	40	90	500	81.18	81.47
2	4	20	150	1100	81.49	81.47
3	4	20	90	500	84.01	83.78
4	5	30	120	200	84.19	84.20
5	6	40	150	1100	89.59	89.10
6	5	50	120	800	87.64	87.97
7	5	30	120	800	77.45	77.12
8	6	20	90	1100	82.17	82.42
9	5	30	60	800	78.06	78.66
10	4	40	150	500	81.43	81.47
11	5	30	120	1400	81.37	81.60
12	5	30	120	800	78.96	78.78
13	4	40	90	500	86.67	86.64
14	4	20	150	500	81.37	81.47
15	5	30	120	800	85.81	86.08
16	4	40	90	1100	81.83	81.47
17	6	20	90	500	83.88	83.73
18	6	20	150	500	79.56	79.38
19	6	40	150	500	84.76	84.24

20	4	20	90	1100	81.22	81.29
21	5	30	180	800	84.29	84.43
22	4	40	150	1100	77.57	77.91
23	5	10	120	800	89.05	89.23
24	5	30	120	800	79.64	79.57
25	6	40	90	1100	90.10	90.51
26	7	30	120	800	83.39	83.24
27	5	30	120	800	81.53	81.47
28	6	20	150	1100	75.83	75.82
29	3	30	120	800	74.23	74.07
30	5	30	120	800	92.28	91.95

4.2.2. Analysis of variance (ANOVA)

Analysis of variance (ANOVA) is required to test the significance and the adequacy of the model. The results of multiple linear regressions conducted for the second order response surface model by ANOVA are given in Table 4.4. The significant of the coefficient term is determined by the value of F and p, and the larger the value of F and the smaller the value of p, the more significant is the model.

Table 4.4 analysis of variance (ANOVA) results for percentage removal

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	535.66	14	38.26	266.34	< 0.0001
x_1 -Cr(IV) concentration	67.34	1	67.34	468.71	< 0.0001
x_2 -pH	6.85	1	6.85	47.67	< 0.0001
x_3 -contact time	12.73	1	12.73	88.62	< 0.0001
x_4 -sorbent dosage	268.94	1	268.94	1872.06	< 0.0001
x_1x_2	3.03	1	3.03	21.07	0.0004
x_2x_3	0.073	1	0.073	0.51	0.4872
x_2x_4	81.99	1	81.99	570.75	< 0.0001
x_1x_3	57.53	1	57.53	400.48	< 0.0001
x_1x_4	23.72	1	23.72	165.09	< 0.0001

x_3x_4	0.59	1	0.59	4.13	0.0603
x_2^2	2.44	1	2.44	17.02	0.0009
x_1^2	2.70	1	2.70	18.77	0.0006
x_3^2	2.78	1	2.78	19.37	0.0005
x_4^2	9.42	1	9.42	65.57	< 0.0001
Residual	2.15	15	0.14		
Lack of Fit	1.93	10	0.19	4.20	0.0634
Pure Error	0.23	5	0.046		
Cor Total	537.82	29			

The higher the F-value and lower the probability P value (< 0.0001) demonstrates significance for the regression model. The p is lower than 0.05, suggesting the model is considered to be statistically significant. The p-values denote the significance of the coefficients. They are important in understanding the pattern of mutual interactions between the variables. Table 4.4 shows the ANOVA results and p-values were ($p < 0.0001$) for individual variables X_1 , X_2 , X_3 , X_4 and interaction X_2X_4 , X_1X_3 , X_2X_4 , and X_4^2 . Where the p-values of X_1X_2 , X_1^2 , X_2^2 , and X_3^2 are 0.0004, 0.0009, 0.0006 and 0.0005 respectively so all the model terms are significant except X_2X_3 the p-value is 0.4872. A lower value of coefficient of variation, $CV = 0.46\%$ indicates the precision with which the experiments were conducted. The smaller, predicted residual sum of squares (PRESS) statistic, better the model fits the data points. The model has high R^2 , significant P-value and an insignificant lack-of-fit indicating its excellency in predicting the solution to our problem. This also shows the best degree of fitness for the model equations.

In addition, the adequacy of the models was also evaluated by the residuals (difference between the observed and the predicted response values). Residuals are thought as elements of variation unexplained by the fitted model and then it is expected that they occur according to a normal distribution. Normal probability plots are a suitable graphical method for judging the normality of the residuals. The observed residuals were plotted against the expected values, given by a normal distribution. The approximate straight lines obtained indicate that residuals are normally distributed. Based on these plots, the residuals appeared to be randomly scattered.

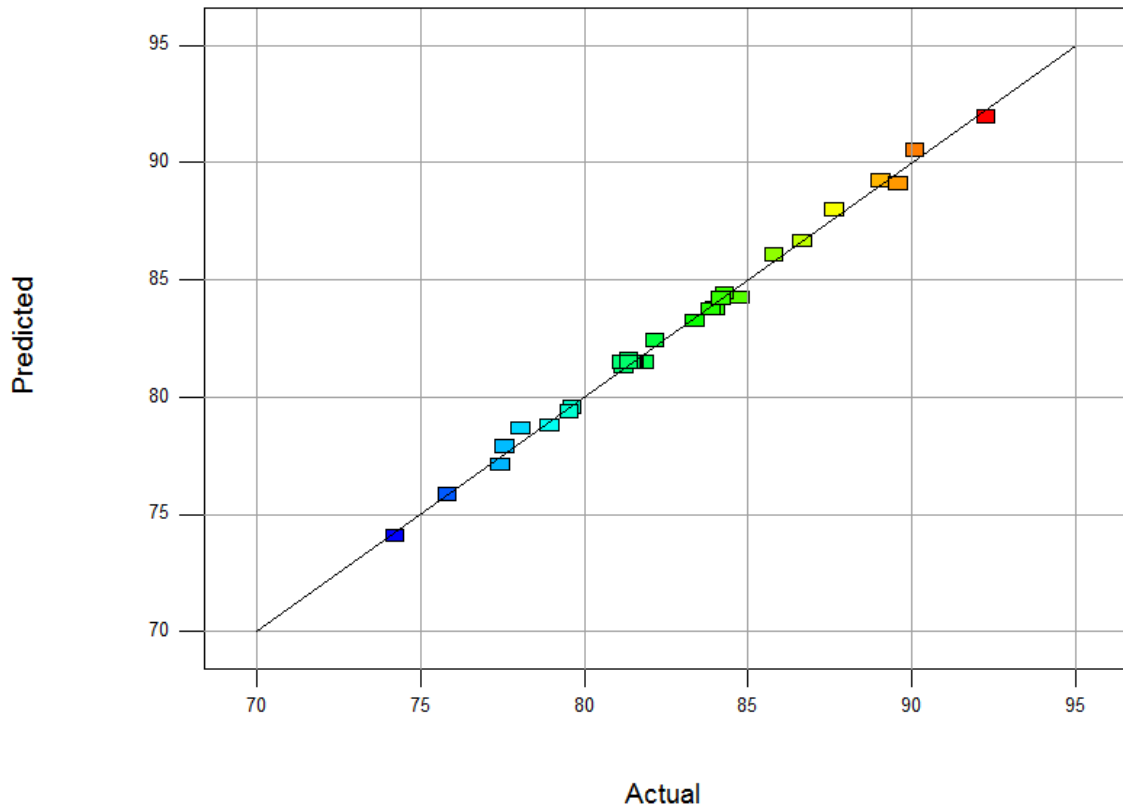


Figure 4.2 Predicted vs. actual plot of response values

4.2.3. Optimization of Response

The optimization of process variables are done to get maximum % removal using response optimizer Design expert 9. In this regard second degree polynomial equation (Eq 4.3) were used to get the optimum values for the variables. Maximum removal of 91.95% chromium was achieved with the magnetic sorbent at initial concentration 20 mg/L, with least sorbent mass of 1100mg, contact time of 90 minutes and at pH 4 and the maximum experimental % removal at this values of variables was 92.28, which shows good agreement between the predicted and experimental values of the maximum removal percentage.

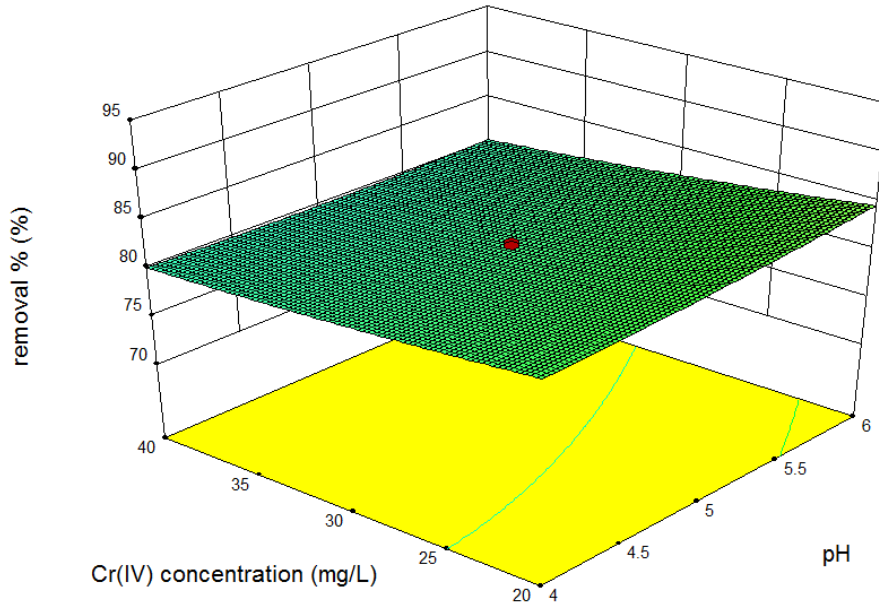
4.2.4. Response surfaces and contour plots

The three dimensional response surface and their corresponding contour plots for removal % against any two independent variables by keeping the other independent variables at zero levels are presented in figures below. These plots show the type of interaction between the tested variables, thereby permitting optimum conditions. The linear contour plot indicates the triviality of

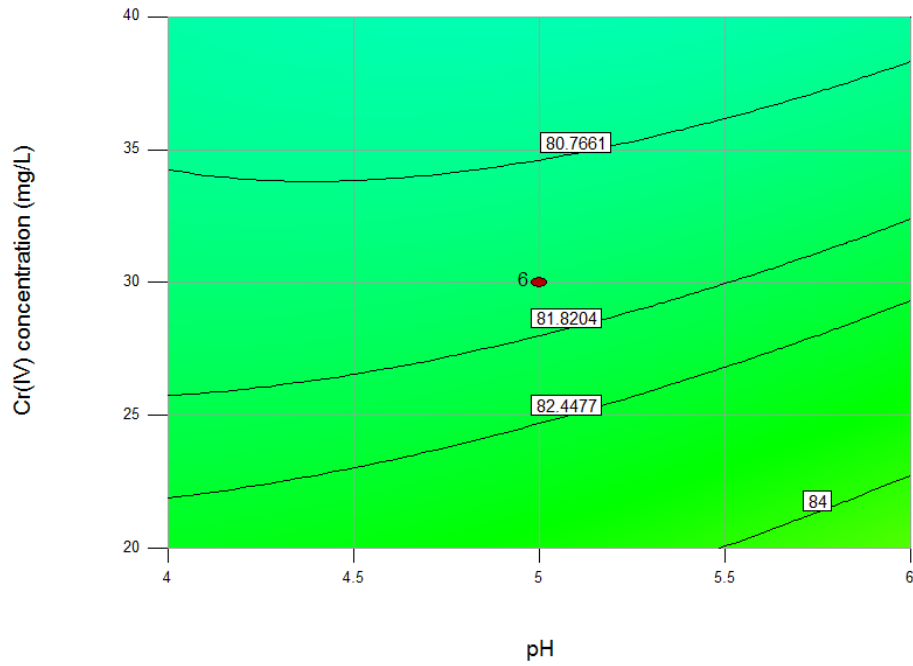
the interaction terms on the response, whereas contour plots of adequate curvature specify the importance and magnitude of interaction terms. A circular contour plot embodies a negligible interaction between the independent variables, while perfect interactions were exemplified by the elliptical contours. The maximum predicted value of the response under the optimum experimental condition is represented by the surface confined in the smallest ellipse in the contour diagram [17].

Interactions between the pH and initial Cr^{6+} concentration are shown in Figs. 4.3 (a1) and (a2), for the sorption %. The result demonstrated the maximum point on the response surface. The sorption % was 84.286 when the initial Cr^{6+} concentration was 20 mg/L and pH 6. The sorption percentages were seen to decrease for increasing concentrations of Cr^{6+} . Maximum removal % of 82.931% was seen for a solution of concentration 40 mg/L and at 150 min. when the sorbent dosage increase from 500 to 1100mg sorption percentage varied from 76.5 to 86.7% and maximum removal percentage is at pH 4. This is expected due to the fact that the higher dosage of magnetic sorbent in the solution resulted in greater availability of exchangeable sites for Cr^{6+} ions. Figure (c1 and c2) show the interaction of sorbent dosage and pH. Fig. 2(d1 and d2) represents the interaction between concentration of Cr^{6+} and time. Figures (e1) and (e2) show the three-dimensional response surface and contour plot of sorbent dosage and Cr^{6+} concentration effect on removal %. Maximum removal percentage of 87.13 was achieved for 20 mg/L of Cr^{6+} concentration and for a dosage of 1100 mg and percentage removal increase with increase in magnetic sorbent dosage and decrease in chromium ion concentration.

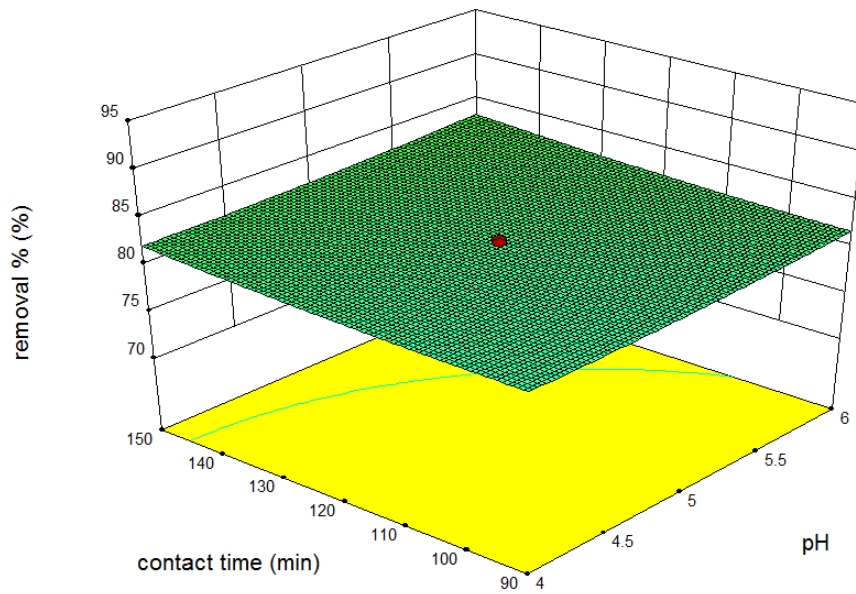
a1



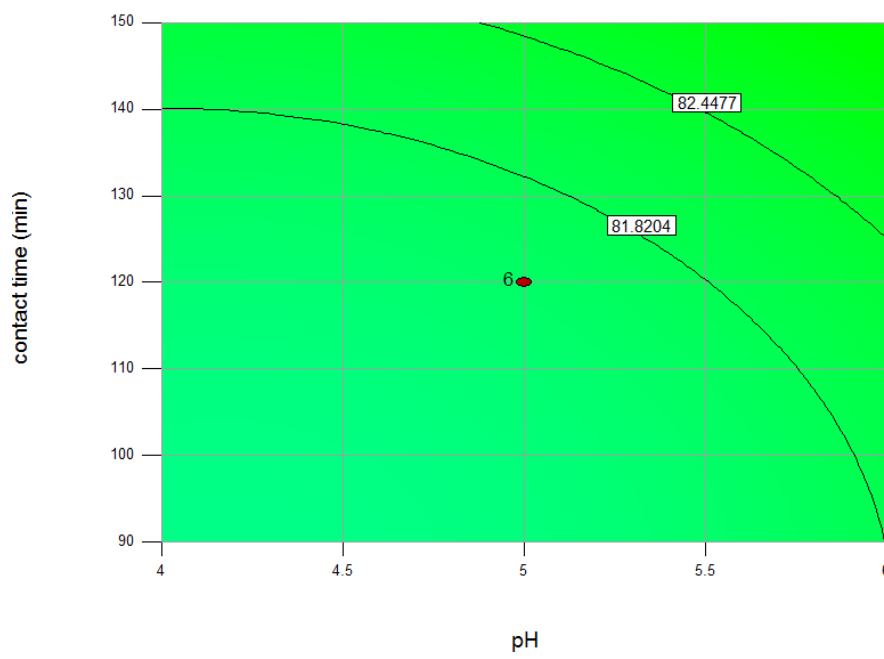
a2



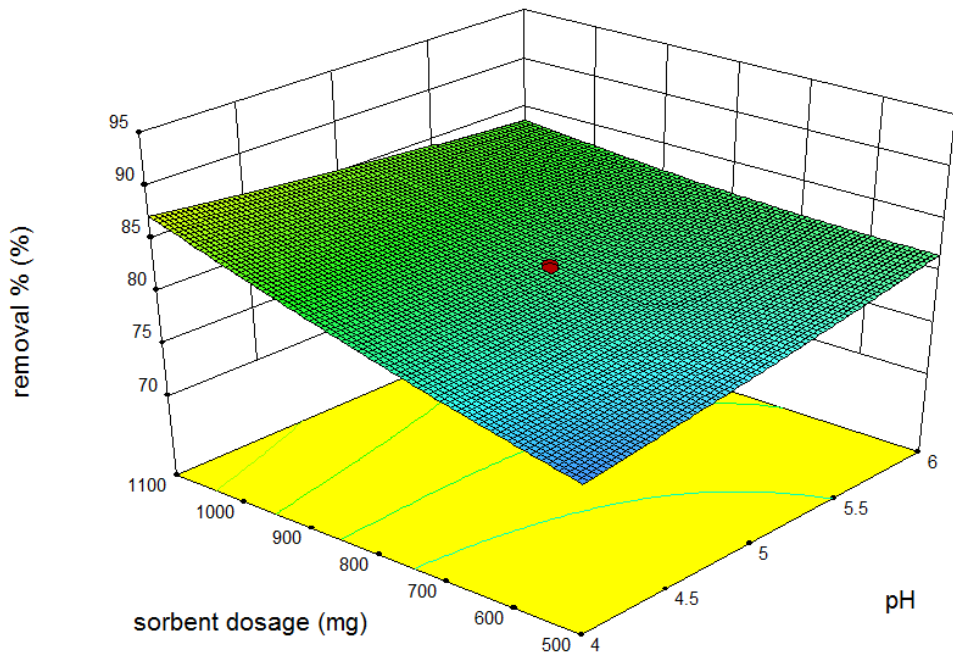
b1



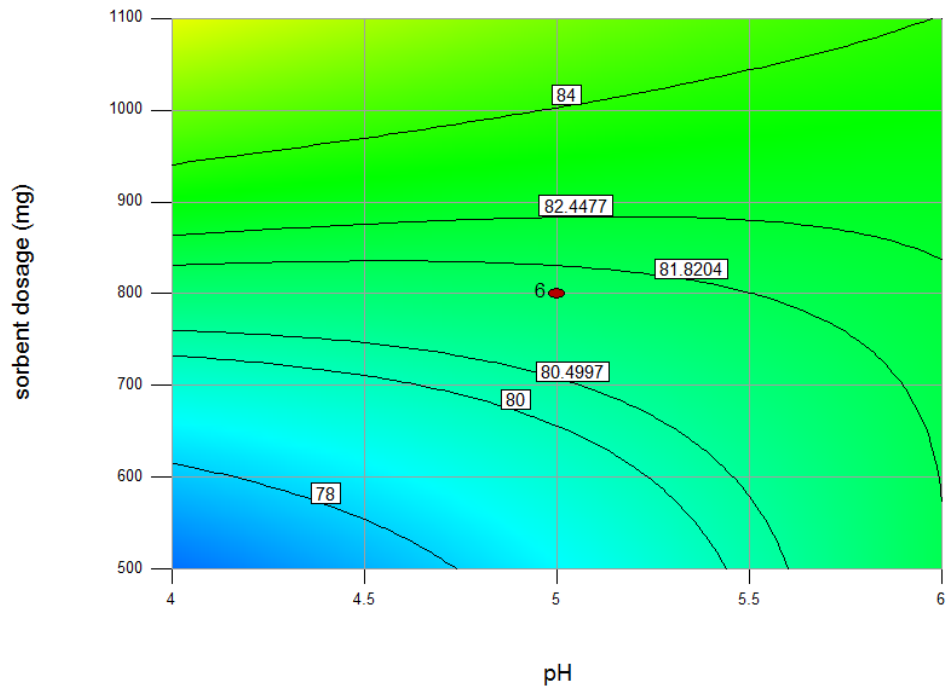
b2



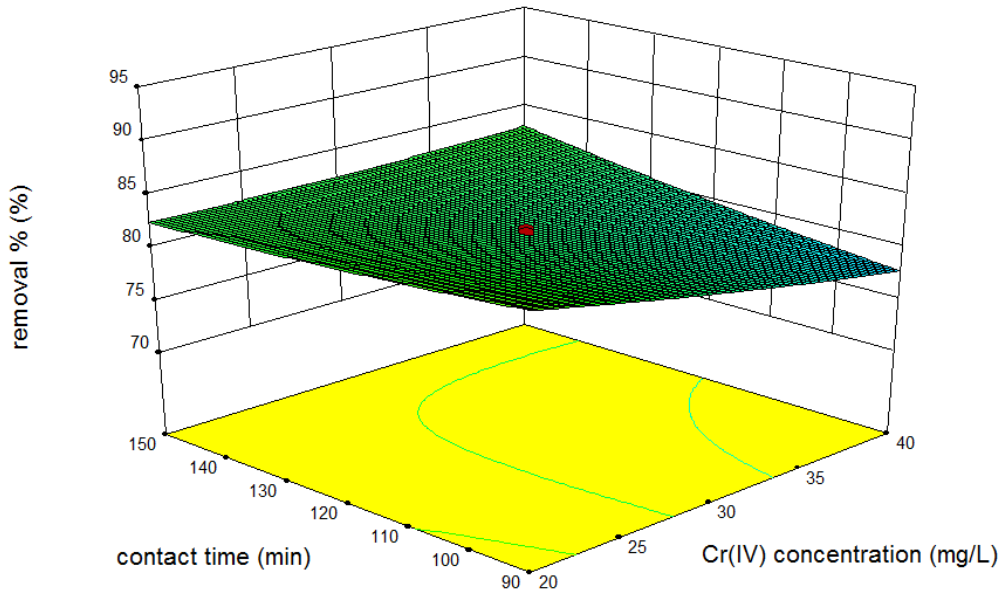
c1



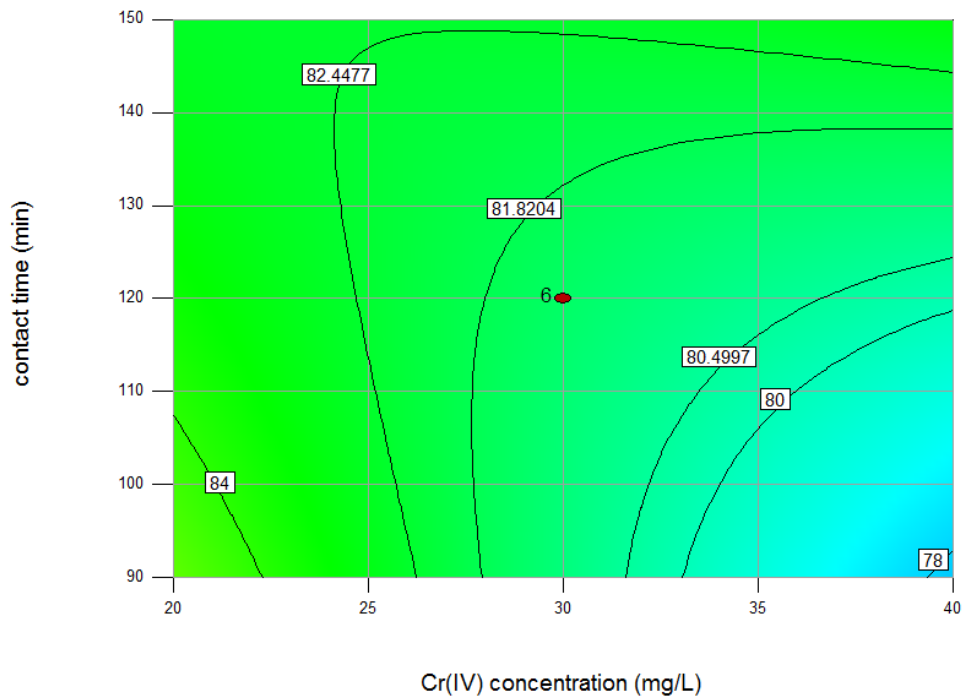
c2



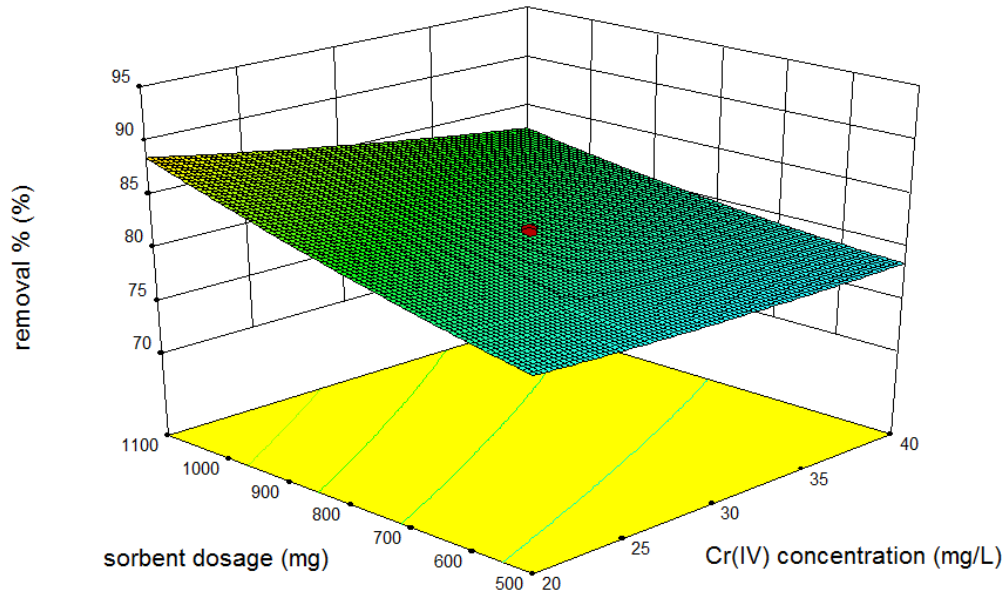
d1



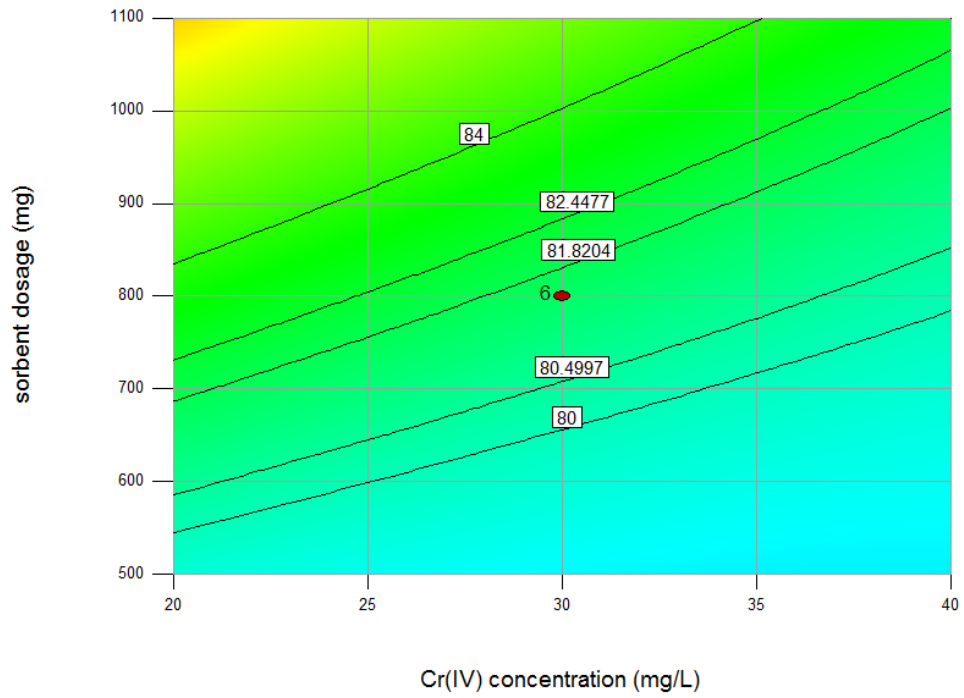
d2



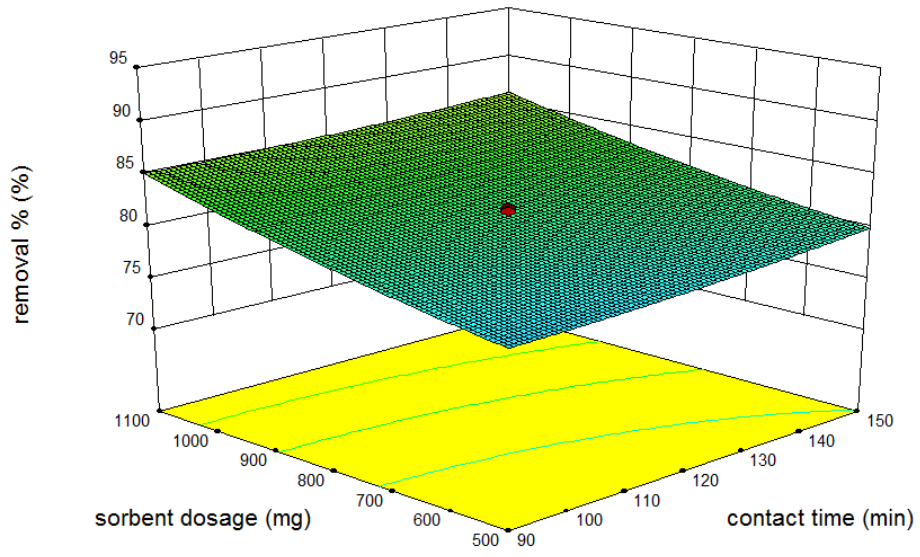
e1



e2



f1



f2

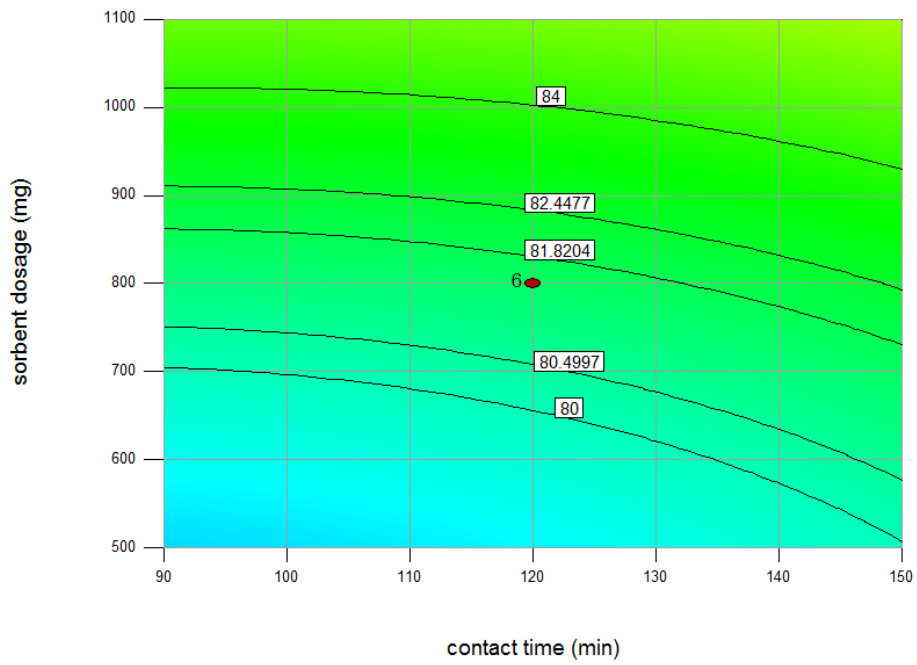


Figure 4.3 Response surface plots

4.3. Factors Affecting the Adsorption

Various factors influence the adsorption capacity of potential adsorbents during the adsorption process. Efficiency of any adsorbent is strongly influenced by the physicochemical characteristics of the solutions such as pH, initial concentration, contact time and adsorbent dosage.

4.3.1. Effect of pH on adsorption

The pH of a solution is a significant parameter in the adsorption process. It affects both the dissociation degree of the functional groups from the adsorbent surface and the solubility of the metal ions. Thus, experiments were performed in order to investigate the effect of initial pH of solution to be treated. During this study, results show that the removal of metal ions was strongly dependent on the pH of the solution. Chromium removal by magnetic sorbent increased varying pH from 3 to 6 and start to decrease.

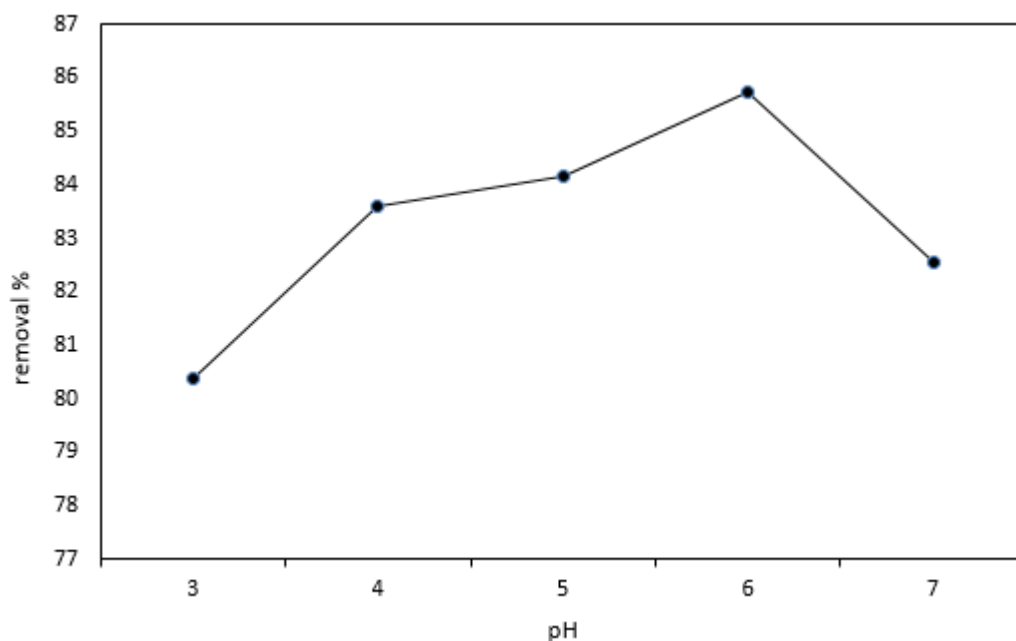


Figure 4.4 Effect of pH on removal %

4.3.2. Effect of initial concentration

Initial concentration of metal ions can alter the metal removal efficiency through a combination of factors such as the availability of specific surface functional groups and the ability of surface functional groups to bind metal ions. Initial concentration of solution can provide an important driving force to overcome the mass transfer resistance of metal between the aqueous and solid phases.

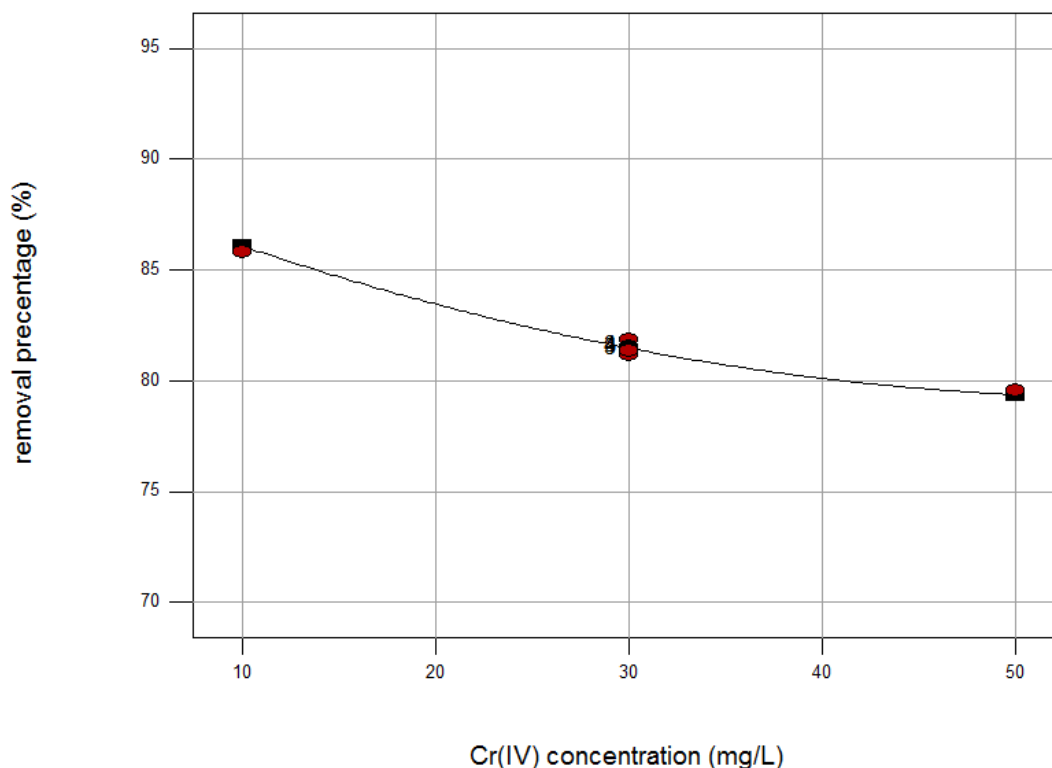


Figure 4.5 Influence of initial concentration of chromium ions on removal (%).

The initial concentration of chromium ions varied from 10 mg/L to 50 mg/L, by keeping other parameters at the optimum values (pH=5, time=120 min, adsorbent dosage= 800mg). The equilibrium curve shows that the overall percent removal of Cr(VI) from solution decreases with an increase in initial Cr(VI) concentration. This may be attributed to the fact that with increase in Cr(VI) concentration/amount of Cr(VI) in solution with fixed amount of adsorbent, binding capacity of adsorbent approaches to saturation resulting in decrease in Cr(VI) removal. At higher Cr(VI) concentration; the number of active sites on adsorbent surface is not enough to accommodate chromium ions, however, at low concentration, the ratio of surface active sites to

total Cr (VI) is high and therefore chromium ions can interact with the active sites on adsorbent surface sufficiently.

4.3.3. Effect of contact time

Contact time is necessarily a fundamental parameter in adsorption. Therefore, it is important to study its effect on the sorption capacity of the magnetic sorbent. Adsorptions can be assumed to be complete when equilibrium is achieved between the solute of solution and the adsorbent. However, specific time is needed to maintain the equilibrium interactions to ensure that the adsorption process is complete.

The adsorption experiments were carried out for different contact times with fixed sorbent dose, pH, and initial concentration. The results were plotted in Figure 4.6, as it is shown, the removal efficiency of chromium by the adsorbent significantly increase during the initial adsorption stage and then continue to increase at a relatively slow speed with contact time until a state of equilibrium is attained. Generally, the removal rate of sorbate is rapid initially, but it gradually decreases with time until it reaches equilibrium.

This phenomenon can be attributed to the fact that a large number of vacant surface sites are available for adsorption at the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases.

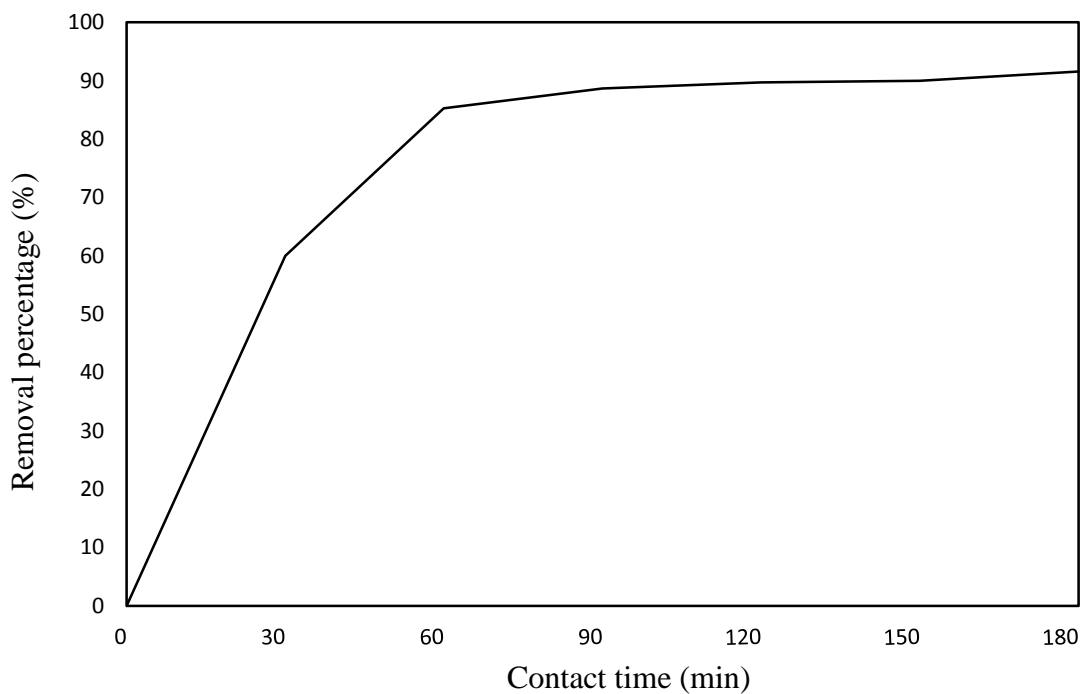


Figure 4.6 Effect of contact time on chromium removal

4.3.4. Effect of adsorbent dosage

Adsorbent dose seems to have a great influence on adsorption process. Figure 4.7 shows that removal increased with increasing the amount of adsorbent dosage. These results indicate that removal efficiency is directly related to the number of available adsorption sites. This suggests that after a certain dose of adsorbent, the maximum adsorption sets in and hence the amount of ions bound to the adsorbent and the amount of free ions remains constant even with further addition of the dose of adsorbent. Amount of adsorbent added to the solution determines the number of binding sites available for adsorption. Metals adsorption efficiency was increased with increase in adsorbent dose. This revealed that the adsorption sites remain unsaturated during the adsorption reaction whereas the number of sites available for adsorption site increases by increasing the adsorbent dose.

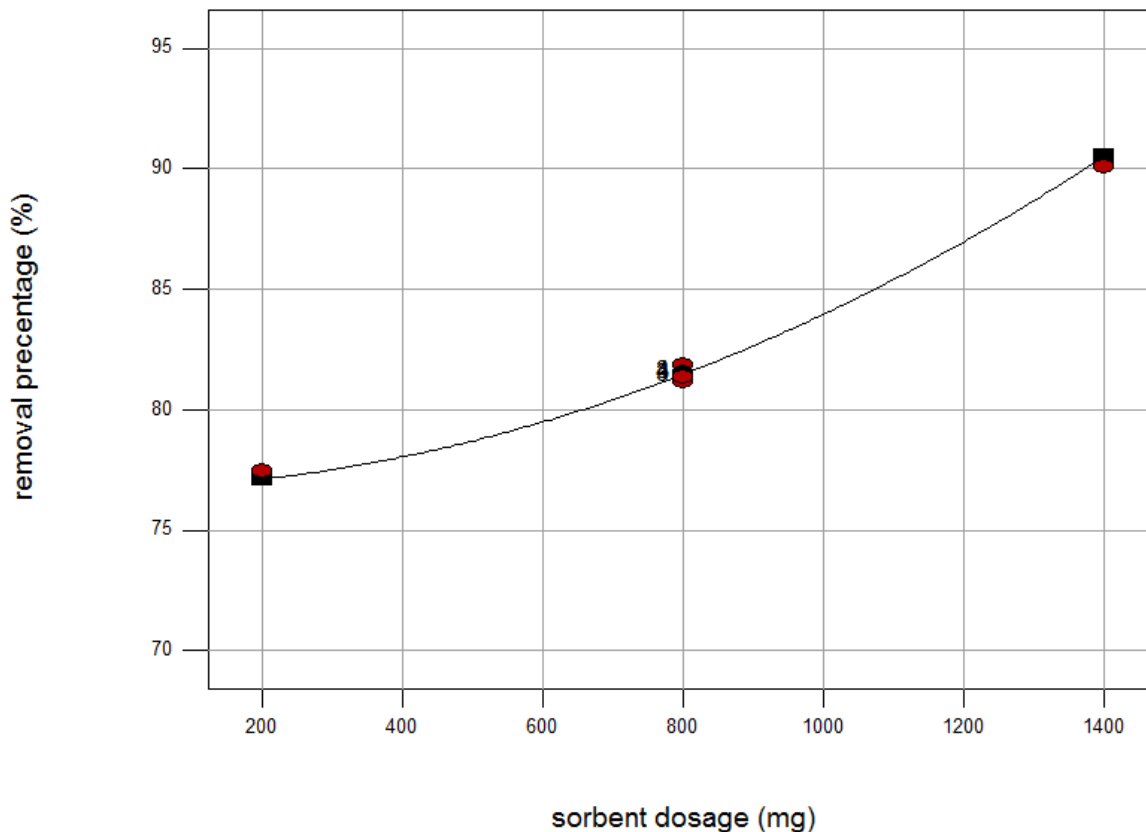


Figure 4.7 Influence of sorbent dose on chromium (VI) removal (%)

4.4. Sorption kinetics

Equilibrium study is vital in determining the efficacy of adsorption. It is also necessary to identify the adsorption mechanism for a given system. Kinetic models have been exploited to test the experimental data and to find the mechanism of adsorption and its potential rate-controlling step that include mass transport and chemical reaction. In addition, information on the kinetics of metal uptake is required to select the optimum conditions for full scale batch or continuous metal removal processes. Adsorption kinetics is expressed as the solute removal rate that controls the residence time of the sorbate in the solid–solution interface. Several kinetic models are used to explain the mechanism of adsorption processes. These models include Pseudo-first-order rate model and Pseudo-second order rate model.

In order to define the adsorption kinetics of heavy metal ions, the kinetics parameters for the adsorption process were studied for contact times ranging from 0 to 12 hours by monitoring the removal percentage of the Cr (VI).

Pseudo first order model

The Pseudo first order rate model based on adsorption capacity of adsorbent and is generally expressed as:

$$\log(Q_e - Q_t) = \log Q_e - k_1 t \quad (4.4)$$

Where, Q_e and Q_t are the amounts (mg/g) of Cr (VI) adsorbed at equilibrium and at time (t), respectively. Plot of $\log(Q_e - Q_t)$ versus t gives a straight line for first order adsorption kinetics which allows computation of the rate constant k_1 .

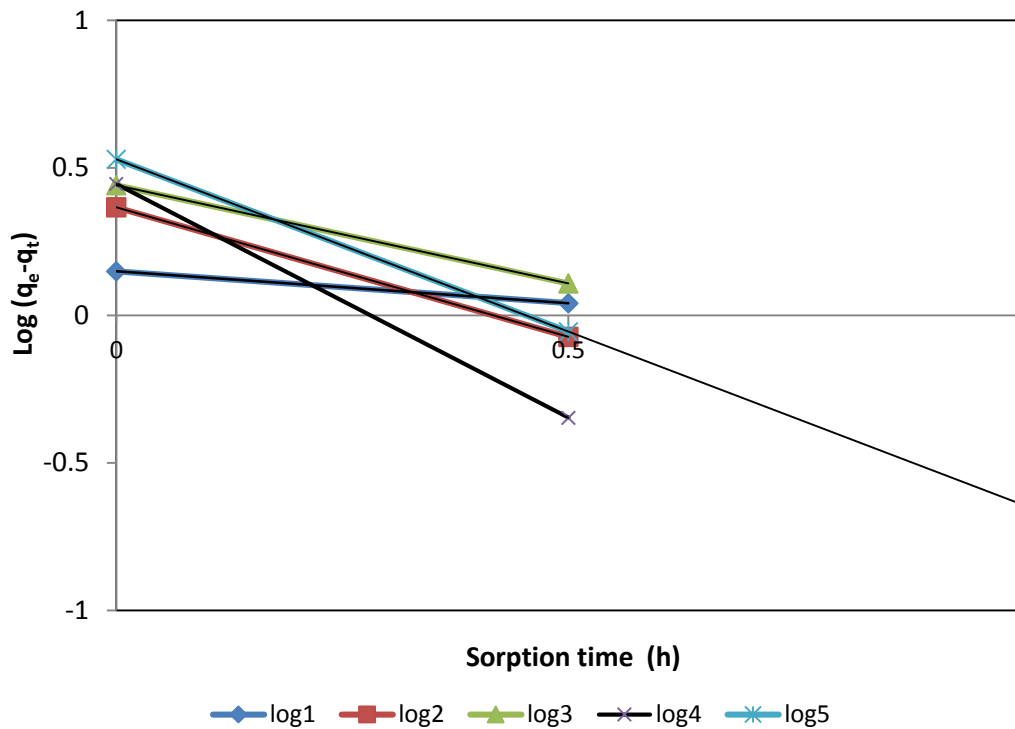


Figure 4.8 Pseudo first order kinetics model

The equation that describes the pseudo-second order model is given in the following linear form

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4.5)$$

Where k_2 is the adsorption rate constant (g/mg-min). The k_2 and q_e are found from the intercept and slope of t/q_t versus t linear plot such that $q_e = 1/\text{slope}$ and $k_2 = \text{slope}^2/\text{intercept}$.

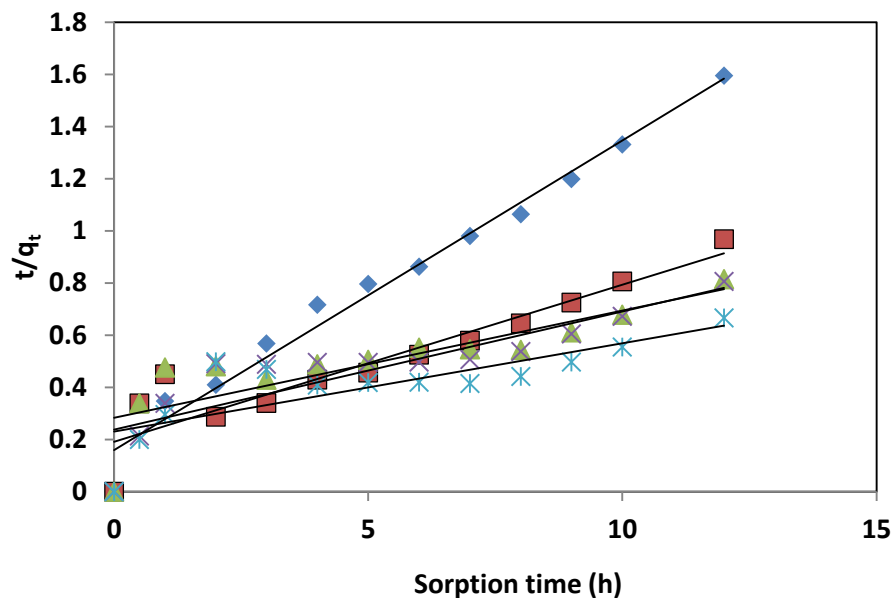


Figure 4.9 Pseudo second order kinetics model

Table 4.5 The adsorption kinetic model rate constants for adsorption of chromium

Initial Cr(IV) ion concentration(mg/L)	Pseudo 1 st order kinetic model			Pseudo 2 nd order kinetic model		
	q_e	K_1	R^2	q_e	K_2	R^2
10	1.81	0.108	0.98	8.37	0.23	0.985
20	6.40	0.44	0.99	16.72	0.042	0.872
30	5.95	0.33	0.98	23.92	0.009	0.737
40	17.29	0.79	0.98	21.74	0.014	0.795
50	12.97	0.58	0.97	28.90	0.007	0.66

The degree of goodness of linear plot of these kinetic models can be judged from the value of the determination coefficient of the plot, which can also be regarded as a criterion in the determination of the adequacy of kinetic model.

The kinetic rate constants obtained from pseudo-first order and pseudo-second-order models are given in Table 4.5. Pseudo-first-order present high correlation coefficients than pseudo-second-order kinetics and the experimental q_e values obtained are closer to those calculated for the first

order model. External mass transfer and intraparticle diffusion represent the experimental kinetics where the effect of pore diffusion and film diffusion are expected to negligible respectively.

4.5. Sorption isotherm

The adsorption isotherm is fundamental in describing the interactive behavior between solutes and adsorbent, which express the surface properties and affinity of the adsorbent. It also plays an important role in the design of an adsorption system. The Langmuir and Freundlich models are often used to describe equilibrium adsorption isotherms.

Langmuir isotherm

The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies with no transmigration of adsorbate in the plane surface. Once a site is filled, no further sorption can take place at that site. This indicates that the surface reaches a saturation point where the maximum adsorption of the surface will be achieved. The isotherm is represented by

$$\frac{C_e}{q_e} = \frac{K_L C_e}{Q_o} + \frac{1}{Q_o} \quad (4.6)$$

Where q_e (mg/g) and C_e (mg/L) are the amount of adsorbed chromium per unit mass of sorbent and unadsorbed chromium concentration in solution at equilibrium, respectively. Q_o is the maximum adsorption at monolayer (mg g^{-1}) on the surface bound at high C_e , and K_L is a constant related to the affinity of the binding sites (L/mg).

The Langmuir constants Q_o and K_L were determined from the intercept and slope of the linear plot of (C_e/q_e) against the equilibrium concentration (C_e).

The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L , which is a dimensionless constant referred to as separation factor or equilibrium parameter.

$$R_L = \frac{1}{1 + K_L C_o} \quad (4.7)$$

Where:

C_o = initial concentration

K_L = the constant related to the energy of adsorption (Langmuir Constant). R_L value indicates the adsorption nature to be either unfavourable if $R_L > 1$), linear if $R_L = 1$, favourable if $0 < R_L < 1$ and irreversible if $R_L = 0$.

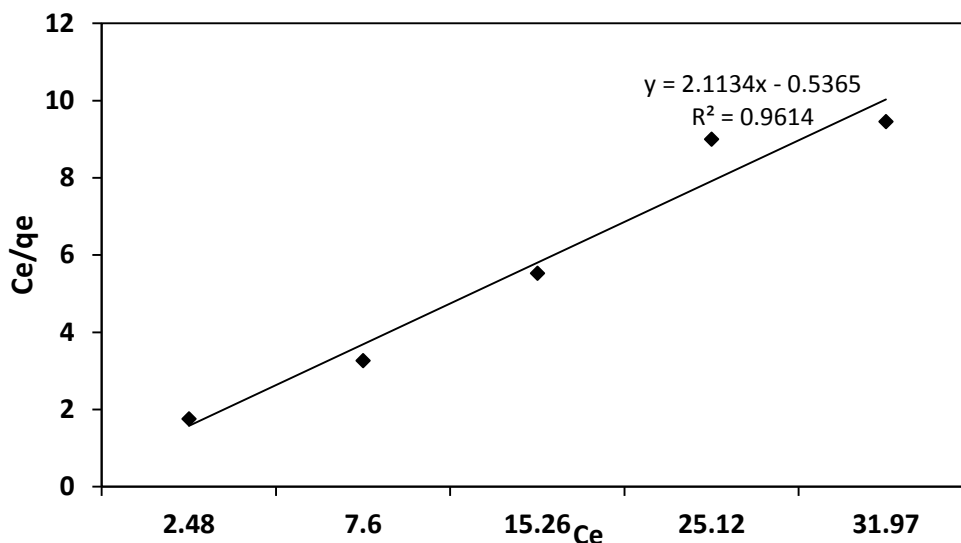


Figure 4.10 Langmuir isotherm for Cr(VI) ion adsorption

From the data calculated, the R_L is greater than 0 but less than 1 indicating that Langmuir isotherm is favorable. From this work, the maximum monolayer coverage capacity (Q_0) from Langmuir Isotherm model was determined to be 1.864 mg/g, K_L (Langmuir isotherm constant) is 3.94 L/mg, R_L (the separation factor) is 0.025, 0.013, 0.0084, 0.0063 and 0.0058 for 10, 20, 30, 40 and 50mg/L of initial concentration respectively. This reflects that in all the cases, R_L values fall between 0 and 1, indicating favorable adsorption of Cr (VI) and the R^2 value is 0.96 proving that the sorption data fitted well to Langmuir Isotherm model.

Freundlich isotherm

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The Freundlich equation is expressed as:

$$q_e = k_f C_e^{1/n} \quad (4.8)$$

Where K_f and n are Freundlich constants with K_f ($\text{mg/g (L/mg)}^{1/n}$) is the adsorption capacity of the sorbent and n giving an indication of how favorable the adsorption process. The magnitude of the

exponent, $1/n$, gives an indication of the favorability of adsorption. Values of $n > 1$ represent favorable adsorption condition [18]. To determine the constants K_f and n , the linear form of the equation may be used to produce a graph of $\ln(q_e)$ against $\ln(C_e)$.

$$\ln q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e \quad (4.9)$$

Values of K_f and n are calculated from the intercept and slope of the plot.

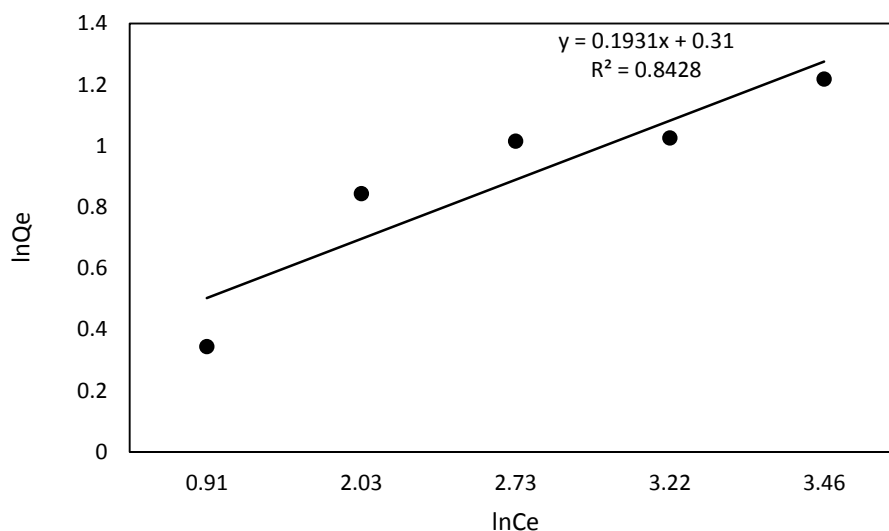


Figure 4.11 Freundlich isotherm model for Cr(IV) adsorption

If $n = 1$ then the partition between the two phases are independent of the concentration. If value of $1/n$ is below one it indicates a normal adsorption. On the other hand, $1/n$ being above one indicates cooperative adsorption. K_f and n are parameters characteristic of the sorbent-sorbate system, which must be determined by data fitting and whereas linear regression is generally used to determine the parameters of kinetic and isotherm models. From the data appendix 2, that value of $1/n = 0.1931$ while $n=5.18$ indicating that the sorption of Cr^{6+} unto the magnetic sorbent is favorable and the R^2 value is 0.843.

Temkin Isotherm

This isotherm contains a factor that explicitly taking into the account of adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease

linearly rather than logarithmic with coverage [18]. As implied in the equation, its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy) was carried out by plotting the quantity sorbed q_e against $\ln C_e$ and the constants were determined from the slope and intercept. The model is given by the following equation

$$q_e = \frac{RT}{b} \ln(A_T C_e) \quad (4.10)$$

$$q_e = \frac{RT}{b_T} \ln A_T + \left(\frac{RT}{b_T} \right) \ln C_e \quad (4.11)$$

$$q_e = B \ln A_T + B \ln C_e \quad (4.12)$$

where $B = \frac{RT}{b_T}$

A_T = Temkin isotherm equilibrium binding constant (L/g)

b_T = Temkin isotherm constant

R = universal gas constant (8.314J/mol/K)

T = Temperature at 298K.

B = Constant related to heat of sorption (J/mol)

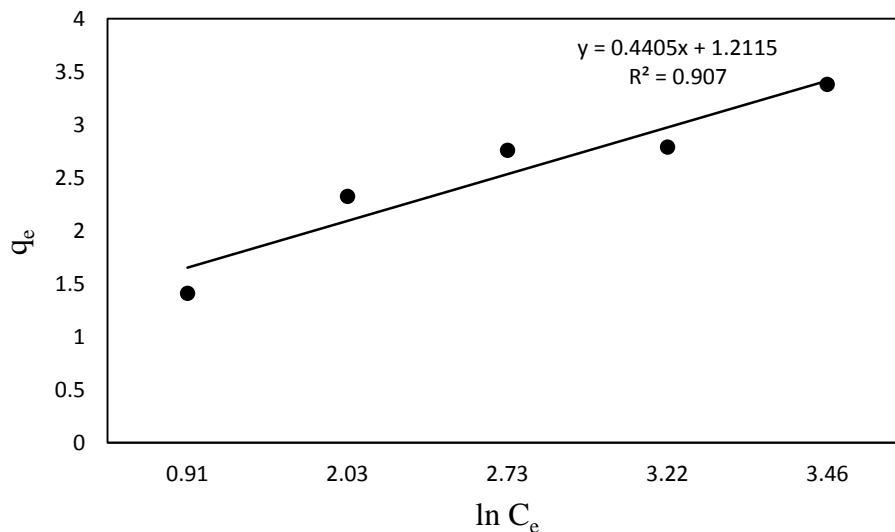


Figure 4.12 Temkin isotherm model

From the Temkin plot shown in Figure 4.12, the following values were estimated:

$A_T = 15.65$ L/g, $B=0.4405$ J/mol which is an indication of the heat of sorption indicating a physical adsorption process and the $R^2=0.907$.

Table 4.6 Langmuir, Freundlich and Temkin isotherm model constants and correlation coefficients for adsorption of chromium

Isotherms	R^2	Estimated isotherm parameters
Langmuir	0.96	$Q_o(\text{mg/g}) = 1.864$ $K_L(\text{L/mg}) = 3.94$
Ferundlich	0.843	$K_f = 1.363$ $n = 5.18$
Temkin	0.907	$A_T(\text{L/g}) = 15.65$ $B(\text{J/mol}) = 0.4405$

The regression coefficient (R^2) for Langmuir, Freundlich and Temkin isotherms are found to be 0.96, 0.843 and 0.907, respectively. Thus, the Langmuir adsorption isotherm is the best model for Cr (VI) adsorption on to the magnetic sorbent followed by Temkin adsorption isotherm model. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogeneous distribution of active sites onto magnetic sorbent surface, since the Langmuir equation assumes that the surface is homogenous.

4.6. Desorption

Recovery of the adsorbed material and regeneration of the adsorbent are also important aspects of wastewater treatment. Attempts were made to desorb chromium (VI) from the magnetic sorbent with various desorption agent, such as hydrochloric and nitric acid solutions and base solutions containing sodium hydroxide and potassium hydroxide. After adsorption experiments, the magnetic sorbent with the adsorbed Cr(VI) ion were separated by magnet from the solution and then added to various stripping solutions and agitated at 60rpm for 90min and the final Cr(VI) concentration was determined.

The results are presented in Table 4.7 the present work showed that effective desorption was obtained with alkaline solutions. These phenomena are consistent with the results observed for the effect of pH. Potassium hydroxide solution was useful for desorption of chromium from the surface of sorbent and the desorption efficiencies with 1M KOH was 82%.

Table 4.7 Influence of the Eluent on the desorption of Cr (VI)

Desorption agent(1M)	Desorption %
NaOH	63.32
KOH	82.75
HCl	12.16
HNO ₃	16.11

Adsorption process: Initial Cr concentration, 20mg/L, sorbent dosage 0.8 g, volume of desorption agent, 100mL, agitator speed 60 rpm

5. Conclusion and recommendations

5.1. Conclusion

It is known that it is expensive and ineffective to remove Cr(VI) ions from aqueous solutions using conventional methods when the chromium concentration is low. An adsorption process using magnetic sorbent, is an ecofriendly and low-cost method that could replace conventional processes for remediating Cr(VI) pollution in aqueous systems. The present study focuses on the preparation of magnetic sorbent from bagasse residue and iron salts for adsorption of Cr (VI) from aqueous solution.

The batch technique is used to study the adsorption as a function of various influencing factors such as initial metal ion concentration, contact time, pH magnetic sorbent dosage and under ambient conditions. The obtained results indicate that the adsorption percentage increases with increasing the amount of dosage and contact time until it reaches the equilibrium values and decrease with increase in the amount of initial metal ion concentration.

Central composite design was adopted to study of effect of variation in parameters like initial chromium concentration, pH, time and adsorbent dosage. ANOVA analysis reveals that the adsorbent linear effect and square was significant. Analysis of variance also showed that a reasonably high regression coefficient of 0.996, ensuring a satisfactory adjustment of the second order regression model with the experimental data.

The knowledge of point of zero charge of the studied materials provides information about the possible attraction and repulsion between sorbent and sorbate but in any case enables to ensure that electrostatic force is one of the mechanisms that takes place in metal sorption.

The percentage removal was found to be dependent on the quantity of sorbent dosage, pH, time, and initial concentration of the sorbate (chromium). Pseudo-second-order kinetics model was found to be the predominant. The equilibrium sorption data fitted the Langmuir isotherms with high correlation coefficients, suggesting that the process followed a monolayer adsorption onto a surface containing a finite number of adsorption sites.

5.2. Recommendation

More research is needed to study the particle size, agitation speed and temperature dependence of the magnetic separation efficiency.

Since bagasse residue is abundant and locally available, magnetic sorbent prepared from bagasse is also a low-cost adsorbent and has a considerable high adsorption capacity, it may be treated as an economically viable for the removal of metal ions from effluents (Biruk, 2011). This needs further research on magnetic sorbent from biomass like bagasse and agricultural wastes for heavy metal remediation on a large scale. The future of magnetic nanoparticles and biomass in water treatment is quite bright, but it needs the collaborative efforts of research and industrial persons to materialize a dream of fast, economical, and feasible water treatment technology. By working together, it will be possible to solve water contamination globally.

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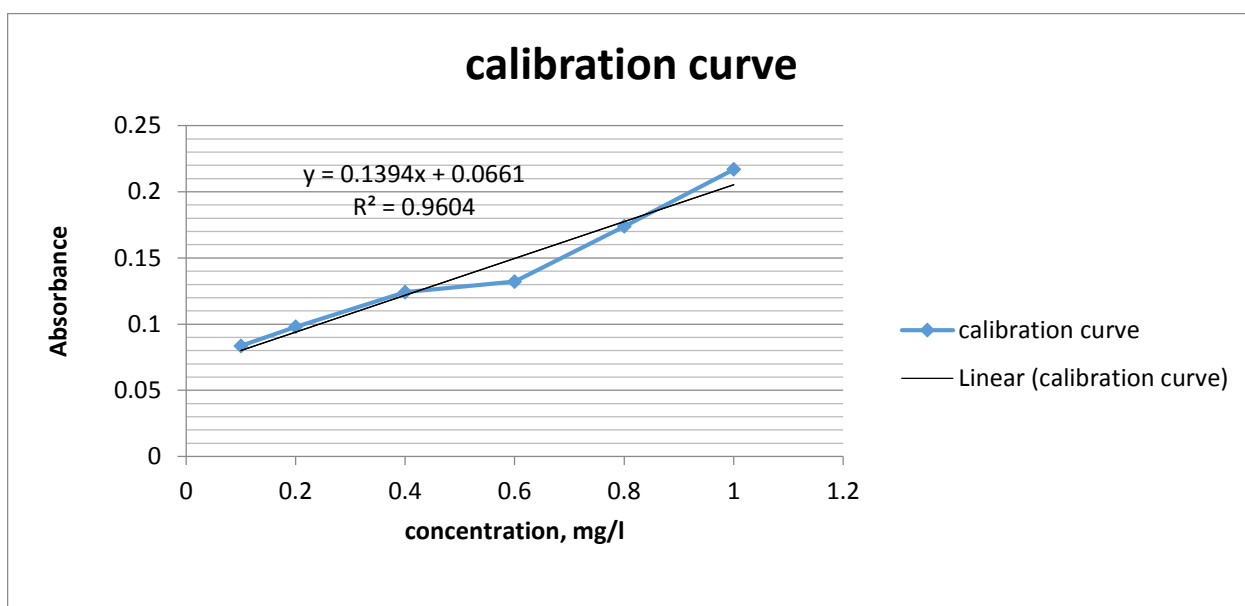
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Appendix

Appendix 1 Calibration curves for Cr⁶⁺



Appendix 2 Parameters for plotting Langmuir, Freundlich and Temkin Adsorption isotherms of Cr(IV)

Co(mg/L)	Ce(mg/L)	1/Ce	logCe	lnCe	Qe(mg/g)	1/Qe	logQe	lnQe	Ce/Qe(g/L)
10	2.48	0.40	0.39	0.91	1.41	0.71	1.238	0.34	1.76
20	7.6	0.13	0.88	2.03	2.235	0.45	0.257	0.80	3.40
30	15.26	0.07	1.18	2.73	2.764	0.36	0.806	1.02	5.52
40	25.12	0.04	1.40	3.22	2.79	0.35	1.113	1.03	9.00
50	31.97	0.03	1.50	3.46	3.38	0.29	0.775	1.22	9.46

Appendix 3 Bagasse powder after washed with distilled water and heated for 24 h at 50°C



Appendix 4 The magnetic sorbent powder prepared from iron salt and bagasse for metal ion adsorption from wastewater.

